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Paint Film Components

M van Alphen

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Contents

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My work in the South Australian Health Commission since 1993 has been directed towards the investigation of child lead exposure and lead smelter emissions with a limited emphasis on paint lead. An early draft of this work emerged after the realisation of the presence of paint film components such as asbestos, mercury, cadmium, and PCBs, among other components that may pose risks; in addition to those of lead. This project emerged (after hours) given the early encouragement of Mark Farfel, Rob Fowler and Nick Kim.

For unpublished paint lead analysis data provided by Dani Boddington of the Broken Hill Environmental Lead Centre, and national paint lead survey data from Phil Anderson of the Australian Institute of Health and Welfare, I owe particular thanks.

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Finally I thank Joe van Alphen - who has shared much practical knowledge, from some 40 years in the painting trade.

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Preface

This work provides an insight into the use of potentially toxic materials in paints, which may be left in the layers of paint films. The historical information presented is a guide to potentially toxic components in paint films and their probable concentrations. For example, it will permit a broad understanding of what paint components may be expected in a 100 year sequence of paint layers. Such a history is a preliminary step in the risk assessment process and will contribute to better informed decisions about the assessment and remediation of homes with old paints.

Simply put, paint is a material that obscures and protects the underlying surface and is able to be pigmented with a range of colours. Paints by their protective functions, have to be environmentally stable, containing long lived materials that will form a waterproof barrier able to withstand biological, physical and chemical attack. The protective requirements of paints have commonly resulted in paint components being used which are potentially toxic as are some brilliantly coloured pigments.

The manufacture of paints and pigments, particularly over the last hundred years, has been driven by the imagination and industry of millions of people and tens of thousands of manufacturing sites world wide. The diversity of raw materials and the different approaches to manufacture are responsible for wide variation in paint film composition. More subtle variations occur, particularly with respect to minor additives, whose concentrations may range over many orders of magnitude.

Diversity in paint formulations is driven by the need for a range of colours, applied to a wide range of substrates, a diversity of paint uses and differing exposure (weathering) conditions. There are many paint properties such as covering or obscuring power, drying time, paint-film-hardness, film flexibility, colour permanence, water resistance, UV resistance, ease of application, control of paint layer thickness, rate of chalking, mould and fire resistance, among others, that are able to be modified by varying the properties and proportions of major components and minor additives. In many situations one component may require the addition of others to balance the physical and chemical properties of the formulation. The constitution of paint materials is highly varied as are the toxic properties of paint. Dusts generated by the abrasion of a number of different paint layers from a number of different surfaces of different ages may readily contain or be derived from several hundred different compounds.

Some answers to questions on the contemporary risks related to old paint lie in the investigation of dried paint films. However, to estimate past exposures, particularly in relation to pesticides, organic mercury, and plasticisers which are sufficiently volatile for a proportion to be lost from the paint film over time, the analysis of original paint stored in good condition in-the-can may be useful. Such materials from the 1950s are rare but may still available from deceased estates or hazardous waste management depots, for example.

The toxic properties of pigment particles or other materials in paint may be substantially influenced, and perhaps mediated, by the manner of encapsulation of that material by paint binding components. Examples of this may be the extent of encapsulation of asbestos fibres or lead-compound pigment-particles by paint binders. The degree of rimming of potentially toxic particulates with paint binder and the nature of incorporation of toxic components with relatively inert components of a paint as well as their means of liberation from a paint film are central to detailed assessment of health risks.

Since the 1950s, technology in pigment manufacture has resulted in pigment particles being individually encapsulated with layers often only nanometres thick of more stable compounds such as silicates. Any experimental, or occupational exposure based assessment of pigment toxicity, that has failed to characterise pigment particle coating, will also fail to represent the long term risk of highly weathered pigment where the pigment particle encapsulation has failed. Most animal studies of pigment toxicity fail to document the status of pigment particle coating.

The 'quick and easy' assessment of the potential health risk of a particular component of paint films will be the total analysis. Matters which may mediate or accentuate risk such as the fate of inorganic and organic paint components; the sandwiching of toxic component rich paint layers among other paint layers, the bioavailability and particle size of toxic components at particular points in time, need to be considered when 'guideline' contaminant levels are being assessed.

At various times, technical details relating to the manufacture of a pigment or the toxic properties of an ingredient may have been secret, poorly understood, or not considered to have been relevant to a particular manufacturing process and therefore not documented. Some details presented here may reflect the imperfect knowledge of the 1950s to 1970s. The use of potentially toxic paint components were frequently detailed in texts pre-1970, whereas such information appears to be rarely found post - 1970.

The chronology of discovery, use and withdrawal from use, of paint components is documented where possible, as is the history of legislation relating to paint. Legislated maximum levels of substances in paint in some situations, sometimes closely reflect actual levels and in numerous situations greatly exceed actual levels. In the 1950s and 1960s it was necessary for manufacturers, wholesalers and retailers, to hold more paint in stock than they do currently. In the past, in relation to already manufactured goods, legislation resulted in progressive declines in use of materials as stocks were cleared. Painting contractors and do-it-yourself painters may also store paints for future use. The date of enacting legislation may not mark the absence of future use of particular materials. In a small, isolated community, dominated by a single industry, it has been common for paints such as red lead and other industrial paints to have been widely used in the community. Aspects of past paint component use, particularly in the mixing of paint components by the user, involve modification of tradition, learned skills and behaviour. Such changes in behaviour are not implemented as rapidly or effectively as when all paint sold is ready to use. Ready-made paints gradually assumed dominance between the 1940s and late 1950s with the painting trade, but were more readily accepted by the do-it-yourself painter, when they were available.

The revolution in paint formulation in relation to lead risk was the reduction in use of white lead as the use of titanium dioxide pigments steadily increased, particularly from the early 1950s to the early 1960s. Over that period, Australia played a dominant role in the supply of titanium dioxide to world pigment markets. Titanium dioxide pigment, like other modern pigment particles, consists of a pigment core coated with a thin layer of material designed to improve the pigment characteristics. Detailed examination of titanium dioxide pigment shows that it has varied greatly over time in terms of its methods of manufacture and trace element chemistry.

A summary of existing data on lead in paint on Australian houses provides useful insights as to what levels of lead in paint may be encountered.

Models to evaluate the potential mass of lead on house walls are explored. Hundreds of kilograms of lead in paint are readily present on the walls of older houses. A 'typical' painting regime is outlined for a house built in 1900, having 280 m^2 of wall area that resulted in a paint lead loading value of 103 mg Pb/cm^2 such that the wall coatings would contain some 288 kg of lead. A worst case scenario indicated that some 364 to 644 kg of lead in paint on the walls is possible.

Insights into the potential magnitude of soil contamination; given particular paint lead settings and scenarios for the incorporation of lead in soil, are readily obtained from models provided in this work. Even low levels of paint loss from an old wall surface will generate high soil lead concentrations. A 4m high wall having a paint lead loading of 80 mg Pb/cm^2 which loses 10% of the lead from the wall will lose 320 grams of lead per linear metre of wall. If 85% of the lead lost from the wall is evenly incorporated into a 0.3m x 0.3m x 1.0m block of soil, the lead added to soil attributable to paint, would account for some 1780 mg of lead per kilogram of soil. A range of scenarios provide useful indications as to the likely ranges of concentration of soil lead attributable to paint lead.

The substrate upon which a paint is applied should not be ignored when evaluating or testing paints for toxic components; lead may be encountered in plasters, putty and PVC. Timber treatment chemicals, and metal substrates, particularly plated metals may pose other problems. The tendency for particular paints to fail on particular substrates can help guide investigations into paint components.

Much of the information on paint manufacture and formulation presented is generic. Most responses to, or comments on, health risks associated with paint will also be generic, based on common practice. However local paint manufacture or painting practice may result in more idiosyncratic use of paint components of which an investigator may need to be aware.

Accounts of past formulation practice in the history presented here are not a complete assessment. Analysis of multi-layer paint films is one means of assessing matters such as the use and abundance of particular potentially toxic paint components suggested by the historical details of paint formulation.

Paint solvents are discussed in this work, but are not investigated in detail.

Paint is a universal component of the built environment and health risks associated with paints potentially impact on large numbers of people. Because of the long-lived nature of paint materials in residential settings, a good historical understanding of paint formulation and manufacture is required prior to undertaking scientifically valid health risk assessments.

1. Legislation affecting paint

1.1 International

One of the early conventions directed towards the control of lead in paint was the International Labour Office (ILO) White Lead (Painting) Convention 1921 (No. 13) (Browne, 1983). According to Grut (1951) 27 countries had ratified the 1921 ILO convention which prohibited the use of white lead or sulphate of lead in 'internal' painting.

The regulation of the use of toxic pigments and dye in the manufacture of edibles, foods and objects of daily use, in Germany, dates back to 1887, (Hess, 1965, p.205).

Recent European regulations on cadmium use in pigments, are referred to in Buxbaum (1993, p.113-114):

> *'In 1981 Sweden prohibited the use of cadmium pigments (with some exceptions) for ecological reasons. In 1987 Switzerland prohibited the use of cadmium pigments in plastics. Exceptions are possible if valid reasons can be given. In 1991 the EC passed a directive to prohibit the use of cadmium pigments as colorants for certain plastics that can be easily be coloured with other pigments. …. In 1996 the use in coating media will be prohibited. Use in artists' colors and ceramic products is still permitted.'*

And also from Buxbaum (1993, p.124):

> *According to Directive EEC 89/178 (Feb 22 1989) and GefStoffV, (April 23 1990), lead-containing coatings and paints with a total lead content exceeding 0.15% of the total weight of the finished product must carry the warning: "Contains lead. Should not be used on surfaces liable to be chewed or sucked by children".*

A range of international, and national pigment manufacture standards and material specifications is listed in Buxbaum (1993, pp2-7).

1.2 Great Britain

Similarities in legislation and standards between Australia and the UK were strong, particularly up to the 1970s.

Regulations as to the methods of manufacture of lead pigments with regard to the control of occupational dust exposures appear to have been in place or introduced between the 1920s and 1940s (Hess, 1965, p.215). Early concerns were for the soluble lead content of paints (Home Office Test for Soluble Lead S.R.&P., No. 1621, 1926).'

The UK, Lead Paints (Protection against Poisoning) Act, 1926 restricted lead in paints as follows:

> *For lead paints to be applied by spraying, the Act lays down a maximum figure (5 percent) for the lead compounds soluble in 0.25% hydrochloric acid, which is the concentration in normal digestive juices. This soluble-lead figure is calculated as lead monoxide (PbO) and is expressed as a percentage on the pigment. (see British Standard 282: 1963) [Morgans,1982, p.39]*

One interpretation of the above is that an extraction of a maximum of 5% lead, (calculated in terms of the PbO compound at 92.85% Pb) using a 0.25% HCl digestion of paint was permitted.

This equates to paint returning an apparent analysis of 4.65 wt.% Pb by the weak HCl digestion method. According to Morgans (1982, p.39) in addition:

> *Under the conditions of this method white lead and litharge are completely soluble, but the soluble lead contents of lead chromes and chrome greens vary according to the composition.*

Morgans refers to the UK Lead Paint Regulations 1927 but does not report the details of this legislation. Hess (1965, p.212-213) notes various views on the restriction of paints for children's toys (BS 3443) as follows:

> *'the maximum of total toxic materials including lead has been restricted to 1 per cent on the dry film' and for other paints 'The British Paint Manufacturers' Executive Committee has recommended to its members that paints containing more than 1.5 per cent toxic materials on the dry film from January 1963 onwards should be labelled as unsuitable for surfaces likely to be chewed by children.'*

An article in October 1961 by Burgess, of London City Council is referred to in Hess (1965, p.66) as proposing '*…limits for the amounts of toxic pigments contained in lacquers for children's crayons and pencils… In the lacquer for each pencil, etc., no more than 10 mgm. of metallic lead, soluble chromium, soluble barium, cadmium, selenium or acid soluble antimony or arsenic should be contained.*'

The above reference to metallic lead as opposed to soluble lead, may suggest some additional caution with respect to lead, Hess notes that the general proposal could be problematic if more than one toxic substance was present.

The British Toys (Safety) Regulations, 1974 set a limit of 250 ppm "soluble" chromium in dry film, presumably to reduce risks in relation to the use of zinc chromates and Cr^{VI} , (Morgans, 1982, p.85).

Many British Standards have in the past been considered *de facto* Australian Standards in the absence of local standards (Table 1). Building codes in the 1970s in various countries continued to require lead-based timber primers, by way of reference to standards despite lead reductions in paint.

Table 1: *Some British Standards from 1961 to 1976 (after Boxall and Frauhoffer, 1980)*

British Standard 217:	1961:	*Red lead for paints and jointing compounds*
British Standard 282:	1963:	*Lead chromes and zinc chromes for paints.*
British Standard 3698:	1964:	*Calcium Plumbate Priming Paints*
British Standard 3699:	1964:	*Calcium Plumbate for Paints*
British Standard 303:	1965:	*Brunswick or lead chrome greens (pure and reduced) for paints.*
British Standard 2523:	1966:	*Lead-based Priming Paints*
British Standard 239, 254, 338, 637 and 1851:	1967:	*White pigments for paints*
British Standard 4313:	1968:	*Strontium chromate for paints*
British Standard 318:	1968:	*Chromic oxide pigments.*
British Standard 3443:	1968:	*Toy Paints: Code of Safety Requirements for Children's Toys and Playthings.* (available prior to 1965 (Hess, 1965, pp.207).
British Standard 4310:	1968:	*Permissible limit of lead in low-lead paints and similar materials*
British Standard 5358:	1976:	*Specification for low-lead solvent-thinned priming paint for woodwork.*

1.3 Australia

1.3.1 Past legislation relating to paint manufacture and sale in Australia

The following section is a *sample* of the legislative regulations of paints. The history of legislative change is difficult to research and detailed understandings of the nature of implementation and outcomes of regulation will be difficult to evaluate. The following represents what was readily discovered in a limited time.

1.3.2 Queensland

A version of the Queensland Health Act (1937), of unknown age, which may or may not have been amended and then consolidated, and whose relationship with the Act of 1922 is unknown, is summarised here.

The Queensland Health Act (1937) prohibited lead, arsenic or antimony in toys, wallpaper, decorative paper, paper serviettes and food wrapping paper amongst other things. In addition Section 127 restricted the soluble lead concentration of paints to 5% and prohibited the use of paints containing lead on roofs. It may well be that the Queensland legislation was very similar to the 1926 UK legislation. Section 127 of the Act did not appear to seek to legislate with respect to lead in interior paints. Structures already painted with 'soluble lead' could have attracted prosecution. Where paints in excess of 5% soluble lead were discovered, the State had the power to enforce the removal of that paint. Section 128 of the Act required the labelling of the name or names of ingredients and the quantity or percentage of each in the paint. It appears that this legislation was not designed to limit the amount of lead in paint (except roof paint) but to reduce the proportion of carbonate of lead to 5% (calculated as PbO), or 4.65 wt % lead soluble in weak hydrochloric acid.

An undated pamphlet produced by the Australian Paint Manufacturers' Federation Inc., between 1993 and 1994, containing an endorsement from the Minister for the Environment, states: *'Prior to 1950 white lead was the principal white pigment used in house paints - although Queensland banned its use in 1922.'* This assertion that white lead use was banned in 1922 has since been widely quoted, however the Queensland Health Act (1937) did not ban white lead; this did not happen until 1956.

According to Hanson (1958), paints in Queensland up to that time were not lead free. More significant provisions relating to lead in paint became law in January 1956. *The Struggle Against Lead Poison in the Painting Trade*, Hanson (1958, p.7) makes the following comments regarding the 1956 law:

> *'The main points of the legislation are:-*
>
> *(1) The manufacture, sale and use of paint containing basic lead carbonate (white lead) is banned in its entirety.*
>
> *(2) Paint containing lead of any description cannot be used on the roof of a house or other building or structure; any exterior portion of any house or other building whatsoever; any fence or gates whatsoever; any interior portion whatsoever of a house; or any household furniture.*
>
> *(3) Paint containing not more than 5% soluble lead chromate may be used on certain places but shall not be used on any exterior portion of a building which is accessible to children under fourteen years of age.'*

According to Hanson (1958, p.8) who quotes The Hon. WM Moore (ALP) from Hansard No 18, p.1295, 11/11/55:

> *'Our goal is now in sight. With the passing of the Bill to prevent the manufacture, sale and use of paint containing white lead, we can confidently look forward to the day when there will not be any white lead on any house in the State.'*

While Alperstein, Reznik and Duggin (1991, p.407) state that *'....Australia led the world in measures to protect children from the hazards of lead poisoning when, in 1922, legislation was passed in Queensland banning the use of lead-based paint on verandahs and outside surfaces that were within the reach of children'* the removal of white lead and reductions of lead in paint were a more drawn out process.

1.3.3 Tasmania

It appears that a 1942 Tasmanian Act relating to paint lead was based on the Queensland Act (pers. comm. Pamela Edwards, 1997). The Tasmanian Health Act 1962, sought to prohibit the sale, manufacture and use of paint containing basic carbonate of lead (Section 123), and sought to enforce restrictions and labelling requirements (Section 124) in relation to the total lead content of paints (Table 2).

Table 2: *Labelling requirements from the Tasmanian Health Act, 1962.*

Up to 1 % Pb	*Containing not more than one percent of lead.*
Between 1 and 5% Pb	*Containing not more than five per cent of lead.*
	For exterior use only -Not to be used on interior work or toys.
More than 5% Pb	*Poisonous. Not to be used where food is or on roofs of buildings fences, or gates.*

In addition, paints containing greater than 5% lead were prohibited from the exterior of a building (Section 125) although this was not obvious from the labelling requirements. Paints containing in excess of 1% lead were restricted from use in house interiors, on household furniture, and things that come in contact with food or water. Schedules were set for the allowable concentration of metals (Section 126) in or on toys, wall-paper, paper napkins or paper for enclosing food.

Table 3: *Class II classification by solvents and amount in the paint, relative to total weight. (Tasmanian Statutory Rules, 1968)*

benzene	›1%
dichloroethane	›5%
dichloroethylene	›10%
dichlorobenzene	›5%
dichloromethane	›5%
methanol	›1%
nitrobenzene	›1%
pyridine	›2%
trichloroethylene	›5%
free organic isocyanates	›0.1%

The Tasmanian Public Health (Paint) Regulations 1968 designated a Class I paint as having Pb >1%, As >0.1%, Sb >5%, Cd >0.1%, Se >0.1%, Hg >0.5% of the non volatile content of the paint. Regulations required that percentages of all Pb, As, Sb, Cd, Se, or Hg be on a label of Class I paints.

Such paints required warnings in relation to exposure of children to paint and were prohibited from:

> *any toy, wallpaper, pencil, wrap, container, or furniture;*
> *the roof or other exterior portion of any house or other building or structure;*
> *any fence, wall, post or gate;*
> *any interior portion of any house or other building or structure intended for the use of human beings;* **or**
> *any household or other furniture or part thereof,* [Tasmanian Statutory Rules, 1968]

Class II paints were regulated in order to control solvent exposures to paint applicators, and risk of fire or explosion (Table 3).

1.3.4 New South Wales

Poisons Regulations under the Poisons Act 1966, contain provisions relating to the labelling of paints. Paints containing more than 1% Pb; 5% Sb; 0.1% As; 0.1% Cd; 5% chromate or dichromate; 0.1% Hg; 3% Sn; or 0.1% Se require the proportion of those compounds to be expressed, presumably on the label. Under 13A(5), *'... In the case of a tinter containing 10 per cent or less of lead calculated as a proportion of the tinter, the proportion of lead contained therein may be omitted from the label.'*

There was a NSW regulation from 14 January 1972 that incorporated a ban on paint lead carbonate (pers. comm., Edwards, 1997).

Also, in relation to motor vehicle and industrial paints (Provision 13A(6)) a paint containing greater than 1% lead will not need to have the lead content printed on the label so long as *'FOR AUTOMOTIVE OR INDUSTRIAL USE ONLY'* is written on the label. Industrial metal spray paints have been seen for sale in a hardware store in Broken Hill NSW, in late 1990 and, as recently as May 1995 similar paints in a range of bright colours with lead contents generally in the range 20-30%, have been seen in hardware stores in Port Pirie and Adelaide. The lead content of these paints is printed on the label.

1.3.5 South Australia

It appears that in SA, until very recently, there has been no regulation of lead or other components in paint as it has been assumed that manufacturers have to conform with the regulations of others so as to trade interstate. In 1991 SA recognised the NHMRC Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP) relating to paints.

1.3.6 Australia

The form of and date of commencement of any national Australian regulations or recommendations relating to paint standards from the 1960s is unknown. Anecdotal information suggests that such regulations existed.

The NHMRC Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP) had a standard that limited lead concentration in paint to 0.5% (in the non-volatile fraction of the paint) in 1990 which on 16 March 1992 was revised downward to 0.25% Pb (pers. comm. Keith McKellar). The use of lead and other chemicals in paints can restrict their use and impose labelling requirements (Table 4).

The SUSDP limits the use of lead carbonate to mirror backings which in SUSDP, 1996 further specified no more than 15% Pb and application to less than 40 microns thickness.

Table 4: *Amounts of chemicals requiring labelling and use restrictions for paints (NHMRC, 1993, Appendix P)*

> 0.25% Pb or Pb compounds
> 5% Sb or Sb compounds other than Sb titanate pigments
> 5% Ba salts except $BaSO_4$ or barium metaborate
> 0.1% Cd or Cd compounds
> 5% Cr as chromates of Ba, K, Na, Sr, Zn or NO_3
> 0.1% Se or Se compounds

The manufacture, sale, supply or use of paints having concentrations of metals exceeding the levels in Table 4 is prohibited for the following applications: roofs or water collection surfaces; furniture; (and except on industrial sites) fences, walls, posts or gates, building interiors and exteriors (other than buildings solely for industrial purposes); and premises used for food processing.

The SUSDP in 1996, notes that after 1 December 1997 there will be additional labelling requirements for paints having greater than 0.1% Pb in the non-volatile fraction, lowering the previous level of 0.25% (NHMRC, 1996, p.249). In the case of zinc-based paints, additional labelling will be required when lead or lead compounds exceed 0.2%.

From 1993, in relation to tinters containing more than 10% lead, the proportion of tinter required to raise the lead concentration of a paint above 2,500 ppm w/w is calculated and a warning is given to the effect that if greater than that certain amount of tinter is used then the use of the paint is to be restricted and labelled with additional warnings. A tinter containing more than 0.1% of lead is now to be labelled with the warnings: '*This tinter contains lead. Do not add to any paint which is for application to any toy, furniture, building (interior or exterior), fixed structure or to anything which may contact food or drinking water,* and the expression KEEP OUT OF REACH OF CHILDREN.

Table 5: *Concentration of solvents in paints, above which labelling is required ([NHMRC, 1993, Appendix P).*

1,2-Dichlorobenzene	5% by wt
1,2-Dichloroethane	5% by wt
Dichloromethane	5% by wt
Ethylene Glycol Monoalkyl Ethers	10% by vol
Toluene	50% by vol
Trichloroethylene	5% by wt
Xylene	50% by vol

The SUSDP lists mercury in Schedule 7, where the warning DANGEROUS POISON is required on a label except where it is at or below 0.01 per cent organic mercury (100 mg/kg) as a preservative in paint (NHMRC, 1996, p.172).

1.4 Occupational health and safety and paint in Australia

The Worksafe Australia standard for the 'Control of Inorganic Lead at Work' through the National Occupational Health and Safety Commission (NOHSC) has the objectives to:

(a) minimise the risk of adverse health effects caused by lead exposure in the workplace by:

(i) providing for assessment of the risk for jobs in the workplace where there is exposure, or potential exposure, to lead and to determine whether the job is a lead-risk job,

(ii) ensuring that employees with potential exposure to lead used in a work activity are provided with information, induction and training on the nature of hazards and means of assessing and controlling exposure to workplace lead and that employee representatives have access to this information,

(iii) ensuring that employers provide certain equipment and facilities, and provide for the testing and monitoring at workplaces where lead processes are conducted, and

(iv) ensuring that emergency services and other relevant public authorities have access to relevant information on lead;

(b) ensure that an employer controls lead exposure at the source in workplaces where lead processes are conducted;

(c) ensure that an employer provides for the health surveillance of employees who work in lead-risk jobs;

(d) prescribe certain duties of prescribed persons at workplaces where lead processes are conducted;

> *(e) prohibit certain activities at workpIaces where lead processes are conducted;*
>
> *(f) ensure that information on lead exposures is available to public authorities (to be defined on a jurisdiction by jurisdiction basis);*
>
> *(g) ensure that this National Standard for the Control of Inorganic Lead at Work [NOHSC: 1012(1994)] and National Code of Practice for the Control and Safe Use of Inorganic Lead at Work [NOHSC:2015(1994)] are reviewed within four years; and*
>
> *(h) progressively reduce lead exposure and blood lead levels to convert existing lead-risk jobs to non-lead-risk jobs.* [NOHSC, 1994, pp.5-6]

The degree to which the Worksafe Australia Standard has been implemented with respect to the average painting contractor who would deal with lead-based-paints, particularly in respect of health surveillence is unknown. The definition of a lead risk job, means *'...a work activity or a sequence of activities at specified workstations within the workplace, in which the blood lead level of the employee might reasionably be expected to rise, or does rise above 1.45 µmol/L (30µg/dl) or the removal level… whichever is the lower'* (NOHSC, 1994, p.8). Where the worker is at or above the removal level, they are transferred from a lead-risk job to a non-lead-risk job. For males and females of non reproductive capacity the removal level is 50µg/dl, 20µg/dl for females of reproductive capacity, and 15µg/dl for pregnant or breast feeding females. (NOHSC, 1994, p.9 & 18).

Based on sampling in the breathing zone, the lead in air exposure standard at October 1994, (the time weighted average concentration over a normal eight-hour working day) was 150 µg/m^3, (NOHSC, 1994, p.13) whereas the Australian ambient lead in air NHMRC goal is 1.5µg of total suspended particulate lead per cubic metre of air (90 day average, 24 hour sample, 6 day cycle).

There are two lead processes, defined in Schedule 1 of the Worksafe Standard that relate to paint:

> *Machine sanding or buffing of surfaces coated with paint containing greater than one per cent by dry weight of lead.*
>
> *Any process whereby electric arc, oxy-acetylene, oxy-gas, plasma arc or a flame is applied, for the purpose of welding, cutting or cleaning, to the surface of any metal which is coated with lead or paint containing greater than one per cent by dry weight of lead.* [NOHSC, 1994, p.23]

In Schedule 2 (NOHSC, 1994, p.24) the following processes are relevant to paint:

> *Spray painting with lead paint containing greater than one per cent by dry weight of lead.*
> *Working in any lead process not listed in Schedule 1*

The above are defined as lead processes to which the national Worksafe Standard applies.

Also in particular relevance to the painting trade, the Worksafe Standard prohibits among other techniques, the use of *'…dry sweeping cleaning methods in lead process areas…'* as well as the requirement to confine contamination by lead, as far as practicable, and ensure that lead contamination of the surrounding environment does not occur (NOHSC, 1994, p.13).

Occupational health regulations in relation to solvents, 'nuisance dusts', and to some extent, heat-gun paint removal and chemical paint strippers have an impact on painting activities, but risks relating to paint components such as asbestos, mercury and other paint components for example are not explicitly recognised.

A survey of 127 painters from North Carolina identified only three with blood lead levels between 20 and 30 mg/dl (Ennever, Zaccaro, Fernando, and Jones, 1995). According to a survey of home renovation in the year 1993-1994 in New York, some 86% of renovation was:

> *'…conducted by persons who were not professional contractors and who may have been unaware of lead hazards and protective measures for safely containing dust and paint chips. Their work primarily involved sanding and scraping, methods that are potentially hazardous but require no training and little financial investment.'* [quoting MMWR in JAMA, 1997, p.1031]

2. The Paint Industry

2.1 The export and import of paints

The Berger company claims to have been a major exporter to Australia prior to the 1900's but was not alone:

> *'Though Bergers were finding the competition tough in the domestic market, they were almost unopposed in their exports to the Colonies. A small but constant demand had been built up in the Australian colonies and almost every ship that left British ports for the months' - long trip to the young settlements carried stocks of Berger colours.'* [Cleary, circa.1956, p.23]

In 1907, one quarter of the British paint industry's product was being exported (Armitage, 1967, p.10).

According to Cleary (c.1956, p.19) the Berger company based in North London in the early 1800's imported the raw materials for their paints, lead and quicksilver, from Spain. Such background information may be useful in relation to lead isotope analysis of paints to evaluate sources of child lead exposure.

A prohibition on the export of white lead from the UK in WW1 appears to have been responsible for the beginning of the large scale manufacture of paint in Australia according to *Technology in Australia 1788 - 1988* (Australian Academy of Technological Sciences and Engineering, 1988).

2.2 The paint industry in Australia

An excellent compilation of the history of Australian Paint Manufacture is contained in *Technology in Australia 1788-1988* (Australian Academy of Technological Sciences and Engineering, 1988).

The following is a chronology, in most part, from that document:

1897	George Henry Taubman: importing painters supplies
1899	George Henry Taubman: manufacturing paint at his Arncliffe home then at St Peters
1904	The earliest recorded patent for a paint invention in Australia
1906	Paint manufacture by H.L Vosz
1911	Berger: had a warehouse in Sydney
1912	Vosz formed the Australian United Paint Company (the first production site was in South Australia)
1915	Wattyl paints started by the Walters family
1916	Berger began to manufacture white lead in oil at Rhodes, (Homebush Bay) Sydney
1918	British Australian Lead Manufacturers (BALM) formed from 3 Broken Hill mining companies and 7 white lead corroders, after the purchase of Australian United Paint Company
1918	White lead exports from the UK were prohibited during WW1
1919	BALM bought the Australasian United Paint Co of Port Adelaide (according to Rowe, 1983)
1920	Prior to this time people generally made their own paints using imported pigments
1920	Solver paint started around 1920 in Adelaide
1921	BALM built a paint manufacture plant at Cabarita, Sydney
1922	BALM had 26 lead stacks for the manufacture of white lead at Cabarita on the Parramatta River (Rowe, 1983)
1923	Berger set up a factory in Wellington, New Zealand
1924	Some time after 1924, ICI took a 40% interest in BALM
1927	Around this time BALM and BHAS set up Commonwealth Litharge and Red Lead Pty Ltd. which appears to have been later bought by Dulux.
1928	Australian Chemical Holdings/AC Hattrick imported phenol formaldehyde resins
1928	Taubman had branches in 5 Australian states and NZ
1930	Taubman became involved with USA paint producer Pinchin Johnson
1932	Berger paint on the Sydney Harbour Bridge
1937	First recorded manufacture of alkyds by BALM

1937	Queensland Health Act (1937) restricted carbonate lead content of paint to 5% of total lead and prohibited the use of lead in paint on roofs
1938	ICI began the local manufacture of nitrocellulose
1940s	Taubmans manufactured ethylenedichloride and DDT
1940s	BALM discovered a quick process for the manufacture of white lead that replaced the 3-4 month acetic acid and tanbark lead corrosion process
1947	ICI obtained a 51% interest in BALM
1950s	Taubmans was Australia's 'second largest' paint company
1955	ICI obtained a 70% interest in BALM
1960	Wattyl became a public company, the third largest paint company in Australia (12% of market) Wattyl acquired Tafel-Shone, Usher, National Paints, Pioneer Chemicals, Kilrust, Davison and Spartan paint producers.
1962	Tasmanian Health Act (1962) prohibition of carbonate of lead in paint and restricted the total lead content of exterior house paint to up to 5%
1966	NSW Poisons Act (1966) paints containing > 1% Pb to be labelled.
1968	Berger took over British Paints
1968	Tasmanian Public Health (Paint) Regulations (1968) required the labelling of paints containing paints containing >1% lead.
1970	Berger became a wholly owned subsidiary of Hoechst
1971	BALM changed its name to Dulux Australia Limited
1986	ICI obtained 100% ownership of BALM

Some technological milestones in industrial coatings with a focus on paint vehicles and paint systems, according to the Australian *Oil and Colour Chemists Association* (1983), include:

1915-20	Phenolic varnish resins
1921-25	Low viscosity nitrocellulose Alkyd resins Anatase (TiO_2)
1926-30	Oil-soluble phenolics
1930-35	Urea formaldehyde-alkyd blends Chlorinated rubber Molybdate orange pigments Vinyl chloride copolymers Phosphating and metal pretreatment
1936-40	Phthalocyanine pigments Polyurethane resins Melamine formaldehyde-alkyd blends
1941-45	Styrenated, acrylated oils Rutile (TiO_2) Silicone Resins UV absorbers
1946-50	Epoxy Resins
1951-55	Light fast organic yellows, oranges, reds, maroons, violets Unsaturated polyesters Polyamide cured epoxies Powder coatings
1956-60	Acrylic automotive lacquers Thermosetting acrylic enamels Urethane oils Aqueous industrial primers Chloride process TiO_2 Coal tar epoxy

Recent paint technology milestones according to Gooch (1993, pp.35-36), were focused more on the developments relating to paint vehicles:

1900s	Kippling synthesized first polysiloxane. Rohm's PhD dissertation on polymerization of acrylic esters.
1901	Glyptal (thermosetting polyester) resins prepared by Smith from the condensation of glycerol and phthalic anhydride.
1907	Baekeland produced first ethanol-soluble novalac; used as a substitute for shellac.
1918	Amino-resins from urea and formaldehyde; patent application filed by John.
1920	Soluble copolymers of vinyl chloride and vinyl acetate; patent applications filed by Reid of Union Carbide, and Voss and Dickahauer of IG Farbenindustrie.
1921	Polyester resins improved by Kienle; applied unsuccessfully for patent for alkyd resins
1923	Cellulose nitrate (trade name Duco) lacquers used in automobile finishes.
1927	Alkyd name officially coined by Kienle for ester oils.
1928	Oil-soluble varnishes patented by Turkington; produced by alkaline condensation with para-substituted phenols.
1931	Glyptal and oleoresinous paint technology (oil-modified polyester resins) used by Kienle to produce superior polymers that were air-curable and more flexible than Glyptals; became known as alkyd resins.
1935	Ethyl cellulose first went into commercial production.
1937	Polyurethane resins originally synthesized by Bayer
1939	Ethyoxyline resins patented by Schlack; became known as epoxy resins.
1944	Polyvinylchloride plastisols were developed.
1946	First styrene-butadiene latex commercialized for paper-coating application; first patents on pigmented paper coating issued in 1954 to S. D. Warren.
1948	First styrene-butadiene latex sold for architectural-coating applications; prototype styrene-butadiene latex copolymer known as Dow latex 546.
1950	Multicolored cellulose nitrates developed.
1953	Powder coatings developed by Gemmer of Farbwereke Hoechst; granted a patent on the fluidized bed method of applying coatings using a powdered polymer. Ethyl acrylate and methyl methacrylate copolymer introduced as binders in house paints; the product was called Rhoplex# AC-33.
1954	Cellulose acetate butyrate resin introduced for general purpose uses.
1956	Acrylic esters replaced some cellulosic automobile coatings by General Motors.
1960	Cellulose nitrate-isocyanate resins introduced. Alkyd-cellulose nitrate blends with copolymers of vinyl chloride and vinyl acetate used. Electrospray gun for applying powder coatings developed by Eraser and Point.
1963	Cellulose nitrate lacquers ranked second among all industrial finishes.
1970	Powder coatings used in Japan on automobiles and to a lesser degree in the United States; powder coatings eliminated volatile organic compounds.
1980s	Powder coatings used extensively on appliances and automobiles as a substitute for enamels, thereby eliminating volatile organic compounds.
1990s	Powder coatings expected to grow to 286 million pounds in North America and 507 million pounds annually in Europe.

Another chronology is available in Dick (1987, p.209).

2.3 Pigment manufacture

Early pigment materials were raw minerals, ground and used on their own or mixed with other minerals. Simple processing such as calcining of pigments, reaction of metals to form oxides and carbonates, and the precipitation of pigment by reaction in solution may produce a range of compounds for use in paint formulation. While a manufacturing process may achieve a high efficiency in the conversion of material to a desired pigment phase, there is the potential for only 90 to 95% of the desired compound to be produced. For example, a range of lead carbonate mineral species might be encountered. Impurities in the raw materials or variations in process conditions may produce a range of different compounds (Table 6). Industrial quantities of pigment materials, particularly pre-1960 were of an industrial grade fit for a technical purpose and not single compound materials or 'chemically pure'. Pigment specifications and standards recognised this and often permitted the presence of a range of compounds.

Table 6: *Lead pigments, manufacturers and chemical compositions (Gooch, 1993, p196)*

Pigment	*Source*	*Composition*
White lead pigment (circa 1950s)	Dutch Boy Co.	1. $Pb_3 (CO_3)(OH)_2$ Lead carbonate hydroxide
		2. $PbCO_3$ Lead carbonate
		3. $Pb_{10}(CO_3)_6(OH)_6O$ Lead oxide carbonate hydroxide
		4. $Pb(BO_2)_2 \cdot H_2O$ Lead metaborate hydrate
White lead pigment (circa 1950s)	Glidden Co.	1. $Pb_3 (CO_3)_2 (OH)_2$ / 95-97% Lead carbonate hydroxide
		2. $PbCO_3$ / 3-5% Lead carbonate
Red lead pigment (circa 1950s)	Sherwin-Williams Co.	1. Pb_3O_4 Lead (II,III) oxide
		2. $Mg_3SiO_{10} (OH)_2$ Talc mica (silicate)
White lead pigment (circa 1970s)	Carter Chemical Co.	1. $3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$ Lead hydroxide carbonate hydrate
Red lead pigment	Carter Chemical Co.	1. Pb_3O_4 Lead (II,III) oxide

The commercial pressures to differentiate products in the marketplace, and the many possible routes to achieve similar bulk products will result in much variety in the mix of accessory compounds in pigment materials.

Variations in the origin and amount of processing of mineral and chemical raw materials may also have a strong influence on accessory compounds in a bulk pigment product as well as an influence on trace elements in bulk pigment samples and trace elements within pigment particles.

Accessory compounds such as lead acetate in the manufacture of white lead, may only have a small impact on the overall lead bioavailability of a particular paint sample, but the risk associated with accessory compounds cannot be overlooked. Particular methods for the precipitation of chromate pigment materials, for example, may increase the potential for the presence of hexavalent chromium or un-reacted hazardous starting or intermediate components in the final pigment.

2.4 The early water paints - whitewash

Previous sections have listed the chronology of technological developments of paint materials from a range of perspectives. One aspect of paints that is poorly documented in the literature appears to be that of essentially chalk and glue - water based paints and similar lime based paints. They have been unchanged in their essential characteristics for a long time. They are cheap materials and as all the ingredients are readily available, perhaps not seen as a major concern of those in mainstream commercial ready-made-paint manufacture.

Water paints were common pre-1960; they cannot be readily compared with what we know of oil and present water-based paints. They were commonly purchased as dry powder in a cardboard carton. The cheapest of these paints when used outdoors have to be regularly applied owing to the high rate of erosion of the paint surface. In some settings where 'water paints' are widely used, the concept of paint layers accumulating in thickness with each generation of painting, to make multi-layer paint films, may not be relevant. In such settings the rate of addition of paint components to soil may be elevated with respect to modern water-based and enamel paints.

Calsimine (also Kalsomine) made by the painter is based on whiting, (chalk, $CaCO_3$) and may also contain glue size, pigments for tinting, and water (Holloway, 1953, Vol.I, p.183). The problems associated with glue and for example casein in paint is that these components may sustain mould growth and there is a need for additives to combat this problem before and after application.

Distempers contain glue (DLNS, 1955) and are probably similar to calsimine.

Emulsion paints include components that don't normally mix and could be oil-in-water (or water-in-oil) emulsions and for example may contain, linseed oil, casein, water and pigment (DLNS, 1955, p.36).

Limewash, is essentially a lime-based thin cement wash, which may contain many of the components of emulsion or water paints and is not able to be painted-over by oil or water paints. It is difficult to remove and for that reason is a troublesome material to use (Holloway, 1953, Vol.I, pp.195-197).

Holloway (1953, Vol. I, p.192) distinguishes between the ordinary calsimine and the washable water paint. The washable material is not so readily removed, and the adhesion may be highly variable. Washable waterpaint poses greater risk of failure by cracking or peeling, as it has relatively poor surface adhesion properties causing problems particularly when additional coats of washable water paint are added on top of this or other material, and its use is associated with '*…some danger of premature failure'* (Holloway,1953, Vol. I, p.193).

Table 7: *Pigments compatible with lime or chalk-based waterpaint (Holloway, 1953, Vol.I, p.185).*

Sienna, raw and burnt	Dutch pink
Ochre	Ultramarine
Umber, raw and burnt	Cobalt blue
Vandyke brown	Viridian
Venetian red	Lime green
Indian red	Red oxide
Cadmium yellow	All the black pigments

White lead or lead chromate pigments are not likely to have been used in lime-based or chalk-based waterpaint but Table 7 lists some compatible pigments.

A later section on paint substrates lists a similar array of pigments that are compatible with cement, lime and plaster.

An early form of plastic paint was available in dry powder or paste form and thinned with water (Holloway, 1953, Vol. II, p.138) and used for thick, textured effects on surfaces. Such early water-based paints may not have been chalk-based. The textured plastic paints appear to have been the forerunners of water-based plastic, chlorinated rubber, PVC, PVA and latex paints which began to replace oil based paints for interior surfaces in the 1960s.

2.5 Pigments and paint formulation practice

Developing technology and the availability of new raw materials has had major impacts on paint formulation over time.

Atlas Chemical Company, Sunderland (1896, p.1) recommended for some pigments the calcining of rough ground mineral ores in a crucible, this mixture was then finely ground. Elsewhere (p.130) fine pigment powder was to pass a sieve containing 80 holes to the inch. Such was the simplicity of early processes.

The paint recipes from Atlas Chemical Company (1896) contain a greater number of formulations utilising bichromate of potash, antimony, chromium oxide, copper oxide and tin oxide than is seen in recipes from about the 1920s onward. This may reflect the more general practice at that time.

According to Cleary (c.1956, p.29), around 1911 in Australia, when the Berger company was operating a depot in Sydney *' White lead and linseed oil were the accepted bases with tradesmen painters; prepared paint was something only amateur painters indulged in'.*

In Australia prior to 1920 painters would mostly have mixed their own paints using imported pigments, due to the absence of local manufacture.

According to Jennings (1926, p.191) by 1926 the grinding of dry pigment in oils '*...is carried on by most of the large manufacturing paint houses, many of whom do not themselves make the dry pigments.*'

Vanderwalker (1944, p.76), notes that:

> *'At some time or other most painters and decorators wonder why they cannot make their own ready-mixed or prepared paints and save some money. They learn that formulas for these materials contain such inert materials as silica, barytes, whiting, asbestine or magnesium silicate; they note that prices on inert pigments are much less than for white lead and zinc, and wonder why they cannot make cheaper paints than they can buy from manufacturers.'*

The author then begins to make a case for the complexity of paint formulation. It appears that the period from the 1920s to the 1950s is one of major transition from paints primarily mixed on site with raw ingredients to paints primarily purchased in a more ready-made condition.

While early use of white lead was as dry powder, in the 1950s white lead was available as a paste, said to be *'...marketed in three different consistencies-stiff, medium, and soft-to meet varying requirements,…'* Holloway, (1953, Vol.I, p.208). Vanderwalker (1944, p.69) was still able to secure white lead as a dry powder, but:

> *'...it is more commonly used as a thick paste which is composed of 92 per cent white lead and 8 per cent linseed oil. Most of the white lead now sold to painters is in soft paste form (also called all-purpose white lead), which is much easier to mix than the older heavy paste lead. Soft paste contains approximately 85 per cent white lead and 15 per cent liquids - linseed oil and turpentine.'*

Basic lead carbonate pigment mixed with linseed oil and turpentine into a painting consistency and left to stand for some days, will be too thick, even after stirring, and will require the addition of more oil (Vanderwalker, 1944, p. 123).

Manufacturers of prepared paints were often just mixers and formulators of paints, dealing in a market with thousands of potential ingredients. Armitage (1967 p.105) considered that a large proportion of paint formulation work was *'...concerned with the examination of new products from raw material suppliers, which are offered in embarrassingly increasing quantities.*'

A useful list of colours associated with metal pigments is given in Crown (1968) *in The Forensic Examination of Paints and Pigments,* the next most comprehensive and historically useful listing may be Jennings (1926) *Paint and Colour Mixing* , and Vanderwalker (1944) *The Mixing of Colours and Paints,* some of which are reproduced in Appendices to this document.

Turczynowicz (1991, p.50), Burgess (1981, p.103) and Morgans (1982, p.282) give similar listings of pigments. Armitage (1967, p.116) states that *'Modern enamels usually have no extender, and relatively poor hiding power, the amount of titanium dioxide present being about 60-70% of the weight of solid binder.'* Such views indicate a lack of acceptance of 'modern' TiO_2 paints.

Table 8: *Typical pigment levels in liquid paints (Boxall and von Frauhoffer (1980, p.38)*

White		*Protective*	
Titanium dioxide	15-20%	Basic lead silichromate	25-35%
Zinc oxide	15-20%	Basic lead sulphate	15-20%
Antimony oxide	15-20%	Calcium plumbate	30-40%
White lead	15-20%	Red lead	30-35%
		Zinc phosphate	25-30%
		Zinc tetroxychromate	20-25%
		Zinc chromate	30-40%
Green		*Blue*	
Chromium oxide	10-15%	Prussian blue	5-10%
Lead chrome green	10-15%	Ultramarine blue	10-15%
Black		*Metallic*	
Black iron oxide	10-15%	Zinc	60-70%
Carbon black	1-5%	Lead	40-50%
Yellow			
Lead chromates	10-15%		
Zinc chromates	10-15%		
Cadmium sulphide	5-10%		

The critical pigment volume concentration is discussed by Patton (1964, pp.186-187). It is a point of compromise between a high gloss, low permeability paint susceptible to blistering and a permeable flat paint with insufficient connectivity of pigment by the binder component to protect the substrate from rusting or other decay. Levels of pigment in liquid paint are usually 10 to 30% (v/v) but can be as low as 1% and as high as 70%.

2.6 Pigment particle characteristics

The mean particle sizes of inorganic pigments according to Buxbaum (1993, p.14) '...lie in the range 0.01 - 10 µm, and are usually between 0.1 and 1µm.'

By another generalised account, paints can contain 20-60% by weight of pigment generally ground to less than 3 microns ranging from 0.5 to 10 microns (IARC, 1989).

Buxbaum (1993, p.24-25) notes how Mie's Theory predicts a maximum in light scattering at an optimal particle diameter, where for example titanium dioxide creates optimal scattering (550 nm wavelength) at some 0.2 ± 0.1 microns. This calculated scattering by titanium dioxide is some 3 times greater than that of zinc oxide and white lead which produce maximum scattering at some 0.5 ± 0.3 microns particle diameter. Such optimal pigment particle sizes are likely to be targeted during pigment manufacture.

TiO_2 pigment particles with a size less than or equal to '...0.2 µm scatter light of shorter wavelengths more strongly and therefore show a blue tinge, while larger particles have a yellow tone.' (Buxbaum, 1993, p.66).

Paint pigment particle morphology will be dependent on the crystallographic form of the pigment compound, and the degree of modification due to grinding or precipitation on the pigment particle surface.

An advance in the grinding and dispersion of pigments in the early 1950s is attributed to the sand or bead mill, (Armitage 1967, p.96 & p.99) developed by Du Pont. Buxbaum (1993, p.98) refers to jet milling (micronisation) as a particle size reduction method. In the examination of sequences of paint layers it is common to see more coarse pigment and filler particles for example in the range from 5 to 15 microns in older layers and in priming and undercoat layers. Asbestos was added to the paint to exploit the properties of its long, slender fibres.

Hess (1965, p.136) notes surface imperfections of 0.5mm can affect gloss and that while aggregates, agglomerates or flocculates of pigment can affect gloss, an effective means of obtaining flattness of finish is to employ relatively coarse inert particles.

While the possibility of pigment agglomeration as a consequence of paint formulation (Hess, 1965, p.88) has been raised, and the potential for agglomerates at 1 to 100Tm (p.136) noted, the prevalence of this phenomenon is unknown. Further, the degree to which most painters would routinely strain paint through stockings or sieves (Brindley, ca.1952, p.20) to remove 'pips' from new and 'used' paint is unknown. This is a matter of workmanship which in the past was an important step in order to obtain smooth glossy top coats.

The use of mixtures of pigment of differing morphology in the one formulation has appeared to have been a strategy employed in the past:

> *‘The shape of the ground-in pigments may also exert a certain influence, i.e. spherical-shaped pigments such as zinc oxide and splinter-shaped particles of barium sulphate if mixed together yield a much denser and more protective texture than if used unmixed. (M. Ragg.) The same applies to needle-shaped structures due to their felting tendencies (Depew) as long as they are not ground too finely or if they are very hard.’* [Hess, 1965, p.292]

Gloss paints and automotive paints are likely to have very finely ground pigment particles relative to, for example, flat paints, fire resistant paints and paints for concrete and masonry (Patton, 1964, pp. 208-209).

The distribution of lead in sandblasting residue, which includes the spent blasting abrasive, is such that no fine or coarse fractionation of lead occurs; it is distributed somewhat evenly across sieve sizes from <6300 to <53 microns (Weyand, 1991, p.879-880). However, knowledge of the sub-sieve size fractionation of such material is also required for risk assessment purposes.

2.7 After-treated and core pigments

Much development of pigment materials has been in the fields of pigment particle size control and the coating of pigment particles to impart required physical properties of durability for example. Details of surface properties are critical to the assessment of risks associated with pigment particles. Pigments such as lead chromates coated with thin layers of aluminosilicate material (measured in nanometres) may be of significantly lower risk than an uncoated particle. However, if the particle rind is weathered or leached, the ultimate risk may be similar.

2.8 World wide pigment utilisation

World consumption of inorganic pigments, for all uses, in 1989 is given in Table 9.

Table 9: *World consumption, in relative terms, of inorganic pigments in 1989 (Buxbaum, 1993, p.8)*

Titanium dioxide	69%
Synthetic iron oxides	11%
Carbon black pigments	9%
Lithopone	5%
Chromates	3%
Zinc oxide	1%
Chromium oxide	<1%
Mixed metal oxide pigments	<1%
Others	<2%

3. Lead pigments

3.1 White lead

3.1.1 Introduction

White lead is usually the basic carbonate white lead and is, or has been known as: Berlin White, Blanc de Plomb, Ceruse White, Corroded White Lead, Cremnitz White, Cremser White, Dutch White Lead, Flake White (also a Bi pigment), Kremser White, London White, Minium Album, Psmithium, Silver White, Slate White (Crown, 1968); and also Foundation White, Nottingham White and Snowflake White (Hess, 1965, p.363).

A pigment mixture known as reduced white lead, also goes by the following names, Dutch White, Hamburg White, Venetian White, and is a mixture of barium sulphate with increasing white lead in the ratios 80:20, 65:35 and 50:50 respectively (Crown, 1968).

White lead is reported as being $Pb(OH)_2{\cdot}2PbCO_3$ (Johnstone, 1954, Hunter 1957, Morgans 1982, Armitage 1967). In addition, Crown (1968, p.32) cites $3\text{-}6PbCO_3{\cdot}Pb(OH)_2$ and $4PbCO_3{\cdot}2Pb(OH)_2{\cdot}PbO$ as other variations of the composition. The precise composition of white lead materials is said to vary considerably according to the method of manufacture (Johnstone, 1954, p.237).

Until the 19th century white lead in linseed oil thinned with turpentine was the principal white paint formulation. Prior to 1920 the available white pigments were basic carbonate white lead, zinc oxide, leaded zinc oxide and lithopone. Atlas Chemical Company, (1896 p.129) consider that *'The basis, or most important ingredient in making the large majority of Paints is White Lead.'* This publication also reveals a use of litharge that is not seen in more recent work. In relation to white lead, Jennings (1926) describes the substance as *'...probably the best known and most largely used pigment in existence'* while also recognising that it was poisonous. Vanderwalker, (1944, p. 67) considered white lead pigment as having *'…been the backbone of the paint industry for over two hundred years'.*

White lead, and lead as a commodity, was once clearly the foundation of the paint industry. For example according to Vanderwalker (1944, pp.252-266), of a listing of 246 paint colours, there were 135 recipes which included white lead as an ingredient, and an additional 38 out of the 246 containing no white lead but other lead pigments such as lead chromates.

The Australian price for white lead in 1938 was 58/6 per hundredweight (1/20th of a ton) (Mayes, 1938, p.303).

3.1.2 White lead manufacture processes

Processes for the manufacture of white lead include the Stack or Dutch method, the Chamber process and the Carter process, according to Holloway (1953, VI, p.27), described as follows:

> ***Dutch Process;*** *'…metallic lead is molded into "wicket" or "buckle" form grids with longitudinal bars within a frame. These are placed in layers on platforms covered with spent tan in a room on the floor of which are open earthenware pots containing dilute acetic acid. A stack is built up of several platforms, each covered with spent tan. Then the room is sealed and the fumes rising cause the tan to ferment, which in turn acts on the lead and corrodes it into hydrocarbonate. The process is over in from 80 to 100 days. To activate the giving off of vapor, bars of lead are sometimes placed in the acetic. On removal the lead is ground between corrugated rollers, screened, ground in water, and then dried in stoves.'*
>
> ***Chamber Process;*** *'…the metallic lead is hung in thin strips over poles in a room which is then closed and suitable corroding gases introduced through stoneware pipes. Oxidation is complete in about eight weeks.'*
>
> ***Carter Process;*** *'…lead is reduced to a powder by means of high-pressure steam blasts, is then placed in wooden drums which are slowly revolved while dilute acetic acid and carbonic acid gas are introduced into them. After twelve days corrosion is complete, and a brilliant white, very fine powder is produced.' [Holloway, 1953, VI, p.27]*

Discussion of the Dutch process is also given in Jennings (1926) and with some detail in Morgan and Pratt (1938, p.149). In addition, Brindley (ca. 1952, p.220) mentions the chamber process, the electrolytic process and the modern Euston lead process. In the 1940s, the British and Australian Lead Manufacturers (BALM, later Dulux) are said to have discovered a quick process for the manufacture of white lead that replaced the 3 month acetic acid and tanbark lead corrosion process (Australian Academy of Technological Sciences and Engineering, 1988).

Variability in the properties of white lead may well be attributable to the impurities of the lead used as well as manufacture process:

> *'The production of the best quality basic carbonate white lead pigment requires the use of high-grade metal, usually described as "corroding lead." The presence in the lead of small amounts of copper or antimony gives the finished white lead a greyish tint and small amounts of silver may cause a pinkish discolouration. Bismuth tends to give greyish tints and its presence is usually not tolerated in amounts over 0.05 per cent. of the lead.'* [Johnstone, 1954, p.237]

3.1.3 Properties of white lead

Brindley (ca. 1952, p.220) notes the properties of white lead as producing '...a durable elastic paint film which weathers by gradually powdering away without becoming brittle or peeling.' This helps to minimise the cost of repainting lead-painted surfaces because powdering paints seldom require "burning off."

It is said that white lead rarely attains a pure brilliant white (DLNS, 1955, p.24), and yellow colouration is counteracted by the addition of a trace of ultramarine (Holloway, 1953, VI, p.27). The variability of colour of white lead from batch to batch is said to be able to be standardised with the addition of blue by Brindley (ca. 1952, p.220).

Holloway notes that 'If a white-lead paint is applied to a surface to which little or no light has access, the paint will become yellow, but will bleach out white again if exposed to the sunlight' (Vol.I, p.28).

Brindley (ca. 1952, p.220) notes that one disadvantage of white lead in addition to its toxic properties is its reaction to black lead sulphide in sulphur polluted atmospheres, producing 'dirty brown stains on the surface of the layer of paint.' Armitage (1967, p.67) does not describe brown stains but a serious yellowing of paints made from white lead due to the effect of industrial atmospheric pollution.

More fine grain size white lead pigment is described by Vanderwalker, (1944, p. 70) ‘Coach and Car Lead, is a very fine white lead ground in refined, bleached linseed oil. It dries hard and sandpapers without gumming'. Flake White, is dry white lead sifted to achieve very fine texture; the lead is ground and reground with refined, bleached linseed oil, and it is sometimes called Cremnitz white, blanc d'argent and silver white.

Not all pure white lead was considered equal. In 1944 Vanderwalker, (1944, p. 118) suggests that there were differences in covering and hiding ability between different brands, suggested to be due to varying proportions of carbonate and hydrate, and the relative fineness of the pigment particles. This variability is also noted by Brindley (ca1952, p.220) saying that the material '…varies in particle size and color, especially when prepared by the older methods.' Such variability may have some impact on the potential health risks of white lead liberated as dust, or wiped from chalking surfaces and have implications for the characterisation of white lead pigment material in house dusts.

Associated Lead Manufacturers Limited produced three standardised grades of white lead through the Octagon process, a High, Medium and Low stain, where the high stain material provided a '*decorative hard gloss finish'* (Martin and Morgans, 1954, p.53).

Chatfield (1962, p.159) notes that the structure of white lead, both chemical and physical (morphology) depended on the manufacture process. He also notes:

> *'If the quantity of normal lead carbonate is decreased and molecular constitution changed by increasing the basic compounds present - yet at the same time maintaining the (analytical) content of carbonate to lie between 66 and 72 per cent-then some control of particle size can be obtained, often in this way giving desirable pyhsical properties.'*

There were some standard specifications for white lead in later years. Part of the British Standard for white lead (BS 239) was for it to contain (after drying at 98°-102°C):

> *'not less than 99 per cent. of hydroxycarbonate of lead, which latter shall consist of not less than 20 per cent., or more than 37 per cent. of lead hydroxide chemically bound with not more than 80 per cent. or less than 63 per cent. of normal carbonate of lead.'* [Johnstone, 1954, p.238]

The Australian Commonwealth Engineering Standards Association (Specification K 9 - 1940) defined their white lead standard similarly specifying levels of 25 to 33% and 75 and 67% in place of the above ranges, and in addition requiring acetates calculated as acetic acid to not exceed 0.15 % (Johnstone, 1954, p.239).

In terms of particle size, raw white lead pigment could consist of no more than some 0.75% or 0.3% retained on a BSI 240 mesh sieve [63 micron] according to the above Australian and British Standards respectively.

A standard specification for white lead (ASTM, 1991, p.29) for dry pigment nominates the lead carbonate content at 62-75% and coarse particles retained on a 45 micron sieve at 1.0% maximum.

There is variability in the constitution of 'white lead' and this brought about a need for testing. An early method of testing the quality of dry white lead was to:

> *'...put half-a-pound in an unglazed cup and get a potter or glass maker to calcine it; let the cup be closely covered to keep out the dust. After being fired, the Lead if pure will be clear and transparent as glass. If it shows any spots, settlings at the bottom of the cup, or dead scum on top, it is certain that the sample contains some impurity,...'*

[Atlas Chemical Company, Sunderland, 1896 p.129]

Vanderwalker (1944, p. 70) describes field tests of white lead; *'You can cut a splinter of a match from a house painted with pure white lead twenty years ago, hold a match under it, blow it gently to increase the heat, and you will notice little beads of bright lead metal forming'*. Similarly white lead powder may be placed on the head of a match and ignited with another.. 'If the lead has been adulterated to any appreciable extent it will not reduce the lead metal.'

A similarly quick test is suggested by Holloway (1953, VI, p.28) where dilute nitric acid is added to white lead and material used to 'adulterate' the lead such as barytes will remain as a residue. White lead carbonate is soluble in acetic acid as is the lead oxide component of the mostly lead sulphate-based pigments (Scott, 1922, p.1189).

Methods for the chemical analysis of white lead, with the designation D1301 (ASTM, 1991, p.212) is an indication of the commercial use of white lead in the 1990s.

In relation to the yellowing of paints, it is noted in Hess (1965, p.358) that: '*The pigments used are also variable in their resistance,*(to yellowing) *white lead-oil paint being inferior to similar paints based on zinc oxide or titanium oxide, and the chamber process white lead being being worse than precipitated white lead.*'

Gooch (1993, p.100) considered that the US white lead production peaked in the 1920s, declined in the 1930s and increased again in the 1940s, saying that lead pigments declined in house paints in the 1950s.

In the US, the Sherwin-Williams and Eagle-Pitcher paint companies were said to have ceased the manufacture of white lead sometime prior to 1953 (Gooch, 1993, p.99) while National Lead continued producing white lead at least into the 1960s.

According an Australian source, DLNS (1955, p.24), *'The consumption of white lead has remained practically stationary in recent years, in spite of the enormous increase in the amount of paint used.'*

While not a direct reference to white lead, it is stated by Freeman (1970, p.647), who had extensive experience of paint lead in NSW, that *'…it is less than 15 years since titanium dioxide to a major degree replaced lead in paint…'.*

The UK published Paint Trade Manual (ca.1960s, p.66) notes the following as manufacturers or agents for white lead, basic carbonate:

Associated Lead Manufacturers

Blyth, Heald & Langdale Ltd

Lonabarc Ltd

Mersey White Lead Co. Ltd

Yorkshire White Lead Works Ltd

Armitage in 1967 (p.67) indicates that wood primers were still manufactured on a linseed-white lead base and Rawlinson and Partners (1969) in *Spon's Architects' and Builders' Price Book for Australia 1969* includes accounts of the area in square feet that may be covered by a gallon of red or white lead and oil. Thus in Australia in 1969 white lead cannot have been entirely out of use.

3.1.4 Imitation mother of pearl - white lead

The use of basic carbonate white lead, so as to imitate the nacreous lustre of pearl (guanine platelets) is described by Buxbaum (1993, p.208). The production of 50nm thick 20mm diameter hexagonal platelets is described (p.212).

In 1993, manufacturers of nacreous basic carbonate white lead pigment were listed as:

J Jaeger GmbH, Viechtach, Germany

Polipearl SA, Argentina

Semo Ltd, Seoul, South Korea

Sudarshan Chem. Ind., Pune, India

Dr Yang Chemical, Tainan, Taiwan [Buxbaum, 1993, p.208]

Also noted is the use *'From 1920 onwards of hydroxides, halides, phosphates, carbonates and arsenates of zinc, calcium, barium, mercury, bismuth, lead and other cations…'* as pearl pigments.

3.2 White basic sulphate of lead

The names given to lead sulphate pigments include: Freeman White, Basic Lead Sulphate, Milk White, Mulhouse White; and for basic lead sulphate pigments, include Bartlett White Lead, and Sublimed White Lead (Crown, 1968), and Freeman's lead, Silver lead and Purex white (Hess, 1965, p.363).

Holloway (1953, Vol. I, p.29) makes the following observation:

> *Until 1932 the description "white lead " was held to apply exclusively to white-lead carbonate, and when the term is used by itself, it is still, in the majority of cases, taken to imply this material. In the year in question, however, a decision taken in the course of a case in the law courts established the fact that basic sulphate could also be described as " white lead," though a qualifying phrase should be added to distinguish it from white lead carbonate.*

This outlines some potential for being misled by generalised descriptions of 'white lead' materials. Further description from that era reveals:

> *'This is a standard white pigment in the United States and approximates to the formula* $PbO \cdot PbSO_4$*. It is usually made, either by vaporizing high grade galena at a high temperature in the presence of air, or by spraying molten lead into a jet of ignited fuel gas and air in a special furnace into which sulphur dioxide is also introduced. …It is usually not such a good white colour as high-grade basic carbonate white lead, but it is claimed to be more stable in colour when used in exterior paints in cities where it is subject to sulphurous gases.*
>
> [Johnstone, 1954, p.239]

Lead sulphate, is made from the addition of sulphuric acid to acetate of lead in dilute solution, and is said to be whiter than lead carbonate, but with very poor hiding qualities (Crewdson, 1943, p.14) whereas sublimed white lead is a basic sulphate of lead obtained by the sublimation of lead ore. Holloway (1953, Vol. I, p.29) describes the sublimed white lead as being *'produced by melting lead ore, or galena, in a furnace and forcing draughts of air through it'.*

Basic sulphate of lead (Crewdson, 1943, p.14), is considered to be an excellent paint when mixed with other pigments such as zinc oxide or carbonate of lead and *'…especially suitable for surfaces that are subjected to conditions such as are to be found in sea-coast locations. Sublimed white lead is a pigment possessing excellent hiding power, and superior wearing qualities.'*

An analysis of a sublimed white lead pigment product based on the daily analysis of product over five months is 76.7% lead sulphate, 17.2% lead oxide and 5.8% zinc oxide (Scott, 1922, p.1178).

In Chatfield (1962, p.160) two alternative methods of production of $2PbSO_4 \cdot PbO$ are said to produce pigment of different molecular constitution and physical properties. The oxidation of lead ore or metal by SO_2 provides some control over the particle size of the pigment, whereas the dissolution of lead metal or oxide in H_2SO_4, provides a means of producing an acicular crystal form of basic lead sulphate.

Table 10: *Standards for basic sulphate white lead and blue lead in paint (Johnstone, 1954, pp. 239-240)*

	BS 637 : 1952 (white lead)	*ASTM specification D82-44 (white lead)*	*ASTM specification D405-41 (blue lead)***
PbO 'chemically combined'	not less than 15 % or more than 28%*	15 - 28%	minimum 35%
$PbSO_4$ 'normal'	not more than 85% or less than 72%	remainder excluding impurities	minimum 45%
$PbO + PbSO_4$	$PbO + PbSO_4$ constitute not less than 94% of the pigment		
ZnO	must not exceed 5%*	limited to 5%	
Other impurities	not > 1%	not > 1%	maximum 5%
Coarse particles	0.1% not passing 63 microns	maximum 1% not passing 45 microns	maximum 1% not passing 45 microns

*ZnO and PbO content varied by agreement between buyer and seller.

** Some error in the source text is likely as a maximum $PbSO_4$ of 5% in blue lead is stated.

3.3 Red lead paint

Vanderwalker (1944, p. 74) describes the manufacture of red lead by:

> *'…melting lead metal in a saucer - shaped kettle. When the lead is held in a metal solution for a certain time it takes up oxygen from the air and forms first a light yellow powder pigment which is litharge. More time and heat change the litharge to a brilliant red which is red lead. If the heat is maintained and the red lead subjected further to oxygen from the air it changes to a very brilliant red called orange mineral. Orange mineral is more commonly made by roasting white lead.'*

Red Lead (Pb_3O_4) is also simply described as being prepared by the oxidation of lead monoxide, (Armitage, 1967, p.67). The standards for red lead in Britain, Australia, Canada and USA (ASTM) are summarised in Table 11.

The anticorrosive action of red lead is described in Buxbaum (1993, p.201):

> *The electrochemical action of red lead results from the fact that lead has valencies of 2 and 4 in lead orthoplumbate: Pb(IV) compounds are reduced to Pb(II) in the cathodic region. The chemical anticorrosive effect is a result of lead soaps that are formed when fatty acids in the binder react with the red lead. The lead soaps permeate the paint film as lamellae, and give good mechanical strength, water resistance, and adhesion to the steel surface. Furthermore, the corrosion-promoting chloride and sulfate ions are precipitated by lead(II) ions.*

It appears that an undesirable property of red lead was for it to thicken, requiring mixing immediately before use; non-setting red-lead, containing greater than some 93% lead as Pb_3O_4 was introduced to combat this rapid setting tendency. A more recent introduction as at 1955 (DLNS, p.28) was the use of dispersive red lead where the pigment is *'…prepared in a particularly fine state of division so as to obtain greater spreading power and improved brushing quality.'*

***Table 11:** Summary of selected standards for red lead.*

	Australian Cwlth. Eng. Standards Assn.	*Canadian Govt. Purchasing Standards Committee*	*British Standards*	*ASTM*
	Specification K 19 of 1941	*Specification 1-GP-14-1946*	*Specification BS 217 : 1952*	*Specification D83-41*
Lead Oxide Content	minimum 99%			remainder
H_2O Soluble Matter	0.5%	(as impurities)	0.3%	(as impurities)
Impurities		not exceeding 1%		not exceeding 1%
Red Lead Pb_3O_4	• minimum 72% for setting pigment • 93 % in non-setting pigment	no less than 95%	• minimum 72% for setting pigment • 93.15 % in non-setting pigment	• 85% • 95% • 97%

Ready-mixed red lead paints from the 1940s to 1960s contain pigment having greater than 93% Pb_3O_4 or greater than some 84.3% Pb as Pb_3O_4 with the remaining material being other lead oxides. The greater the proportion of Pb_3O_4 the more red the colour. Lower grades were likely to be yellow-orange in colour.

A red lead primer formulation from Boxall and von Fraunhoffer (1980, p. 113) having a pigment concentration of 38% is:

Non-setting red lead	79.4%
Asbestine	4.0%
White spirit	2.0%
Acid refined linseed oil	13.9%
6% Cobalt napthenate	0.7%

The asbestine was added as a pigment suspending agent.

Red lead primers were often reserved for 'highly exposed' surfaces such as windowsills and doorway sills. Areas having exposed woodwork and that become cracked, prior to repainting, are commonly 'spot primed' with red lead primer for example. The common use of such primers may be an additional variable to consider in analysing dust in the vicinity of windows. While the lead content of top-coat paint materials had decreased in the 1960s the use of red-lead in primers was still high until the early 1970s.

According to Hess (1965, p.105):

> *'It is a general custom in countries with a damp climate, e.g. Great Britain, to prime all wooden window and door frames to be lined with masonry with a coat of white lead and red lead, in Holland mainly with red lead and barium sulphate, in order to protect them against penetration from moisture…'*

Red lead primers based on linseed oil are described by Boxall and von Fraunhoffer (1980, p. 113) as *'the finest anti-corrosive primers that can be formulated for on site application to mild steel'.* Red lead paint formulations have been strongly backed by British Standards. Building specifications even into the 1960's and 1970's will have specifically required particular paint formulations based on paint performance and the track records of products such as lead-based primers.

According to Brindley (ca. 1952, p.52) there appears to be some caution shown with respect to the use of red lead for rainwater collection surfaces in Australia, however, *'In cities with a separate water supply, the use of red lead as a first coat on roof work will be found quite satisfactory.'* A later undercoat roof paint formulation suggested a formula of 1 part red lead to 2 parts red oxide for such a non-water collecting roof. The alternative, for presumably rainwater collecting surfaces, (p.232) included the use of 3% Terebine (lead containing driers). Irrespective of intention to collect rainwater off roof surfaces, the overlapping surfaces of corrugated iron have in the past commonly been painted with red lead to prevent rusting. This is somewhat more noticeable in Port Pirie than Adelaide, from some 30 houses observed in each area.

Thirty years ago a roof may have been painted with red lead primer perhaps with knowledge of the associated risks, and no intention to drink rainwater, but new occupants to the house, unaware of the use of red lead, may choose to install a rainwater tank for the supply of drinking water.

An English architect, Prof. Lethaby, is cited in Kelly (1929, p.113) as favouring the use of 'pure colours', such as red lead and ochre and avoiding pigment mixtures, the impact of such taste or fashion on the choice of red pigments is unknown. Red lead is not known for colour permanence.

Hanson (1958, p.24) lists trades where red lead is used in Queensland, and notes that *'…as with white lead, the tide of history is running against the red lead advocates*' and makes the claim that Queensland Railways were rather backward in sticking to the use of red lead.

The blistering of red lead paint in sea water is said to be due to the formation of chlorine gas (Hess, 1965, p.107). According to Hess (1965, p.354) '*Exposed red lead films tend to form a whitish surface within a year'*. There is little information available on the relative bioavailability and fate of red lead and white lead.

According to Hunter (1957) the London Tower Bridge used 25 tons of lead paint each year and the Sydney Harbour Bridge used 90 ton of red-lead and 250 tons of battleship grey at each painting. Very large quantities of lead can be expected to be liberated if there is any uncontrolled or 'historical' sandblasting of bridges and other old structural steel items.

Red lead was widely used into the early 1970s in Australia, and is readily found on galvanised iron fences, on the laps of a galvanised iron roof, as a primer on timber window sills and on the hulls of wooden boats for example. Red lead painted domestic surfaces appear to be more apparent in settings where such paint had continued to be available through local industrial sources. It is not uncommon to see red lead still being applied by generally more elderly people who may have acquired a can of this paint some 20 or more years ago.

3.4 Sublimed blue lead

> *'A variety of basic sulphate of lead collected from the fumes arising from lead smelting has a bluish colour due the presence of a small amounts of sulphide of lead and carbon. It is known in the United States as "blue lead basic sulphate" and is stated to be useful for coating metallic surfaces.* [Johnstone, 1954, p.239]'

Sublimed blue lead is described by Crewdson, (1943, p.14) *'…mixed with pure linseed oil and not too much drier, it makes an ideal rust-proofing paint for all metal surfaces, and will form a coating the elasticity of which is far above that required by any deformation that can take place by expansion or contraction of the metal to which it is applied.'*

3.5 Calcium plumbate

This beige pigment, Ca_2PbO_4, has an important use in the coating of galvanised steel, where 'The pH change occurring on hydrolysis of the calcium plumbate etches the zinc surface which improves adhesion of primers…' (Buxbaum, 1993, p.202).

Calcium Plumbate, $2CaO{\cdot}PbO_2$, is formed by the heating of calcium hydroxide and litharge at 700° C for 8 to 10 hours (Morgans, 1982, p.120). It appears to have been used very successfully on galvanised iron, and its use may have been due to its ability to pass lead solubility tests and the desire to find 'less soluble' lead-based paints in addition to being more rapidly manufactured relative to basic carbonate of lead.

Chatfield (1962, p.436) notes claims having been made as to the cathodic and anodic inhibition provided by calcium plumbate, but considered information on the mechanism of protection and intermediate products formed was needed.

3.6 Lead titanate

Dry lead titanate pigment material consisting of 88% $PbTiO_3$, 9% $PbSO_4$, and 1% PbO (Table 12) will contain 67.2% elemental lead.

Table 12: *The ASTM D 606-42 standard specification for Lead Titanate ($PbTiO_3$) pigment (Johnston, 1954. p.565)*

Lead titanate ($PbTiO_3$), min.	88.0 %
Lead sulphate ($PbSO_4$), max	9.0 %
Lead monoxide (PbO), max.	1.0 %
Total titanium calculated as TiO_2, min.	23.0 %
Titanium dioxide (TiO_2), uncombined, max.	3.0 %
Matter soluble in water, max.	1.5 %
Moisture and other volatile matter, max.	0.5 %
Coarse particles on a 44 micron sieve, max.	1.0 %

Lead titanate is said to be commonly used in primers and in architectural finishes in Holland (Crown, 1968, p.36). A lead titanate pigment called Titanox L is listed by Hess (1965, p.216).

Analogous to the lead titanates are the lead silicates. *A nontoxic paint prepared by first forming a chelated compound of Pb and then incorporating it into an oleo-resinous paint vehicle* according to inventors Mount and Walker in 1958 may be typical of a desire to maintain a use of lead in paint (abstract 4074 in Campbell and Mergard, 1972, p.777) and remain within the requirements of legislation. A basic Lead Silicate pigment, first available in 1947 (Crown, 1968) consisted of a SiO_2 core with a rind of $PbSiO_3$ and $2PbSO_4 \cdot PbO$. This composition would appear to be a response to concerns about health aspects of white lead.

3.7 Lead chlorides in paint

A listing of pigment materials containing lead by Hess (1965, p.215-216) include a number of pigment names for oxychloride of lead, Cassel yellow, English yellow, Mineral yellow, Montpellier yellow, Patent yellow and Turner's yellow. A basic chloride of lead, named Pattinson white lead was also listed, and also mentioned (p.363) was Verona yellow and Caledonian white (chloro-sulphite).

Lead chlorides in paint are unlikely to have been extensively used. Perhaps it is found in a number of regions where availability of raw materials, local manufacture and customary use existed. The alteration of lead pigment particles at the paint surface, or in the soil to lead chlorides may be a localised phenomenon in near-sea settings.

3.8 Lead chromates

> *'Lead chromate ($PbCrO_4$) is usually prepared by the addition of a sodium dichromate solution to a solution of a lead salt or a suspension of a less soluble lead compound. The colour varies from green-yellow to yellow-red. The pigment exists in two crystalline forms, the rhombic form being stable at room temperatures. Co-precipitation with lead sulphate gives primrose and lemon hues; precipitation in alkaline conditions gives rise to a basic salt $PbO \cdot PbCrO_4$ with a redder shade. Co-precipitation with lead molybdate produces a scarlet pigment. The ternary precipitation of lead chromate, lead molybdate and lead sulphate is also known'.* [Armitage, 1967, p.68]

***Table 13:** Manufacturers and their treatments to improve chrome yellow pigments.(Buxbaum, 1993, p.119)*

Company	*Material added*	*Characteristic improved*
DuPont	silicate and alumina	Temperature, light and chemicals
DuPont	metal oxides of Al, Ti, Mn	Lightfast
Bayer	silicate containing solutions of $Sb^{(III)}$ $Sn^{(II)}$ or Zn compounds	-
ICI	Sb compounds and silicates	Light and weatherfast
Ten Horn	-	Low acid solubility
BASF	silicate coating by the hydrolysis of magnesium silicofluoride	Temperature stable
Heubach	alternate precipitation of metal oxides and silicates	Good temperature resistance and low acid solubility

Lead chromate, $Pb(Cr,S)O_4$ is known as chrome yellow. The pigment is insoluble in water but soluble in acids and alkalis and is discoloured by hydrogen sulphide and sulphur dioxide and can have poor lightfastness and darken due to redox reactions (Buxbaum, 1993, p.118). DuPont, Bayer, ICI, Ten Horn, BASF and Heubach all have aftertreatment or production processes for chrome yellow pigments rendering them more stable (Table 13).

The degree to which these coatings moderate human health risk by, for example, minimising gut absorption is not comprehensively documented. Particle coatings are probably responsible, at least in part, for the poor detection of lead in lead chromate paints using test reagents such as sodium rhodizonate and weak leaching solutions.

In terms of risk modification the processes of Ten Horn and Heubach in Buxbaum (1993, p.119) are interesting:

> *Ten Horn describes a process for the production of lead sulfochromate containing at least 50% lead chromate* [J.J. Einerhand *et.al.* (1976)]. *This has a low acid-soluble lead content (<5% expressed as PbO, by BS 3900, PartB3, 1965).*

and

> *Heubach has developed a process for the alternate precipitation of metal oxides and silicates* [Ressler *et.al.* (1988 & 1989)]. *A homogeniser is used to disperse the pigment particles during stabilisation. Products obtained have a very good temperature resistance and very low lead solubility in acid (<1% Pb by DIN 55 770, 1986 or DIN/ISO 6713, 1985).*

While the application of chromate coatings is mostly an industrial coating process, it is referred to here due to its widespread use in WWII and subsequently. According to IARC (1989) zinc chromate coatings were little known before 1914 but widely used during WWII.

'Chromate conversion coatings were widely used during World War II for protection of zinc and cadmium plated parts in tropical service.' (Burns and Bradley, 1960, p.552). The "Cronak" process chromate coatings are deposited in a bath containing hexavalent chromium and mineral acid to form a film that may contain 8.68% hexavalent chromium and 28.2% trivalent chromium. Such films may vary in colour from olive drab to iridescent yellow to clear.

There is little explicit evaluation of the proportion of and fate of hexavalent chromium in household and other paints as well as the risk which may be posed by Cr^{VI} in paint. Standard methods (DIN 53780) for the determination of water and 0.1 mol/L HCl soluble Cr^{VI} in paint are cited in Buxbaum (1993, p.4 & 16).

Despite a lack of instruction as to water quantities or instruction as to whether the raw pigment is then dried and ground, the following is instructive in outlining an 1896 formulation of Lemon Chrome:

> *24 pounds of Nitrate of Lead powdered and dissolved in hot water in a wood cask; then in another tub dissolve 6 pounds Bi-chromate of Potash in hot water; then dissolve in an iron drum 6 pounds of Crystal Soda in hot water, and in another drum 6 pounds Glauber Salts, then let it stand one day to cool.*
>
> *After cooling mix Salts and Soda together and throw into the Bi-chromate of Potash, then add 1 part of this mixture to 3 parts of the Nitrate of Lead mixture and put into a pinewood cask.*
>
> *Get 24 pounds of Terra Alba (White Earth) made into a paste with cold water and add to the above mixture and stir well. This is genuine Chrome it can be still reduced by adding more Terra Alba up to 56 pounds for the same quantity of mixture.*
>
> [Atlas Chemical Company, Sunderland. 1896 p.154-155]

It would be instructive to collect recipes for making lead chromate and recreate the products and determine what likelihood there is of generating hexavalent chromium and readily bioavailable lead co-products.

In the final stage of production of lead silicochromate, (Buxbaum, 1993, p.198), the following reaction takes place to produce a rind on the surface of silica cores:

$$4(PbCrO_4{\cdot}4PbO) + 3SiO_2 \rightarrow 4(PbCrO_4{\cdot}PbO) + 3(SiO_2{\cdot}4PbO)$$

A pigment consisting of 47 wt.% PbO, 5.4wt.% CrO_3 and 47.6 wt.% SiO_2 is formed.

Buxbaum (1993, p.121) considers Chrome Orange ($PbCrO_4{\cdot}PbO$) to be no longer of technical or economic importance. He notes that the particle size and thus the hue of chrome orange could be varied between orange and red. It has been a popular pigment.

4. The mixing of lead and zinc in paint

In relation to the mixing of zinc oxide and white lead:

> *'For interior paints the question of durability doesn't enter, when mixing enamels, enamel undercoats and paints; but for exterior house paints which are subjected to temperature changes, sun, wind, rain, hail and frost, too much zinc may make a paint film so hard and inelastic that it will crack and scale off. White paint used on the sea coast and subjected to moist, salt air continually is especially in need of 15 or 20 per cent of zinc to 85 or 80 per cent of white lead.'* [Vanderwalker, 1944, p. 114]

Holloway (1953, Vol I, p.29) notes that:

> *Leaded zincs are prepared in the same way as is basic sulphate of lead, the galena being replaced by mixed ores of lead and zinc. The proportions may be varied. The product is generally sold in paste form, and it is claimed that it combines the qualities of white lead and zinc oxide.*

Leaded zinc oxide consisting of ZnO and $PbO{\cdot}2PbSO_4$ is marketed in grades of 5, 15, 35 and 50% lead sulphate (BS 1481, Table 13) and:

> *'…can be used in combination with lithopone, titanium oxide, barytes, whiting, asbestine and floated silica for both house decoration and for the protection of metal structures. It is often made by heating a mixture of galena, zinc ore and coal in a reverbatory furnace where it is further oxidised. The product is next desulphurized and whitened.' … 'During World War II, the production of leaded zinc oxide increased considerably, mainly owing to the fact that it could be produced directly from the ore. Roughly about 80 per cent. of the product contained between 5 and 35 per cent. lead sulphate, whilst the 35-50 per cent. grade accounted for about 10 per cent.'* [Johnstone, 1954, p.646-647]

***Table 14:** BS 1481 for leaded zinc oxides, 1952. (Johnstone, 1954, p.759)*

	35 per cent. leaded	*25 per cent. leaded*	*15 per cent. leaded*
Zinc oxide, ZnO %	62-67	72-77	82-87
Basic lead sulphate, $PbO{\cdot}2PbSO_4$ %	31.75-36.75	21.75-26.75	11.75-16.75
Impurities, excluding moisture and volatile matter, max. %	1.25	1.25	1.25
Volatile matter at 98-102°C., max %	0.75	0.75	0.75
Matter soluble in water, max. (Aqueous extract must be neutral to methyl red) %	1.0	1.0	1.0

[The ZnO and $PbO{\cdot}2PbSO_4$ may be co-fumed (eg direct from ore) or a physical blend of the components.]

A selection of leaded zinc oxide paint formulae are given in The Chemical Formulary (1943, Vol. VI, p.276-278).

In 1958, according to Kent (1962, p.759):

> *Approximately 15 per cent of the zinc oxide pigment used in 1958 was "leaded" zinc oxide. This pigment is essentially a mechanical mixture of zinc oxide with 5 to 50 per cent of either lead sulfate or basic lead sulfate.*

Hess (1965, p.216) noted a grey coloured pigment material called Zinc oxide (grey) containing 5 to 7 per cent. lead sulphate.

It appears that while white lead use was declining there was use of substantial quantities of lead in lead-zinc pigment mixtures largely based on zinc oxide and lead sulphate. No account of the use of lead sulphate in Australian paints has been located. The use of proportions of lead sulphate so the paint film would pass the weak acid solubility criteria of <5% Pb calculated as PbO (4.65 wt. % Pb) is possible.

5. Zinc in paint

5.1 Zinc oxide

'In 1796 a specification suggested the use of zinc oxide in paints as an alternative to white lead, although commercial exploitation of this pigment was not to become important for another 50 years' (Armitage, 1967, p.9).

According to Brindley (ca.1952, p.220) the zinc oxide pigment is known for its intense whiteness and sometimes a slightly bluish cast. In proximity to sulphurous fumes it is affected but does not discolour in the manner of white lead.

Armitage (1967, p.67) records that zinc oxide pigments were exported from the UK to tropical and sub-tropical countries owing to its fungus-resistant properties. Boxall and von Fraunhoffer (1980, pp.31-32) consider that some 30-40% ZnO in paint will provide fungicidal properties. Armitage (1967, p.67) suggests that the particle size of zinc oxide may vary from 0.1 to 0.5 microns.

The pigment crystal morphology is said to play a role in the brittle fracture of zinc oxide:

> *'The use of the acicular form of zinc oxide (American process) leads to a very considerable improvement and gives much more durable paints than the amorphous (French process) zinc oxide which consists of small round particles. "Instead of the end of their life being signalised by the usual checking of the film, such paints showed no signs of it and finally began to disintegrate much later by chalking."* [including a quote from Jolly in Hess, 1965, p.242]

And further;

> *'…in the case of acicular zinc oxide paint, failure "begins with small uniform cracking which relieves strain and prevents more intensive failure", and that very high acicularity is undesirable because it involves too high an oil absorption.*
>
> [including a quote from Eide & Easley in Hess, 1965, p.242]

The benefits of amorphous zinc oxide pigment particles, are said to be better gloss and suspension properties (Robertson in Hess, 1965, p.242).

The poorest physical property of zinc oxide pigment is where the *'peculiar hardening action of zinc upon the various binding oils created a tendency for the paint to become brittle and deteriorate by peeling or flaking.*' The development of oils which were *'more elastic and less prone to harden than raw linseed oil'*, along with combining pigments were measures against the peeling tendency. Brindley (ca.1952, p.220) also notes the common mixing of white lead and zinc oxide and titanium white and zinc oxide and notes the modification of characteristics, *'for example the brittle nature of the zinc is countered by the powdering action of the lead.'* And it is also noted that *'For some time after the war, there were a number of grades of zinc white which had the weakness of "chalking" excessively'.*

> '*Zinc oxide is claimed to be the only white pigment that appreciably absorbs ultra-violet light. '...It also reinforces the paint film mechanically and combines with drying oils to form tough, flexible films which delay chalking. Zinc oxide is used in conjunction with other pigments, such as those containing lithopone, antimony or titanium, for hard gloss paints and in iron oxide paints for metal protection… Successful formulations of such* (zinc oxide - lithopone) *pigments depends upon balancing the chalking tendency of lithopone against the hardening effect of zinc oxide, i.e., to reduce chalking without introducing cracking failure. The correct balance is frequently obtained more easily by the judicious use of mineral extenders'.* [Johnstone, 1954, p.645]

Embrittlement of paint films is largely blamed on zinc oxide but, alkyd enamels are also implicated:

> *'Films of alkyd enamels may become brittle prematurely if their pigments consist largely of white lead or of a zinc oxide with high lead content. The same observation has been made with regard to some kinds of umbers.'* [Bauer in Hess, 1965, p.242]

The effect of zinc oxide is said in Hess (1965, p.242) to have a '*...hardening effect on films of various media, especially on highly polymerised oils.*', whereas most general accounts do not recognise 'paint binder - zinc oxide - embrittlement' associations.

British Standards for zinc oxide pigments BS 254 : 1952 (Table 15) included the possibility of 3% PbO in bulk zinc oxide (2.8% Pb).

Table 15: *BS 254, 1952 for zinc oxide pigments (Johnstone, 1954, p.646)*

	Type I	*Type II*
Zinc oxide, min.	99 %	95 %
Lead calculated as oxide, max.	0.3 %	3.0 %
Matter soluble in water, max.	0.5 %	1.0 %
Volatile matter at 98-102°C., max.	0.5 %	0.5 %

Buxbaum (1993, p.82), notes a classification of more recent grades of zinc oxide (Table 16) wherein given the possible cadmium concentrations, the cadmium content of older ZnO pigments would be important to evaluate.

Table 16: *The process path produced variations in ZnO pigments (Buxbaum, 1993, p.82)*

		A *Indirect process*	B *Indirect process*	C *Direct process*	D *Wet process*
ZnO (min.)	wt%	99.5 %	99%	98.5%	93%
Pb (max.)	mg/kg	40	2500	2500	10
Cd (max.)	mg/kg	10	500	300	10
Cu (max.)	mg/kg	5	30	50	10
Mn (max.)	mg/kg	5	10	50	10
Water Soluble Salts (max.)	wt%	0.02%	0.1%	0.65%	1%
Loss on ignition (max.)	wt%	0.3%	0.3%	0.3%	4%
Specific Surface Area	m^2/g	3-8	3-10	1-5	25 (min)
Acidity,	g H_2SO_4/100g	0.01	0.1	0.3	0.2

Clearly, not all zinc oxide is the same.

In a discussion of the more recent grades of zinc oxide and the addition of ZnO, at a mean particle diameter of 0.11 - 0.22 micron, to priming formulations, Buxbaum (1993, p.203) states '*The lead content of commercial zinc oxide depends on the manufacturer and is in the range 0.002 - 1.5%.*' *For a zinc oxide coating to be considered lead-free, the lead content must be less than 1.5%.'* Clearly, past practice has shown that the lead content of industrial grades of ZnO can readily exceed 1.5%.

American specifications for dry zinc oxide (ASTM, D79-44) and 35 % dry leaded zinc oxide (ASTM, D80-41) are similar, notably zinc oxide has no specified lead contents and where prepared by the American (direct) Process (the reduction of roasted ore by carbon and the oxidation of resultant zinc vapour by air and CO_2) may contain 2% impurities and by the French Process (using metallic zinc as a starting material) 1% total impurities. Pigment produced by the American Process will have a higher percentage of lead than that from the French (indirect) process according to (Johnstone, 1954, p.645-647). Buxbaum (1993, p.80) notes the use of zinc concentrates, metallization residues, by-product zinc hydroxide and zinc dross from casting furnaces or galvanising as raw materials for the American process. A wet process, where precipitated basic carbonate is washed, filtered and calcined, is a method for producing ZnO with a high specific surface area (Buxbaum, 1993, p.81).

Zinc oxide paints are hard and when they fail they do so by cracking.

According to Crewdson, (1943, p.15), the qualities of zinc oxide pigment are as follows:

- very fine texture
- practically unaffected by chemical reaction when mixed with other pigments
- extremes of outdoor temperature cause failure in zinc oxide only paint films
- brittle failure tendency can be overcome with mixing with a large percentage of white lead

The production of 0.1mm to 0.5mm euhedral and acicular ZnO pigment particles is described by Chatfield (1962, p.160).

> *Zinc oxide pigments, particularly the acicular grades and the co-fumed acicular zinc oxide, basic lead sulphate and lead silicate pigments, possess good tint retention properties, probably due to the high U.V. absorption. The inclusion of a small portion of zinc oxide in rutile titanium whites used for tinting purposes can give improved tint retention. This may be due to a combination of U.V. absorption and to the delay of breakdown by chalking. The use of high concentrations of zinc oxide, however, may lead to a hardening effect which causes breakdown by checking and cracking.*

> *The fading of dyestuff titanium white mixtures in light can sometimes be reduced by addition of zinc oxide (H. Wagner).* [from Hess, 1965, p.355]

Sulphurous fumes have an effect on zinc oxide, but, such degradation is nowhere near as common or deleterious as the attack of SO_2 on white lead:

> *'Atmospheres containing sulphurous acid (sulphur dioxide) may even attack paint films containing suitable percentages of zinc oxide (Hallet).'… 'Water-soluble zinc sulphate is formed thereby, and this compound is washed out of the film by rain, inducing discolouration.'*
>
> [Hess, 1965, p.272]

The use of chalk resistant grades of rutile in an alkyd-resin media may be incompatible with zinc oxide according to Hess (1965, p.310). The use of such rutile and paint binders and the reduction of use of zinc oxide to mediate the weathering of paints containing white lead may explain a reduction of zinc oxide, in any quantity (>1% say) as evident to the writer from analyses of post 1960s paints. With the use of less zinc oxide, may come the need for other UV absorbing additives, other components with antifungal properties and other additives to increase the hardness of the paint film where those properties are required.

6. Lithopone

White pigments based on zinc sulphide were first developed and patented in France in 1850 (Buxbaum, 1993, p.71). According to Crown, (1968, p.29) lithopone was discovered in 1847, produced commercially in 1874, with light fast types being produced since the 1920s. Lithopone, was first prepared in the 1870s according to Hounshell and Smith, (1988, p. 209). According to Jennings it was invented in 1880. Chatfield (1962, p.161) notes the probable discovery in mid nineteenth century, and the introduction of a calcining process in 1874 in the UK.

Lithopone is also called 'Enamel White', 'Diamond White', 'Chinese Permanent White' 'Albanol' 'Graves White', 'Griffith's White', 'Jersey Lily White' 'Knight's White', 'Ponolith', 'Snow White' 'Zincolith' (Crown 1968, p.210) and in earlier times was known as 'Charlton White', 'Orr's White' and 'Beckton White' according to Jennings (1926, p. 312), 1st edition, 1902).

Jennings (1926, p. 312), 1st edition, 1902), gives some indication as to the adoption of lithopone during the 1890's '... ten years ago very few paint manufacturers used it at all...' and '...within the last seven or eight years lithopone has come into its own...'.

In discussing the use of lithopone, Kelly (1929, p.121) notes, 'It is the whitest paint, it is cheaper than white lead, and is non-poisonous.'

The use of lithopone appeared to peak in the 1920s and 30's and in the white pigment market: 'The share of lithopone, a coprecipitate of 28-30% zinc sulfide and 70-72% barium sulfate, introduced before the First World War, rose to 60% by about 1928 but fell to 15% by 1945.' according to Brunner, (1978, p. 592) and IARC, (1989, p. 330).

Lithopone is produced by the interactions of solutions of zinc sulphate and barium sulphide which results in the co-precipitation of zinc sulphide and barium sulphate.

The proportions of $ZnSO_4$ and BaS can be varied (Buxbaum, 1993, p.73) so as to produce co-precipitates as follows:

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4 \qquad (29.4\text{ wt.\% ZnS})$$

$$ZnSO_4 + 3ZnCl_2 + 4BaS \rightarrow 4ZnS + BaSO_4 + 3BaCl_2 \qquad (62.5\text{ wt.\% ZnS})$$

The reaction to 62.5 wt% ZnS appears to have had limited application, based on the overwhelming reference to 29% ZnS in lithopone.

According to Johnstone (1954, p.643) in order to achieve a good white colour the raw materials have to be relatively impurity free; problems occur with:

Pb, Cu, Mn	rapid greying of the pigment
Fe, Co, Ni	greying occuring slowly
Cd	yellow tints
Mn	brownish tints
Sb, Th	may give reddish tints

Buxbaum (1993, p.73-75) notes the use of zinc in pickle liquors from galvanising plants, zinc dross and other sources where impurities such as Fe, Ni, Cr, Mn, Ag, Cd, Pb, Cu, Th, In are removed so the ZnS will not grey in sunlight.

Cobalt may be incorporated in the ZnS lattice at 0.02 to 0.5% in order stabilise the final product against light (Buxbaum, 1993, p.74); this is noted more generally in Chatfield, (1962, p.161).

Hess (1965, p.359) notes that: *'If lithopone in a paint is not perfectly fast to light, exposure to sunlight may cause blackening of the white films due to the formation of finely distributed zinc.'* And it is further noted that lithopone is not preferred for outdoor application and if used should be a light fast form and not the sole paint pigment in use.

Due to the fact that it had better properties as a flat paint and early formulations changed colour in sunlight, lithopone pigments were commonly used in interior paint. Brindley (ca.1952, p.221) notes that '*Early forms of this pigment tended to turn black on exposure to strong light, but that weakness has been more or less eliminated.'* and that *'…its use in exterior paints has been limited because of its affinity to water. This brings about the saponification of the oil binder.'*

Holloway (1953, Vol.I, p.30) describes lithopone as having the body equal or superior to white lead and as being certainly superior to white lead in its ability to be spread over a large surface. It is however a pigment that cannot be used outdoors, breaking down, under normal conditions after about a year (Holloway,1953, Vol.I, p.30). During early use of the pigment it was commonly known to darken to a deep grey/dull lead colour after a few hours exposure to sunlight and to resume its original whiteness at night time.

Such criticisms of lithopone are not reflected by Gooch (1993, p.96-97):

> *By 1920, New Jersey Zinc had introduced a light, stable lithopone that provided good quality at low cost (Protective and Decorative Coatings, 1941). In 1924, Glidden introduced Zinc-O-Lith®, a lithopone product, as a new kind of house paint. In European countries where the use of white lead in paint was prohibited, a product similar to Zinc-O-Lith®, which produced the same results at a lower cost, was used (Haynes, 1945-1956). Lithopone production surpassed white lead in 1926 and peaked in 1929 (Lead and Zinc Pigments, 1955). During this period, both types of pigment were used primarily in paint (85% of all white lead and 75% of all lithopone), but lithopone cost one-third to one-half less than white lead and when mixed with zinc oxide and calcium carbonate, it could be used on exterior surfaces as well. In addition to its nontoxic qualities, lithopone was cheaper to use in paint than white lead.*

***Table 17:** Lithopone pigment specifications according to ASTM D477-45* and part of BS 296:1952 (Johnstone,1954, p.644).*

	Lithopone BS 296:1952	*Lithopone**	*Titanated Lithopone**
Barium and Zinc Compounds	not less than 99 %		
Zinc sulphide, min.	26-32%	26 %	-
Zinc oxide, max.	1 %	1 %	1 %
Zinc sulphide + TiO_2, min.		-	35 %
Titanium dioxide, min.		-	13 %
Matter soluble in water, max.		0.8 %	0.8 %
Moisture and other volatile matter, max.	0.5 % & 0.5 %	0.5 %	0.5 %
Barium sulphate, min.	remainder	95 % of remainder	95 % of remainder
Strontium sulphate	up to 5% of lithopone		
Coarse particles retained on a 44 micron sieve, max.		1 %	1 %

USA Specifications for zinc sulphide pigments do not refer to any lead compounds (Table 18).

***Table 18:** USA specifications for zinc sulphide pigments according to ASTM D477-45. (Johnstone 1954, p.644)*

	Zinc sulphide	*Zinc sulphide barium pigment*	*Zinc sulphide magnesium pigment*
Zinc sulphide, min.	97 %	45 %	45 %
Zinc oxide, max.	1 %	1 %	1 %
Alumina, max.	-	-	5.5 %
Matter soluble in water, max.	1.5 %	0.8 %	1.0 %
Moisture and other volatile matter, max.	0.5 %	0.5 %	1.0 %
Barium sulphate, min.	-	95 % of remainder	-
Magnesium silicates, with or without added micaceous silicates, min.	-	-	95 % of remainder
Coarse particles retained on a 44 micron sieve, max.	1 %	1 %	3 %

While ZnS has had use in lithopone and fluorescent paint, information indicating other modes of use of ZnS as a pigment were not located.

Countries producing lithopone in 1990, listed in order of increasing quantities, were Yugoslavia, Czechoslovakia, Germany, Soviet Union and Peoples Republic of China (Buxbaum, 1993, p.78).

The optimum size of barium sulphate and zinc sulphide is suggested by Chatfield (1962, p.161) to be controlled in the calcining stage, Buxbaum (1993, p.75) uses an illustration of lithopone having 1.0µm barium sulphate and 0.3µm diameter zinc sulphide particles.

7. Titanium Dioxide

7.1 Introduction

> *Although it was introduced shortly after 1918, it* [titanium dioxide] *was not used widely because of its high cost. The first titanium dioxide pigment was a composite of 30% titanium dioxide (anatase crystal structure) and 70% barium sulfate. ... by 1945* [TiO_2] *represented 80% of white pigment on the market. Concomitantly, the use of white lead in paints fell during 1900-1945 from nearly 100% to less than 10%.* [Brunner, 1978, p. 592 and IARC, 1989, p. 330]

The reduction in the use of white lead has been dependent on local regulations that vary with time and place. The above statement, that TiO_2 represented 80% of white pigment on the market in 1945, does not appear to be supported by the observed use of zinc white, white lead, lithopone, and lead sulphate. More original data on pigment consumption would be useful in this matter.

The early adoption of titanium dioxide is noted by Gooch (1993, p.97) as follows:

> *In 1924, the Bureau of Standards issued proposed master specification for a lead-free exterior white titanium and zinc paint (Minerals Yearbook, 1924). Tests comparing titanium dioxide to white lead demonstrated the former to be a technologically competitive pigment (Tyler et al., 1929; Campbell Paint Brochure, 1924). Moreover, by 1929 titanium pigments had assumed an important role in European countries that had legislatively restricted the use of white lead in paints (Minerals Yearbook, 1929).*

According to (Brindley, ca.1952, p.221), 'Owing to the immense opacity of titanium oxide, it has exceptional value in enamels and other high gloss coatings, where pigment content must be kept to a minimum in order to avoid loss of binder gloss.'

Because of the chemically inert nature of the TiO_2 pigment, 'the binder receives no assistance in drying' (Brindley, ca.1952, p.221), this may mean that as lead was removed from the pigment component of paint formulations, somewhat minor quantities of lead invariably had to be added through products such as the lead, manganese, cobalt (LMC) driers.

The shortcomings of TiO_2, the softness of the film and its chalking tendencies, are overcome with ZnO to produce a harder film, while the lack of drying action of TiO_2 and the need for driers can be reduced by the addition of white lead (Holloway, 1953, Vol.I, p.31).

Detailed knowledge of the history of TiO_2 manufacture is the basis of understanding the great differences in the major and minor element chemistry of TiO_2 pigments. Using tools like electron microscopy, and a detailed analytical database it may be possible to determine the source of raw materials, the manufacture process and year of production for TiO_2 in particular paint layers.

7.1.1 TiO_2 from ilmenite

Paints containing the white pigment titanium dioxide produced in the USA prior to 1949 would appear to have been predominantly manufactured using ilmenite as the raw material (Johnstone, 1954, p.558).

The production of TiO_2 from ilmenite ($FeTiO_3$) as described by Johnstone, (1954, p.560-561) takes the following path:

- ilmenite attacked by 72-95% sulphuric acid
- resultant cake of sulphates of iron and titanium are dissolved in water
- ferric iron in solution reduced to ferrous by means of scrap iron
- solution clarified by settling after adding a wetting agent
- 60% of the ferrous sulphate is crystallised out of solution and removed

The next stages involve the hydrolysis of the titanium sulphate and the precipitation of the hydroxide. TiO_2 from the hydrolysis of sulphate solution is of the anatase variety, whereas if the precipitate is from chloride or nitrate solutions the TiO_2 is of the rutile form. It is also stated in Johnstone, (1954, p.560) that rutile may be obtained by seeding the sulphate solution with a small quantity of TiO_2 prepared from titanium tetrachloride. Calcining of precipitate with additions of $CaHPO_4$ was customary so as to produce the anatase form of TiO_2 having 0.35% P_2O_5.

When ilmenite is discovered in petrographic, X-ray diffraction or electron microscopy type examinations of paint material it is probably as a remnant of the ilmenite raw material used in TiO_2 manufacture and may be indicative of the paint having been manufactured pre 1949. Where the rutile form of TiO_2 is the sole Ti phase, the paint may have been produced from 1941 onward.

In 1954, in relation to mineral resources it was said that '*rutile is of much less frequent occurrence than ilmenite*' (Johnstone, 1954, p.554).

7.1.2 Anatase and rutile forms of TiO_2

The anatase polymorph of TiO_2 *'has some tendency to chalk if exposed to general weathering'* (Brindley, ca.1952, p.221) and was used mostly indoors. Antimony oxide was used as a white pigment in early formulations to reduce the chalking tendency of anatase TiO_2. The anatase form of TiO_2, with a lower refractive index and light scattering ability is not as photochemically stable as the rutile form, (Boxall and von Fraunhofer, 1980, p.16) and can chalk, hence the greater demand for the rutile-based pigments.

DuPont and ICI joined forces and 'developed' means of producing industrial quantities of rutile, which came into production from 1941 (Hounshell and Smith, 1988, p.217). With a higher refractive index and 20% more hiding power (than anatase), rutile became a significant basic raw material for the newly developed DuPont chloride beneficiation process in the 1950s.

7.1.3 Trace components of titanium dioxide pigments

Table 19: *U.S. Federal Specification, TT-T-425A, (pre 1954) for TiO_2 pigment (Johnstone, 1954, p. 564 - 565)*

	Free chalking Anatase	*Semi-chalking aluminium treated Rutile*		*Chalk-resisting silicon-aluminium-zinc treated Rutile*	
	Type I	Type II		Type III	
	min.	min.	max.	min.	max.
Titanium Dioxide (TiO_2)	98 %	97 %	-	93 %	-
Alumina ($Al_2 O_3$)	-	0.5 %	1.5 %	1.8 %	2.4 %
Silica (SiO_2)	-	-	-	0.6 %	2.0 %
Zinc Oxide, (ZnO)	-	-	-	0.5 %	1.4 %

A similar classification (Table 20) of titanium dioxide pigment grades in 1962, indicates higher TiO_2 concentrations and perhaps more refined, thinner, particle coatings of aluminosilicate material:

Similarly, ASTM D476-48 for unextended TiO_2 specifies a minimum of 94% TiO_2 in chalk-resistant rutile. Low levels of aluminium, at 0.95 to 1.27 wt.%; silica, at 0.28 to 0.94 wt.%; and zinc at 0.40 to 1.12 wt.% should be expected in association with titanium in chalk-resistant rutile of the 1950s.

***Table 20:** Classification of titanium dioxide pigments from 1962 (Chatfield, 1962, p. 158)*

	Anatase		*Rutile*			
	Type 1	*Type 2*	*Type 1*	*Type 2*	*Type 3*	*Type 4*
Titanium Dioxide (TiO_2)	98.0	97.0	98.0	97.0	95.0	95.0
Alumina (Al_2O_3)	-	0.5-1.2	trace	0.5-1.2	1.5-2.2	0.5-1.0
Silica (SiO_2)	-	-	-	-	0.5-1.0	0.6-1.0
Zinc Oxide (ZnO)	trace	trace	0.8-1.0	0.3-0.5	0.8-1.0	0.8-1.2

The production of TiO_2 by the sulphate process, uses ilmenite or titanium slag as raw material whereas the chloride process can use ilmenite, leucoxene, natural and synthetic rutile, titanium slag and anatase (Buxbaum, 1993). An older chlorination process known as fixed bed chlorination is said to be hardly used today, with fluidised bed chlorination (Du Pont process) being started in 1950 (Buxbaum, 1993, pp. 56-57).

World production of TiO_2 in 1965 was 1.25 Mt (million tonnes) by the sulphate process (eg Bayer AG) and 0.14 Mt by the chloride process (eg Du Pont process) and an estimate of production in 1995 is 2.0 Mt and 2.1 Mt respectively (Buxbaum, 1993, p.44). According to Buxbaum (1993, p.58), '*Pigments produced by the chloride process (chloride pigments) have better lightness and a more neutral hue than pigments produced by the sulfate process (sulfate pigments)*'.

According to Buxbaum (1993, p.65) and Ward (1977, p.327-328) Australian manufacture of TiO_2 is exclusively by the sulphate route, at Burnie and Bunbury, using ilmenite concentrates from the Western Australian Capel deposits. A plant to produce TiO_2 near Bunbury was established by Laporte Titanium (Australia) Ltd in 1964 (Baxter, 1979, p.117) although it was also said to be commissioned in November 1963 by Ives (1965, p.145). Western Titanium in 1968 establishing a beneficiation plant at Capel to convert ilmenite to synthetic rutile (Baxter, 1979, p.117). According to Johnson (1987, p.191) AMC (a subsidiary of RGC) is said to have been first to produce synthetic rutile as a commercial product in 1969, with a variously resurrected 10,000 tpa (tonnes per annum) plant and followed by a 30,000 tpa plant in 1974. Australian Titan Products at Burnie expanded its pigment plant in mid-1963 (Ives, 1965, p.145).

Annual TiO_2 consumption in Australia is said to have risen from 14,000 tonnes in 1958 to 22,000 t in 1963 with stable consumption of 22,000 tpa from 1965-67. Consumption increased in the late 1960s to estimated levels of 31,000t in 1973, and declined to some 27,800t in 1975 (Ward, 1977).

Imports of TiO_2 pigment to Australia in the 1970s appear to have been a small proportion of annual consumption with 724 tonnes in 1974 and 249 tonnes in 1975 (Ward, 1977). According to Livingstone (1965, p.140) Australia was 100% self sufficient in rutile as a commodity in 1952, 53, 62 and 63 where statistics happen to be quoted and with respect to ilmenite also 100% self sufficient in 1962, 1963 with ilmenite statistics listed as not available for 1952 and 1953.

During the production of rutile pigment, prior to calcination, using the sulphate process, rutile nuclei (<10%) are added, with ZnO, Al_2O_3 and/or Sb_2O_3 (<3%) sometimes also added to stabilise the crystal structure (Buxbaum, 1993, p.55). In manufacture by the chlorine process, the presence of $AlCl_3$ added at up to 5 mol. % promotes the formation of finely divided rutile. (Buxbaum, 1993, p.58). These practices may have had an impact on the trace element constitution of rutile pigment.

'After-treatment' of titanium dioxide pigment particles:

> '*…improves the weather resistance and lightfastness of the pigmented organic matrix, and dispersibility in this matrix. The treatment consists of coating the individual pigment particles with colorless inorganic compounds of low solubility by precipitating them onto the surface. However, this reduces the optical performance of the pigment approximately in proportion to the decrease in the TiO_2 content. The surface coatings prevent direct contact between the binder matrix and the reactive surface of the TiO_2*' [Buxbaum, 1993, p.58-59]

Examples of the thin rinds of post treatment 'armouring' materials are given in Buxbaum, (1993, p.59), with references to patents by Du Pont, Tioxide, British Titan Products and Kronos Titangellschaft:

> *Three groups of pigments have very good lightfastness or weather resistance:*
>
> *1) Pigments with dense surface coatings for paints or plastics formed by:*
>
> > *a) Homogeneous precipitation of SiO_2 with precise control of temperature, pH, and precipitation rate [Du Pont, 1956]: ca. 88 % TiO_2.*
> >
> > *b) Two complete aftertreatments, calcination is performed at 500-800°C after the first or second aftertreatment [Tioxide, 1960]: ca. 91% TiO_2.*
> >
> > *c) Aftertreatment with Zr, Ti, Al, and Si compounds, sometimes followed by calcination at 700-800°C [Kronos Titangellschaft, 1960; British Titan Products, 1965]: ca. 95 % TiO_2.*
>
> *2) Pigments with porous coatings for use in emulsion paints obtained by simple treatment with Ti, Al, and Si compounds, giving a silica content of 10% and a TiO_2 content of 80- 85 %.*
>
> *3) Lightfast pigments with dense surface coatings for the paper industry that have a stabilized lattice and a surface coating based on silicates or phosphates of titanium, zirconium, and aluminum: ca. 90% TiO_2.*
>
> *Co-precipitation of special cations such as antimony or cerium can improve lightfastness further [Du Pont, 1984].*

[Note: the original text cited the references as index numbers]

Pigment particle coatings also described by Buxbaum (1993, p.59) include materials such as:

- chlorides and organometallics
- oxides, oxide hydrates, silicates, and/or phosphates of Ti, Zr, Si, and Al
- B, Sn, Zn, Ce, Mn, Sb or V compounds for special applications

The addition of organophosphates to TiO_2 effectively making the pigment particle surface hydrophobic is described by Buxbaum (1993, p.60).

The potential for rare earth element (REE) contamination of older TiO_2 products should be considered owing to the association of Ti-bearing minerals and heavy mineral beach sand deposits. No specific contaminants are suggested in paint TiO_2 products, but elements such as Zr, Th, Yb, Er, La, Ce, Nd, Dy, P, Cr may be associated with Ti phases such as rutile or ilmenite or be contained in associated minerals such as monazite, xenotime and zircon (Macdonald,1973).

7.1.4 Extended TiO_2

So called 'extended' TiO_2 pigments contain *'...appreciable quantities of precipitated barium or calcium sulphate, magnesium silicate or natural calcium carbonate'* (Johnstone, 1954, p.562). Some forms of extended TiO_2 were more common, combinations such as:

- rutile form TiO_2 with calcium sulphate
- anatase form TiO_2 with barium sulphate

7.1.5 Was TiO_2 a well known pigment in the 1940s?

Vanderwalker, (1944, pp.252-266), in a listing of 246 paint colour recipes had no paint formula that included TiO_2, but the pigment was recognised as available (p.71 & 121). While Vanderwalker mentions the *'claims made for titanium oxide'* as to having '*greater opacity, or hiding power, than any other white pigment'* (p.72), it is also clear that the author believed that *'White lead is the most opaque white pigment known to chemistry for exterior painting'* (p.68). Vanderwalker, despite a lack of inclusion of TiO_2 in his own colour formulas notes that *'...the bulk of titanium oxide is used by paint manufacturers in combination with other pigments to make up prepared materials'* (p.72).

While separate pigment materials such as white lead and zinc white were still available to the painter in the 1950s as dry powder or paste ingredients, it appears that titanium-based pigments were not generally available in such forms but were readily found in already prepared paint materials (DLNS , 1955, p.26).

Crewdson, (1943, p.15) did not recognise TiO_2 as being a pigment component in its own right according to this definition, *'Titanium Dioxide. This is one of the most used of the newer white pigments and* is *composed of about 25% titanium dioxide and 75% artificial barium sulphate'.* This may be a reflection of how titanium dioxide was not used alone in order to make cheap paints, and that it did not substantially displace existing paint components. Brunner, (1978, p. 592) also recognised the early use of TiO_2 in pigment mixtures.

The following paint formulation from 1935 is worth noting as it contains Titanox, (likely to be a product of the US National Lead Company), in addition to large quantities of lead carbonate in a formula where pigments may amount to 60% of the total product.

Synthetic resin house paint

Pigment		
Titanox B	*49%*	
Lead Carbonate	*49%*	
Litharge	*2%*	
Vehicle		
No. 1319 Beckosol Solution	*44%*	
Raw Linseed Oil	*55%*	
Cobalt Drier (2% Cobalt)	*1%*	[The Chemical Formulary, 1935, p. 101]

The Chemical Formulary (1951, pp.370-371) gives numerous examples of Pb, Zn, Ti mixtures including:

No. 3	
Anatase Titanium Dioxide	*132 lb.*
Zinc Oxide	*148.5 lb.*
Basic Carbonate White Lead	*292 lb.*
Magnesium Silicate	*308 lb.*
Refined Linseed Oil	*238 lb.*
P-296 Beckosol	*342.5 lb.*
6% Cobalt Drier	*2.5 lb.*
24% Lead Drier	*5.25 lb.*
Antiskinning Agent	*2 lb.*
No.4	
Anatase Titanium Dioxide	*222 lb.*
35% Leaded Zinc Oxide	*444 lb.*
Magnesium Silicate	*222 lb.*
Refined Linseed Oil	*187.5 lb.*
"X" Viscosity Linseed Oil	*180.5 lb.*
24% Lead Drier	*6 lb.*
6% Manganese Drier	*3 lb.*
Mineral Spirits	*179 lb.*
Weight per gallon	*14.4 lb.*

No. 7 [Lead-free fumeproof]

Titanium Dioxide	*104 lb.*	
XX Zinc Oxide	*277 lb.*	
Magnesium Silicate	*243 lb.*	
Mica	*69 lb.*	
Heat Bodied Linseed Oil	*11.7 gal.*	
Refined Linseed Oil	*36.2 gal.*	
16% Lead Drier (as a paste?)	*1.9 gal.*	
4% Manganese Drier	*0.2 gal.*	
Weight per gallon	*12.6 lb.*	[The Chemical Formulary, 1951, pp.370-371]

Similarly from Kent (1962, p.764) the following Pb-Zn-Ti exterior house paint formula was obtained from a label dated 1949.

Component	*Overall*	*Pigment (61%)*	*Vehicle (39%)*
Basic sulfate-white lead	*11.1%*	*18.2%*	...
Zinc oxide	*20.7*	*34.0*	...
Titanium dioxide	*10.5*	*17.2*	...
Magnesium silicate	*13.5*	*22.2*	...
Silica	*5.1*	*8.4*	...
Linseed oil	*29.7*	...	*76%*
Driers	*0.7*	...	*1.8*
Mineral Spirits	*8.7*	...	*22.2*

Those painters mixing pastes themselves up to the 1950s probably used little TiO_2. TiO_2 made its way into use, initially mixed with other pigments in pre-prepared paints sold in cans at the hardware store - in the 1950s. It was not until the late 1950s to 1960s that paints almost exclusively pigmented by TiO_2 came into common use. The extended titanium pigments, lead-titanium pigments, titanated lithopone and lead zinc titanium paint mixtures soon became irrelevant when the titanium industry 'took off ' in the early 1960s.

8. Lead, Zinc Oxide, Lithopone and TiO_2

DuPont was the largest producer of lithopone in the USA in 1930, producing 33,000 tons in 1914 and 200,000 tons in 1928. According to Gooch, (1993, p.97)'*... the first U.S. commercial production of titanium white began in 1918 by Titanium Products (Haynes, 1945-1956). In 1920, National Lead purchased an interest in Titanium Products and acquired the remaining interest in the company by the 1930s.'* DuPont soon entered the TiO_2 business but could not sell TiO_2 as a pigment without infringing patents held by the US National Lead Company, so it manufactured titanated lithopone. With the depressed price of zinc in the 1920s titanated lithopone was cost competitive relative to otherwise superior TiO_2 products. At that time U.S. National Lead and Commercial Pigments Corporation controlled the anatase TiO_2 pigment patents. DuPont and US National Lead came to an agreement in 1933 relating to TiO_2 manufacture (Hounshell and Smith, 1988, p. 217) and US National Lead and British lead industry and other interests joined together in 1932 (Rowe, 1983, p.345).

The following passage from Gooch (1993, p.99), outlines the control of the USA paint market in relation to lead by a few key players:

> *In 1946, the Federal Trade Commission charged the following companies with effecting monopolies, lessening competition, and restraining trade in the sale of lead pigments, including white lead (National Lead v. Federal Trade Commission, 1953):*
>
> *National Lead*
>
> *Eagle-Picher Lead*
>
> *Sherwin-Williams*
>
> *International Smelting and Refining*
>
> *Glidden.*
>
> *During the 1930s and early 1940s, these companies accounted for practically the entire lead pigment production in the United States (National Lead v. Federal Trade Commission, 1953).*

Control of the developing TiO_2 industry was also resting with a few key companies.

The worlds larger TiO_2 producers according to Johnstone, (p.561) around 1954 were:

British Titan Products Ltd	UK
National Titanium Pigments Ltd	UK
National Lead Co. Ltd	USA
Titangesellschaft GmbH	Germany

The National Lead Co. (USA) was working hard-rock ilmenite at Storgangen, Norway (Johnstone, 1954, p.553). Hard-rock ilmenite was also developed by Jersey Zinc and Kennecott Copper Corporations with Quebec Iron and Titanium Corporation as the operating company (Johnstone, 1954, p.554).

According to Rowe (1983, p.348): *'For two decades until about 1950 the expansion in sales of lead-based paint was to prove a useful profit earner for ALM* (the UK Associated Lead Manufacturers) *but thereafter the competition from titanium-based paints was to become severe.'*

8.1 TiO_2 in Australia

While the non-communist-world production of ilmenite amounted to 320,000 long tons in 1939, and 857,000 long tons in 1950, the corresponding world production of raw mineral rutile was 1690 and 18400 long tons, with Australia producing 99.5% of world mined rutile in 1950 (Johnstone, 1954, p.558). Some 95% of the non-communist world's production of rutile was sourced from Australia in 1965 (Hunter, 1967).

According to Berkman (1982, p.92) Australia produced more than 80 percent of the world's natural rutile and 25% of the world's ilmenite. Berkman notes that ilmenite (Australian?) *'…is almost entirely used in the manufacture of titanium white (by the sulphate route), which produces large volumes of iron sulphate as a pollutant by-product.'* other methods of beneficiating ilmenite concentrates are discussed.

Major international interests in titanium, U.S. National Lead Company, DuPont, Associated Lead Manufacturers, UK, Goodlass Wall and Lead Industries, ICI, RTZ and Imperial Smelting, also had interests in Australian resources or production.

Australia, having 95% of the world rutile resource in 1965 was central to the growth in use of titanium dioxide in paints.

8.2 Summary: TiO_2 in paint

The composition of paint has been a formula based on the balance of available technology, costs of raw materials and their availability, the demand for particular standards of performance, tempered by any legislative restrictions. The worldwide use of lead in petrol and car batteries reached high levels after 1950 and began to aggressively consume lead otherwise used in paint products. Aspects of the development and rise in use of titanium dioxide occurred in close parallel with reduction in use of lead in paint.

In white paints manufactured after 1960, it is common to find titanium dioxide as the only inorganic component at levels in excess of 1-2 wt.%. Descriminating between such paint layers is often by the minor and trace components. The quantitative elemental analysis of individual paint layers, 20 to 40 microns thick, is readily carried out by electron microprobe. By this method the variability of titanium dioxide-based paints is readily appreciated. Methods for the evaluation of paint polymers and organic pigments are not so readily applicable to thin paint layers. In relation to characterising the rimming of pigment particles with coating materials such as those designed to minimise chalking, transmission electron microscopy may be the most applicable investigation method. The variability of TiO_2 materials needs to be considered when considering anything more than a generic risk assessment.

Many of the trace components in and morphological characteristics of titanium dioxide pigment, may be useful in confirming the age of paint layers, based on local knowledge of the history of pigment technology. The matching of particular paint layers from different parts of buildings may also be assisted by detailed characterisation of the 'bulk paint layer' and the characterisation of titanium dioxide pigment particles.

A review of TiO_2 pigment manufacture and use preceeds a review of some biological data relevant to evaluating the health risks of TiO_2 (IARC, 1989, pp307-326). It is unlikely that the wide range pigment particle coating compounds and the wide range of trace element constituents of new and aged nominally TiO_2 bulk industrial materials have been considered in assessment of the risks of TiO_2. Conventional wisdom suggests that biologically, TiO_2 is a relatively inert compound.

9. Other pigment materials

9.1 Antimony

According to Johnstone (1954, p39-40), official figures showed that in 1950, 2,040 long tons of antimony were consumed for the production of antimony white pigments and 696 long tons for other antimony pigments in Great Britain, although 'trade sources' suggested that antimony use in pigments amounted to 4500 long tons. In contrast, in the United States antimony use in paints and lacquers was lower and declining steadily between 1944 and 1950, where use for the years 1944, 1946, 1948, 1949, and 1950 were 2223, 1484, 1150, 780 and 239 long tons respectively.

Antimony trioxide is used as a paint pigment, and one standard (BS 338: 1952) specifies that the pigment material should *'…contain not less than 99% of antimony expressed as its oxide,* Sb_2O_3*, calculated on the product after drying at 98°C.'* (Johnstone, 1954, p.42).

It is said by Holloway, (1953, Vol.I, p.31) it was not until 1919 when antimony oxide was introduced under the proprietary name of 'Timonox' that it proved successful. Listings of trade or brand names in the Paint Trade Manual (ca.1960s, p. 226) refer to 'Timonox' as being owned by Associated Lead Manufacturers.

Chatfield notes that *'Antimony trioxide of optium particle size and particle size distribution is probably the whitest of all pigments if free from impurities such as the tetroxide (*Sb_2O_4*) and traces of iron, lead, arsenic and other heavy metals.'* (1962, p.161). While it is noted that economically Sb_2O_3 could not compete with rutile in 1962, it had continuing use, probably mixed with other pigments. It is noted by Hess (1965, p.310) that '*Combinations of anatase titanium oxide with up to 10 per cent* *antimony oxide show good retardation to the onset of chalking*.' and such a description may indicate use for these properties.

Antimony is a somewhat rare component in house paints, the limited experience of the author (based on about 400 paint analyses) suggests that less than some 0.5 per cent of old paint films may include > 2% Antimony.

In an evaluation of Sb_2O_3 IARC (1989, p.302) considered the compound being '*possibly carcinogenic to humans' (Group 2B).*

9.2 Arsenic

Scheele's Green, $CuHAsO_3$ or $3CuAs_2O_3 \cdot xH_2O$ and Paris Green $CuOAs_2O_3 \cdot Cu(C_2H_3O_2)_2$ or $Cu(C_2H_3O_2)_2 \cdot 3CuAs_2O_4$ are two green pigments considered to be obsolete in architectural finishes (Crown, 1968, p.45-46).

Realgar and Orpiment are mineralogical names for Arsenic Orange and Arsenic Yellow pigments (Crown, 1968, p.198), and Arsenic Purple is a pigment also referred to as Cobalt Violet Light. Alternative names for these pigments abound, the following apply to either Scheele's Green or Paris Green:

> *African Green, Deck Gruen, Emerald Green, English Green, King's Green, Leipzig Green, Meadow Green, Mineral Green, Mittis Green, Parrot Green, Patent Green, Schweinfurt Green, Swedish Green, Verde Ceniza, Vert Cendre, Viennese Green* (Crown, 1968)

While it would appear that arsenic in paint would not have been found readily in paints produced in the 1950s, comments by Holloway, (1953, Vol. I, p.38), do not totally preclude the possibility. Emerald Green is described as a pigment having '*...the most brilliant greens which can be obtained, but it possesses the disadvantage of being very poisonous...'* having an average composition of '*about 33 per cent. of copper oxide and 58 per cent. of arsenious oxide'*. It is said that Emerald Green should not be mixed with pigments containing sulphur. Holloway states that the actual use of the pigment is largely restricted to that of an insecticide (Paris green).

In 1965, Hess appears to suggest that the arsenic sulphide pigments Auripigment, Orpiment, Royal yellow, Realgar, Kings's yellow and Ruby sulphur are scarcely used but he makes a limited, somewhat cautious endorsement of the use of arsenic:

> *'The most important pigments containing arsenic, which must therefore be used only in exceptional cases involving no risk of poisoning are:*
>
> *Schweinfurt green (copper arsenite acetate)*
>
> *Emerald green (as far as this contains Schweinfurt green)*
>
> *Scheele's or mineral green (copper arsenite)*
>
> *Lime-arsenic green (containing copper arsenite)*
>
> *Neuwied green (containing copper arsenite)*
>
> *Paris green (copper aceto-arsenite)'* [Hess, 1965, p.205-206]

Would painters be able to exercise appropriate judgement as to where there may be no risk of poisoning? No specific information is available on the durability and modes of failure of arsenic/copper pigmented paints.

9.3 Barium

Barite is generally used in paint as an extender. The light scattering capability of barite as a function of particle size is poor relative to accepted white pigment materials (Buxbaum, 1993, p.25).

A higher grade of barium sulphate at 97% $BaSO_4$, which is precipitated material as opposed to a minimally beneficiated mine concentrate is known as blanc-fixe, whereas the more typical material contains a minimum of 94% $BaSO_4$ according to ASTM Standard D 602-42 (Johnstone, 1954, p.67).

Natural barium sulphate is noted as having a better influence on paint durability than blanc-fixe (Wolff in Hess, 1965, p.17).

> *'In the past, and much less today it was used as an adulterant of lead paints and to confer weight on paints generally, but since the practice of buying paints by weight has largely disappeared, barytes is now often used for its other special properties'* [Chatfield, 1962, p.225]

This passage from Hess (1965, p.17) gives some support to the addition of $BaSO_4$:

> *'The covering power is reduced only in case of very considerable additions of barium sulphate, and only then if the pigments contained exhibited a comparatively low covering power. In presence of red lead, up to about 20 to 30 per cent of the pigment mixture can be added. But even in the case of white lead a protective effect is obtained with an addition of about 30 per cent (H. Wolff).'*

And further, (p.286):

> *'Red lead can be extended with barium sulphate with negligible effect on performance, and considerable cost reduction. The German State Railways specify an addition of 20 per cent barium sulphate to the red lead paint.'*

Barium is generally present in paint in the form of the sulphate barite, which is highly inert. According to Johnstone (1954, p. 72) witherite (barium carbonate) has also been used in paints. $BaCO_3$ may be somewhat more toxic than the sulphate as it was a component of rodent poisons in the 1920s and 1930s. Specification BS 1795: 1952 *'…for Extenders for Paints requires natural witherite to contain not less than 93 % of barium carbonate'*, (Johnstone, 1954, p.72).

An analysis of a mineral witherite product in Chatfield (1962, p.212) consists of 91.1% $BaCO_3$ with a particle size at 37 microns, (too coarse for paint use unless ground) whereas the precipitated product (Laporte Chemicals) is more pure at 99% $BaCO_3$ and being between 0.2 - 5.0 microns.

The use of $BaCO_3$ is claimed to neutralise atmospheric acids and those acids generated within the paint during weathering: *'Less chalking of titania of both rutile and anatase types, and of zinc sulphide as such and as lithopone, is observed. Coloured pigments which fade in acid conditions are protected by barium carbonate.'* (Chatfield, 1962, p.213). Where $BaCO_3$ is able to play such an acid neutralising role it is possible that toxic Ba^{++} ions may be liberated.

There would clearly have been opportunities for the use of $BaCO_3$ in the formulation of paints between the the 1940s and 1960s when both lithopone and chalking varieties of TiO_2 were in use.

Barium carbonate would appear to have been considered relatively non-toxic by Hess (1965, p.176) wherein it is stated *'Very large quantities have been handled by workers for many years under normal factory conditions without injurious effects.'* and a reference to Muddiman from 1942 in Hess (p.203) notes, *'Barium carbonate pigment may, therefore, be used in paint as freely as, say, zinc oxide or lithopone, although there are obviously unwise applications, such as in paints for food containers.'* Such historical appraisals appear to lack caution or have adequate consideration of child exposure, and require critical evaluation. The potential for the evolution of Ba^{++} ions from the use of $BaCO_3$ is greater than that from $BaSO_4$ and more investigation is warranted.

A formulation containing barium carbonate, intended for metal surfaces is as follows:

Paint No. 748. Priming Coat	***Per cent by Weight***
Barium chromate	*8.7*
Ground witherite (barium carbonate)	*17.5*
Talc	*13.1*
Medium (see below)	*47.8*
White spirit	*12.9*
Pigment/binder ratio by weight	*1.8 : 1*
Total volatile content by weight	*39%*

Weight per gallon	*12.1 lb.*

Natural bitumen/Dehydrated castor oil medium (vehicle)

Natural bitumen (Gilsonite)	*29.5*
Dehydrated castor oil	*14.8*
Litharge	*0.2*
White spirit	*55.3*
Cobalt naphthenate (6% Co)	*0.1*
Manganese naphthenate (6% Mn)	*0.1*

[Fancut & Hudson, 1957, pp.87-88]

More information is required on the use of barium carbonate in paint. The toxicity of barium sulphate and carbonate is suggested to be low (ATSDR, 1992, p.7) owing to the insolubility of these compounds. However more details appear to be required in the case of the carbonate and any circumstances under which Ba^{++} ions could be readily derived.

Bioactive additives noted by Boxall and von Fraunhoffer (1980, pp.31-32) include Barium metaborate at 15-20 %. Hess (1965, p.206) refered to barium chromate as not being regarded as toxic or requiring special precautions. There is a lack of information as to the use of barium chromate in paint and more information as to human health risk is required.

9.4 Bismuth

Bismuth vanadate molybdate ($4BiVO_4 \cdot 3Bi_2MoO_6$) is a greenish yellow pigment having a mean particle diameter of 0.25 microns and coloristic properties closely resembling CdS and $PbCrO_4$-$PbSO_4$ pigments, (Buxbaum, 1993, p.115). This pigment is used in the manufacture of lead-free, weather resistant, brilliant yellow colors for automobile finishes and industrial paints.

Bismuth oxychloride (BiOCl) is used as a synthetic pearl imitation pigment and is said to be replacing the use of hexagonal platelets of basic carbonate white lead (Buxbaum, 1993, p.213).

9.5 Cadmium pigments

> *Cadmium sulphide has been used for artists' colour for a long time, but its use in commercial paints is relatively new. It is made by precipitation when barium sulphide is added to a solution of cadmium sulphate; the product is filtered, washed and calcined, when the particle size is controlled. By co-precipitation with zinc sulphate or by replacing part of the cadmium sulphide by cadmium selenide, hues can be produced from yellow to red. The pigments have good light fastness and heat resistance, and may be used in good quality stoving enamels.'*
>
> [Armitage, 1967, p.69]

The regulation of cadmium pigments has probably only occurred since the 1960s.

Listings of cadmium pigments for paints in the Paint Trade Manual (ca.1960s, p. 54-56), each of which is available through a number of agents or manufacturers. The pigment and number of UK suppliers are listed here:

- cadmium green (3)
- cadmium lithopone (10)
- cadmium and selenium maroon (12)
- cadmium and selenium orange (13)
- cadmium and selenium red (14)
- cadmium yellow (14)

Buxbaum (1993, p.107) states that 'All cadmium pigments are based on cadmium sulfide and crystallize with a hexagonal , wurtzite lattice…' in which '…the only substitutions which are used in practice are zinc and mercury for the cations and selenium for the anions.'

The addition of zinc produces greenish yellow pigment while mercury and selenium produce orange, red and deep red shades (Buxbaum, 1993, p.108).

A particle diameter of 0.2 microns is prevalent in CdS pigment, and some 0.3-0.4 microns in the cadmium sulphoselenide.

While the use of CdS appears to have been widespread in plastics, accounting for 90% of consumption, it is declining in paints and coatings (Buxbaum, 1993, p.111-112) being <5% of consumption of this product.

CdS is slowly oxidised to soluble sulphates according to Buxbaum (1993, p.111), indicating that the use of this pigment on exterior surfaces, or in porous mediums, would result in accelerated deterioration.

9.6 Chromate pigments

9.6.1 Introduction

Chromate pigments, the yellow lead chromate and the red or orange lead molybdate have brilliant hues, good tinting strength and hiding power (Buxbaum, 1993, p.117).

Other chromate pigments include chrome orange, the lead chrome green pigments, zinc chrome greens and anticorrosive pigments such as zinc chromate, zinc tetraoxychromate and strontium chromate.

Understanding of the process of darkening of chrome pigments in the 1920s and 1940s led to manufacture where there was strict control of the ratio of reactants used to produce a stable crystalline form and also the development of pigment particle coating (Chatfield, 1962, p.162).

Buxbaum (1993, p.123) notes the risks associated with chromates as follows:

> *'Lead chromate pigments are classified as substances suspected of having carcinogenic potential. However, extensive epidemiological investigations have given no indication that the practically insoluble lead chromate pigments have any carcinogenic properties. Such properties have been reported for the more soluble zinc chromate and strontium chromate pigments.'*

The uncertainty as to the carcinogenicity and risks associated with chrome pigments are more prudently reviewed in ATSDR (1993, p.36-39). Lead chromate still poses risks attributable at least to its lead content and degradation, albeit over longer time frames.

Chromate pigment materials, prior to the 1920s, were made from relatively impure raw materials, possibly mixed with a lack of precision, resulting in the potential for poorly reacted raw materials to remain in low grade pigment products.

After the 1950s with the advent of coated pigment particles, the potential health risk of chromates may have been modified.

9.6.2 Chrome green and fast chrome green

Buxbaum (1993, p.121-122) describes chrome green as *'...combined or mixed pigments of chrome yellow and iron blue with the formula* $Pb(S,Cr)O_4/Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot xH_2O$', while fast chrome greens are *'...combinations of chrome yellow and phthalocyanine blue or phthalocyanine green.'*

Buxbaum notes that *'...pigments consisting of zinc potassium chromates combined with blue pigments are no longer of importance.'*

'*Chrome greens are essentially mixtures of lead chrome with either Prussian blue or phthalocyanine blue..*' (Armitage, 1967, p.69).

Chrome greens are better known in Australia through the Brunswick Green 'heritage colour' and are described further here in a section on Prussian Blue. The distinction between a Chrome Green and Brunswick Green may differ with location and era - according to DLNS (1955, p.30) Brunswick

Green contained a large proportion of an inert base such as barytes while Chrome Greens did not. More recently the term Brunswick Green would have only have referred to the colour and not to aspects of the composition of the paint.

9.6.3 Chromium oxide

'*Chromium oxide green is a relatively modern pigment, made by calcining sodium dichromate in a reducing gas.*' (Armitage, 1967, p.69). Raw materials can include sulphur or charcoal as the reducing agents and $Na_2Cr_2O_7$ could be replaced with $K_2Cr_2O_7$ (Buxbaum, 1993).

> *'Chrome oxide green, which consists essentially of 97-99 per cent. of chromic oxide (Cr_2O_3), is usually made by roasting sodium or potassium bichromate, either mixed with a reducing agent or in a reducing atmosphere. After cooling, the roasted product is washed to remove soluble salts, dried and ground. Chrome green is one of the most light-fast of all green pigments and is often used in protective paints, as it is unaffected by alkalis or acids in concentrations likely to be met with in normal use.'* [Johnstone, 1954, p.129]

Chromium oxide green is rare as a single compound (Cr_2O_3) green pigment, whereas many inorganic greens are a mix of yellow and blue pigment materials. It is a pigment insoluble in water, acid or alkalai and thus stable when exposed to sulphur dioxide and when applied to or mixed in concrete (Buxbaum, 1993). DLNS (1955, p.30) consided chromium oxide green to be *'a pigment of great opacity and bright enough in colour to be acceptable for most painting purposes'*.

Buxbaum (1993, p.97) notes the particle size of chromium oxide pigments being between 0.1 and 3 microns with mean values in the range 0.3 to 0.6 microns, with the lighter green and yellowish hues from fine pigment material and darker bluish tints with coarser pigment.

Pigment properties of chromuim oxides are modified to produce yellow-greens by the precipitation of hydroxides of titanium and aluminium for example, followed by calcining (Buxbaum, 1993, p.98).

Related to chromium oxide green is the chromium oxide hydroxide and the hydrated chromium oxide pigments known as Guignets Green. Buxbaum (1993, p.96) considers these *pigments no longer of industrial importance* being of low opacity, excellent lightfastness and good chemical resistance.

The particular value of the Cr_2O_3 pigment in the 1950s was in '*exterior painting and for tinting kalsomines, water paints, and emulsion paints'* (DLNS, 1955, p.30) for which the brunswick green pigments at that time were in most part much less suited.

9.6.4 Zinc chromate

The zinc chromate pigment is known as zinc yellow or zinc chromate yellow for example being basic zinc potassium chromate, $K_2CrO_4 \cdot 3ZnCrO_4 \cdot Zn(OH)_2$, and is prominent in its use on light metals used in aircraft construction. It can be specified as a reaction precipitate of soluble chromates and a suitable zinc compound (Johnstone, 1954, p.648). The ASTM specification, D478-49 (Table 21) for zinc chromate requires the pigment to be free from extenders, carbonates and organic colour.

A 'recent' zinc chromate pigment for metal priming according to Johnstone in 1954, (p.649) was zinc tetroxychromate having the formula $ZnCrO_4 \cdot 4Zn(OH)_2$.

According to Holloway (1953, Vol.I, p.144) Lead and Zinc Chromes *'based on the chromate pigments are expensive and this, no doubt, limits their use...'*, although subsequent to the more general reduction of lead in paint from the 1960s onward, they will have come into greater use.

Table 21: *Summary of ASTM and aircraft materials specifications for zinc chromate pigment (Johnstone, 1954, p.648-649).*

	ASTM D478-49		*Aircraft Materials Specification D.T.D. 377A**
	Type I (%)	Type II (%)	(%)
Zinc, calculated as ZnO	35-40	35-40	36.5-40.0
Chromium, calculated as Cr_2O_3, min.	41.0	41.0	not less than 43%
Sulphates, calculated as SO_3, max.	.2	3.0	
Chlorides, calculated as Cl, max.	.1	0.8	
Alkaline salts, calculated as K_2O, max.	13.0	13.0	10.0 - 12.0
Matter insoluble in acetic acid (1 : 9) at 80° C., max.	0.3	0.3	
Moisture and other volatile matter, max.	1.0	1.0	
Coarse particles retained on 44 micron sieve, max.	1.0	1.0	

* not stated if the specification is in terms of the element or oxide content

9.7 Cobalt

A mixture of oxides of cobalt and zinc known as Cobalt Green, and an oxide of cobalt known as cobalt blue, are known cobalt pigments, however only the former is likely to have been used in any volume, (Holloway, 1953, Vol. I, p.38). Buxbaum (1993, p.100) notes that '*Except for the expensive cobalt green, chromium oxide is the only green pigment that meets the high colour stability requirements for building materials based on lime and cement.'*

9.8 Copper

Copper is generally more common in marine paints than in household paints but may be considered as a potentially useful indicator element to use to screen for arsenic in the case of very old green paints. Quantitative analysis for copper could readily use the same sample acid digests as for lead.

Table 22: *Copper pigments (Hess 1965, p.364)*

Copper phthalocyanine blues and greens;	
Copper Hydroxides;	*Bremen blue, Copper green.*
Copper Bronze Powders;	
Copper Acetate;	*Verdigris.*
Copper Carbonates;	*Blue verditer, Copper blue, Green verditer, Malachite, Mineral green, Mountain blue, Verditer.*
Copper Iron Cyanides	*Florentine brown, Hatchess brown, New brown.*
Copper Aceto-Arsenites	*Emerald green, English green, Paris green, Schweinfurth green, Vert Anglais.*
Copper Arsenites	*Mineral green, Scheele's green.*

9.9 Iron

Iron occurs in paints as ferric ferricyanide (prussian blue) and in iron oxide pigments (Table 23).

***Table 23:** Iron oxide pigments (Buxbaum, 1993, p.85).*

goethite	*green yellow to brown yellow with increasing particle size*
lepidocrocite	*yellow to orange with increasing particle size*
hematite,	*light red to dark violet with increasing particle size*
maghemite	*brown*
magnetite	*black*

Umbers, from Cyprus for example, containing 45-70% Fe_2O_3 and 5-20% MnO_2 are deep brown to greenish brown in the raw state and dark brown with a red undertone when calcined (burnt umbers). Buxhaum (1993, p.86) also describes Siennas as being mainly found in Tuscany with an average Fe_2O_3 content of ca. 50% and <1% MnO_2, being yellow brown in the natural state and red brown when calcined.

Synthetic iron oxides appear to be more popular in recent times compared to directly mined materials owing to the ability to create consistency with the synthetic product. Reactions and processes for iron oxide pigment manufacture are summarised by Buxbaum (1993, p.88).

An iron oxide compound at 0.1 micron, can be red with a yellow tinge, while the same material at 1.0 micron can give violet hues. Buxbaum (1993, p.94) notes yellow iron oxide pigment particles being 0.3-0.8 microns long and 0.05-0.2 microns in diameter, and also the availability of spheroidal particles. Particles of some 0.1-0.6 microns diameter for the black magnetite pigment are noted (Buxbaum, 1993, p.95).

It is noted in Hess (1965, p.311) that chalking iron oxide paint coatings on iron substrate provide more anti-corrosive protection than non chalking iron oxide. It is no surprise that chalking iron oxide paints are relatively common. In the case of excessive chalking under tropical conditions, it is suggested that zinc oxide be added to the paint. The addition of high levels of lead to red iron oxide paints is likely to be in the form of red lead or lead chromate.

9.10 Manganese

Manganese compounds to assist the drying of paints include; pyrolusite, manganese sesquioxide (Mn_2O_3) and the hydroxide, napthenate, borate, resinate linoleate or oxalate. (Johnstone, 1954, p.321).

9.11 Mixed metal oxide pigments

'The term mixed metal oxide pigment denotes a pigment that crystallizes in a stable oxide lattice, and in which the colour is due to the incorporation of coloured cations in this matrix.' [Buxbaum, 1993, p.101]

These compounds (Table 24) are usually based on either the spinel, rutile or hematite lattice structure, being solid solutions having a large amount of variability in possible compositions and properties (Buxbaum, 1993, p.101).

These pigments are suited to application by baking and powder coating, and are also utilised in plastics. Nickel in rutile yellow pigment is replacing cadmium yellow use in plastics.

***Table 24:** Some mixed metal oxide pigments (Buxbaum, 1993, p.103-104).*

	Pigment Name	*Approx. composition*	*Colour*
Rutile Structure	Nickel rutile yellow	$(Ti_{0.85}Sb_{0.10}Ni_{0.05})O_2$	light lemon yellow
	Chromium rutile yellow	$(Ti_{0.85}Sb_{0.05}Cr_{0.05})O_2$	light to medium ocher (buff)
Spinel Structure	Cobalt blue	$CoAl_2O_4$ with Cr substituting for Al (+/- trace Zn, Mg)	brilliant blue to a greenish blue with Al:Cr = 3:7
	Cobalt Green	$(Mg, Co, Zn)_2\ TiO_4$	blue to green hues,
		$NiCo_{0.5}Zn_{0.5}TiO_4$	brilliant cobalt green
		$Li_2(Ni,Co,Zn)\ TiO_4$	turquoise
	Zinc Iron Brown	$ZnFe_2\ O_4$ (+/- Al, Cr, Ti, Li)	brown, red brown, dark brown
	Spinel Black	$CuFe_{0.5}Cr_{1.5}O_4$ $CuCr_2O_4$ $Cu(Cr,Mn)_2O_4$	black
Hematite		Mn + Cr in Fe_2O_3	brown

An overall evaluation from IARC (1990b, p.411) indicates that while nickel compounds are carcinogenic to humans there was inadequate evidence in experimental animals for the carcinogenicity of a number of nickel compounds including nickle titanate.

9.12 Molybdate red and orange pigments

Molybdate red and molybdate orange have the general formula $Pb(Cr,Mo,S)O_4$ and are related to the chromate pigments such as chrome yellow but differ in that they contain 4-6% of MoO_3 (Buxbaum, 1993, p.120).

> *Their hue depends on the proportion of molybdate, crystal form, and particle size. Pure tetragonal lead molybdate, which is colorless, forms orange to red tetragonal mixed-phase pigments with lead sulfochromate. The composition of molybdate red and molybdate orange pigments can be varied to give the required coloristic properties; commercial products usually contain ca. 10% lead molybdate.* [Buxbaum, 1993, p.120]

The tetragonal crystal structure of the molybdate needs to be stabilised by treatment and there is also the need to stabilise the pigments as per the particle coating methods for the chromates. The function of particle coating is to maintain high color brilliance, fastness properties, light resistance, weathering resistance, and protection from sulphur dioxide and temperature. Coating can also produce a low yield of acid soluble lead (Buxbaum, 1993, p.120). These pigments are mixed with organic red pigments in a manner analogous to the use of chrome yellow and prussian blue (and phthalocyanine blue) to give an extended color range.

9.13 Organic pigments

Some 176 synthetic organic pigments are listed in Crown (1968, p.63-91) and reproduced in Appendix 3. Many of these organic pigments are of unknown toxicity.

9.13.1 3,3'-Dichlorobenzidine

While yellow pigments such as the lead chromates and the cadmium sulphides were recognised as having toxic properties in the late 1960s, pigments such as the Benzidine Yellow pigment (Crown, 1968, p.63) were identified as having use '*…in nontoxic finishes' ;* subsequently there is now sufficient evidence that 3,3'-dichlorobenzidine is carcinogenic in mice, rats, hamsters and dogs (IARC, 1982, p.251).

IARC (1982, p.242) notes that 8 pigments based on 3,3'-dichlorobenzidine were produced in the US and 7 such pigments are listed in Crown (1968).

According to IARC (1982, p.242) the use of 3,3'-dichlorobenzidine was steady in the years 1971-1979 and noted considerable growth in the sales/production of two benzidine yellow pigments that were previously noted by Crown (1968, p.63) to be in minor use.

9.13.2 Benzidine

Benzidine, is more common as a dye than a pigment and has been found to be associated with an increased risk of bladder cancer in workers in the dye industry. It is also known as a skin irritant and has not been manufactured for sale in the US since the mid 1970s (ATSDR, 1995, p.2).

Benzidine was used in the paint pigment Pyrazolone Maroon (Pigment Red 39, Color Index No. 21080) and is described as benzidine coupled with 3-carbethoxy-1-phenyl-5-pyrazolone (Crown, 1968, p.80).

9.13.3 para-*Chloro*-ortho-*toluidine*

The pigment described as Permanent Red F4RH (Pigment Red 7, Color Index No. 12420) is described by Crown (1968, p.76) as 5-chloro-o-toluidine coupled with 4-chloro-3-hydroxy-2-naphtho-o-toluidide and is produced from a *para*-Chloro-*ortho*-toluidine intermediate (IARC, 1990a, p.125). While *para*-Chloro-*ortho*-toluidine and its strong acid *salts are probably carcinogenic to humans (Group 2A)* (IARC 1990a, p.133) the paint pigments which incorporate such chemicals have not been specifically assessed as to risk.

9.13.4 5-Nitro-ortho-*toluidine*

According to IARC (1990a, p.170), 5-Nitro-*ortho*-toluidine has been used as an intermediate in the synthesis of Pigment Red 17 and Pigment Red 22. According to Crown (1968, p.82), Pigment Red 22 (Color Index 12315) is known as *Solfast Scarlet Dark* being 5-nitro-o-toluidine coupled with 3-hydroxy-2-naphthanilide. The Pigment Red 8 (Color Index No.12335), called *Permanent Red F4R* and is described as as 5-nitro-o-toluidine coupled with 4-chloro-3-hydroxy-2-naphthanilide (Crown, 1986, p.76).

5-Nitro-*ortho*-toluidine *is not classifiable as to its carcinogenicity to humans (Group 3)* (IARC, 1990a, p.176), and there is limited evidence of carcinogenicity in experimental animals.

9.14 Prussian blue: ferric ferrocyanide

Discovered in 1704, by Diesbach, the pigment was first produced on an industrial scale in the early nineteenth century by Milori (Clauss (1960) in Buxbaum, 1993, p.132)

Iron blue is also known as Prussian blue, Berlin blue, Milori blue, Chinese blue, Turnbull's blue, Hamburg blue, Paris blue, Toning blue and Nonbronze blue (Gooch, 1993, p.88; Buxbaum, 1993, p.132; Windholz *et al*. 1983, p.578).

Prussian blue *'...is prepared by mixing a solution of ferrous salt with one of potassium ferrocyanide'* (Holloway, 1953, Vol.I, p.38).

The pigment has the formula $M^{I}Fe^{II}Fe^{III}(CN)_6 \cdot H_2O$, where M^{I} is preferably K, producing excellent hues, but could include Na or CH_3 (Buxbaum, 1993, p.132). Chatfield states that *'Until World War I all iron blues were made from potassium ferrocyanide, but the scarcity of potassium caused the rapid development of 'soda' blues.'* And notes the equivalence with older materials (1962, p.168).

> *Prussian Blue.-A very deep intense blue which is extremely strong in staining power. One part of blue to 600 parts of white will give a tint of blue. This material is transparent in oil,*

> *although on account of its hardness there is difficulty in combining it with that medium. It stands exposure reasonably well, and when mixed with white produces soft, greenish-blue tints. Prussian blue is decomposed by alkalis. When using this pigment as a staining medium in paint, exceptional care is necessary to avoid over-staining.* [Brindley, c. 1952, p.222]
>
> *'Many pigments discolour over alkaline surfaces such as new cement, plasters, etc., …Prussian and other iron cyanogen blues turn brown under alkaline conditions. When greens containing Prussian blues are subject to alkaline attack, e.g. from lime, cement, etc., the loss of blue colour can result in a change to a dirty yellow. This may be patchy according to the concentration of alkali present (e.g. mortar, lime plasters, asbestos cement). In tropical exposure, Brunswick (chrome) green paints tend to fade by yellowing rather than by blueing in contrast to the effect observed in temperate climates due to the acid atmospheres.'*[from Hess, 1965, p.354]
>
> *Iron blue is one of the most widely used blue pigments in the coatings industry because it combines low cost, good opacity, high tinting strength, good durability, and good heat resistance. Unfortunately, it offers very poor resistance to alkalies and cannot be used in water-based paints.* [Gooch, 1993, p.88]

Some variation in colour of streakiness of greens made from Prussian Blue might be expected: *'Greens obtained by blending Prussian or phthalocyanine blues with chrome yellows (lead chromes) are more prone to blueing, i.e. flotation of the blue component, than when the colour is obtained by use of a co-precipitated pigment.',* (Hess, 1965, p.81).

Some grades of Prussian blue are likely to be as a by-product of coal gas manufacture. With the demise of coal gas such Prussian blue becomes less common. Buxbaum (1993, p.137) notes that the world production of iron blue pigment permanently declined from the early 1980s.

The average size of aggregates of iron blue pigment is some 5µm for commercial grade material and 2µm for micronised material, with the primary particles being a mean 40nm in diameter, 45nm in the case of coated primary particles (Buxbaum, 1993, p.134-135).

According to Turczynowicz (1993, p.281) '*the acute toxicity of ferri- and ferrocyanide complexes themselves is low with their toxicity dependent on any subsequent release of free cyanide.*' Buxbaum (1993, p.139) states that *'No harmful effects of iron blue pigments have been found on humans or animals after several decades of investigations'* but notes toxic effects on bacteria. A health based soil criteria for complexed cyanides has been suggested at 500 mg/kg (Turczynowicz, 1993, p.284).

An uncoated grade of iron blue is used at 3-8 wt % to colour copper based fungicide for use on vines in Mediteranean countries. Iron blue is also used as a fertiliser for grape vines (Buxbaum, 1993, p.135-138).

9.14.1 Brunswick Green

Prussian blue was a component of Brunswick Green which is a paint that is important owing to its popularity in use in Australia in the period from 1910 to 1950, it is currently more commonly recognised as the name of a 'heritage' colour as opposed to the name of a pigment.

Brunswick or Chrome Green, (BS 303 : 1938) is referred to by Johnstone (1954) as if it were exclusively a chromium-zinc based pigment:

> *'…requires the colour of the material to be due wholly to salts of chromic acid, and to be free of other dyes, whiting or added zinc oxide. Lead compounds present must not exceed 0.2 per cent., calculated as Pb, and not over 0.2 per cent. of compounds of other metals is permissible (except zinc, chromium, potassium and sodium.)'* [Johnstone, 1954, p.649].

Brunswick Green has a range of definitions:

> *'This is a composite pigment, prepared by combining a small proportion of Prussian blue with a pale chrome yellow, both pigments being precipitated together in the wet state, together with large proportion of an inert base, such as barytes.'* [DLNS, (1955, p.30)]

and by Holloway (1953, Vol.I, p.37) as:

> *'...is made from Prussian blue and chrome yellow, with barytes...'*

The chrome yellow component in Brunswick Green could readily be chromates of lead or zinc.

9.15 Ultramarine

While the pigment was previously mined as the mineral lapis lazuli, current production appears to result in a synthetic mineral ultramarine having a typical lattice repeat unit of ($Na_{6.9}Al_{5.6}Si_{6.4}O_{24}S_{4.2}$) with pink and violet variants (Buxbaum, 1993, p.124). While Buxbaum considers the mineral to be a zeolite it is not a hydrated mineral zeolite but of the sodalite group closely related to the mineral haüyne, specifically the mineral lazurite which occurs in the often gem quality material known as lapis lazuli often found on the margins of metamorphosed limestones (Deer Howie and Zussman, 1996, pp.496-502). These *pigments are not recommended for colored, air-drying paints for outdoor use in urban atmospheres*, (Buxbaum, 1993, p.130) but are used widely in *'...plastics and surface coatings for toys, children's paints and finger paints, modeling compositions, colored paper and crayons*. (ibid, p.131)*'* These pigments find their way into a wide range of household products including cosmetics and soaps, and detergents and have even been used to whiten sugar (ibid, p.131).

Utramarine is unsuited to outdoor use due to swelling from moisture absorbtion (Hess, 1965, p.58). The mineral groups to which lazurite belong are readily gelatinised in acid (Deer Howie and Zussman, 1996, p.496).

The mean pigment particle size is some 0.7 to 5µm, Buxbaum (1993, p.127) with the finer pigment being lighter in shade and greener than more coarse grades, the pigment gives a transparent blue in gloss paints and opacity is provided with the addition of small quantities of a white pigment. One of the previous uses of ultramarine pigment has been to whiten pigments such as basic carbonate white lead (Holloway, 1953, VI, p.27) and titanium dioxide (Chatfield, 1962, p.159).

The particle size of ultramarine quoted by Chatfield, (1962, p.172) is 0.5µm to 5µm.

It is said that a useful test for ultramarine pigment is the evolution of hydrogen sulphide with acids (Buxbaum, 1993, p.128) however there are grades of ultramarine resistant to transient exposure to acids by virtue of particles having an impervious silica coating.

According to Buxbaum (1993, p.132) there were only 3 major corporate producers of high grade ultramarine world wide who have manufacture sites in Japan, Spain, France and the United Kingdom, with smaller producers in Austria and Colombia. This apparent production base may reflect some geographic limits to the utilisation of the pigment. However in 1942, (Chemical Industries Buyers Guidebook Number, 1942, p.417-418) there are numerous suppliers of (artificial) ultramarine in the USA.

The mineral and synthetic material potentially has a wide ranging chemical composition due to substitutions of available elements. Synthetic forms should not be assumed to be simply ~ $Na_7Al_6Si_6O_{24}S_3$ for example.

10. Paint additives

10.1 Introduction

Modern paints have become complex with the need for numerous additives (Table 25) to achieve the required properties:

> *Other types of additives include wetting agents, which help disperse pigments during the manufacturing process, and defoamers, which help break up foam generated during agitation and application. Antisettling agents reduce pigmentation settling when paint is stored. Preservatives and fungicides are additives that improve the paints' storage stability by destroying organisms that grow on certain kinds of cured paint films, causing unsightly dark blotches. Ultraviolet-screening agents that absorb ultraviolet rays from the sun in exposed coatings and reduce ultraviolet degradation in the film, which drastically reduces the life expectancy of certain vehicles, such as the vinyl chloride resins. Plasticizers increase the flexibility and adhesion of film formers; in fact, many of the important film formers, such as the vinyl chloride resins, would not be usable without them. Acid accepters accept and neutralize acids formed by certain important resins, such as chlorinated rubber, during storage, thereby preventing these acids from causing the film former to deteriorate rapidly. Antiskinning agents reduce or prevent paint skinning in the can, especially during long storage or after some of the paint has been used.* [Gooch, 1993, p.57-58]

***Table 25**: Functional componants or additives found to be present (+) or absent (-) in acrylic and alkyd paints in the Netherlands. (van Faassen and Borm, 1991)*

Functional Component	*Acrylic Dispersion Paint*	*Alkyd Paint*
Binder	+ (polyacrylate)	+ (alkyd resin)
Pigment	+	+
Filler	+	+
Organic Solvent	+ (0-15%)	+ (about 50%)
Ammonia	+	-
Amine	+	-
Preservative	+	-
Surfactant	+	-
Corrosion Inhibitor	+	-
Thickner	+	+
Drier	-	+
Anti-skinning Agent	-	+
UV absorber	+	-

Typical addition levels are also reported for a range of paints. More details of the properties of paints, which additives are often required to modify, are listed in Dick (1967, p.215).

10.2 Mineral whites, fillers or extenders

Barytes, China clay, silica and asbestine are called either mineral whites, fillers or extenders and according to DLNS , (1955, p.26*), 'Their inclusion in a paint is justified only to the extent that they may act as correctives with pigments which lack "tooth" or "texture", or have excessive chalking or settling tendencies'.*

Calcium carbonate, is cited by Hess (1965, p.272) as impeding the weathering resistance of outdoor paints:

> *'On account of the hygroscopic properties of chalk, oil paint containing it must not come in contact with moisture, in order to prevent the formation of blisters. Where this requirement cannot safely be fulfilled, the chalk should be replaced with barium sulphate.'*

10.3 Asbestos

10.3.1 Asbestos, asbestine and other nomenclature

When reading paint formulations it would be wise to interpret listed components with care. The discussion from Crewdson (1943, p.23) outlines some of the nomenclature for asbestos in paint:

> *Magnesium silicate, or asbestine, is another popular paint extender and is used almost as much as barytes in the paint manufacturing industry. It is low in cost because it is made out of asbestos which is a very cheap material. This material is also known as French chalk and talc.*

Chatfield (1962, p.221) describes a range of mineral extenders under the heading, Magnesium Silicates, including *'…talc, asbestine and some forms of asbestos and sepiolite*.' The apparent difference between asbestine and asbestos was not explained, however it appears that special coatings requiring the reinforcement of asbestos fibre, used 'asbestos', while asbestine is the more fine particle size extender and suspension agent. Chatfield notes the use of asbestos minerals such as actinolite, tremolite, chrysotile, amosite, anthophyllite and crocidolite in selected products and special applications only.

Boxall and von Fraunhoffer (1980, p.24) and Armitage (1967, p.63) mention the use of talc as an extender in paint. In some cases where the term magnesium aluminium silicate is used, 'talc' additives or asbestos could have been utilised, both are or can be magnesium aluminium silicates, or described as such although the asbestos minerals generally contain iron and potentially other elements.

Asbestine is prepared by *'dry pulverizing followed by air flotation'* according to Morgans (1982, p.76).

In relation to both talc and asbestine, *'Particle sizes vary and some grades may contain particles up to 40µ'.* (Armitage, 1967, p.63). An asbestine sample in Chatfield, (1962, p.222) has an average particle size of 2.3 microns. According to Johnstone (1954, p.52) short asbestos fibres and floats, that were not useful in asbestos cement, woven products or as paper and millboard fillers were used as *'…fillers in asphalt, paints and putties, plaster, stucco, plastic mouldings, etc.'* Given that premiums were paid for long asbestos fibre product (Berkman, 1982) it is suggested that the use of very fine but clean low cost or even by-product asbestos in paints would have been commercially attractive.

10.3.2 The function of asbestos in paint

The use of asbestos in paint spanning many years will be demonstrated. Asbestos would appear to be more readily justified as an additive from the point of view of function by some. Jennings, (1926, p.191) in referring to paint additives mentions adulterants, barytes, whiting or paris white and gypsum which have as their most important purpose to cheapen the finished article. A more functional additive was Asbestine which is defined by Jennings (1926, p.302) as:

> *'A white powder made by grinding asbestos and used in small proportions in ready mixed and other paints with two objects, first to prevent settling of the pigments and, secondly, to ensure that when the paint film needs repainting, that it is in a somewhat rough and fit condition to receive another coat of paint without much preparation.'*

A paint product is advertised in such a manner in Mayes (1938, p.303), that would suggest that *'Ormonoid Asbestos Paint. For protecting all bitumen and iron roofs and metal structures.'* is being promoted with asbestos in the product name because asbestos was either a substantial paint component or an essential functional component.

Traffic paints described in The Chemical Formulary (1943, VI, p.254-257) have asbestine at levels in excess of 50% of the pigment fraction in order to achieve optimum wearing qualities, and infra red reflecting paints for military applications, generally have >60-70% extenders in the pigment fraction, with asbestos nominated as the 'extender' in 2 formulae (ibid, pp.298-300).

Asbestos is described by Vanderwalker (1944, p.74) in a similarly descriptive manner as a material used in ready to use prepared paints as opposed to being a component used by the painter who largely mixed his own raw paste or dry powder materials. Its use in paint is described as follows:

> *'Its particles are rather long and narrow fibres, rather than round, and it is used as sort of a reinforcement in paints just as hair is used in plaster. Its other prime purpose is to help to hold the paint pigments in suspension in the liquids.'*

It is probable that asbestos was used in paint in Australia from the following passage from Brindley in *Australian Home Decorator and Painter* (c. 1952, p. 221):

> *'Asbestine.- A crushed waste mineral asbestos used in the production of fillers and washable distempers, asbestine is sometimes used in flat oil paints because it improves the grip or tooth of the paints with the surface'.*

The reference to asbestos being a waste mineral, or by-product by Brindley (c.1952) and Johnstone (1954) respectively is an indication that its use in a paint product was probably not restricted by cost.

The use of the suspending properties of asbestine, particularly in the heavy paint primer pigments, red lead and calcium plumbate, is noted by Chatfield (1962, p.223).

More recently, Morgans (1982, p.76) remarks on the anti settling properties from the addition of asbestos and that it '*...increases the mechanical strength of certain types of paint film*' giving some indication of continuing use of the material.

Asbestos has been recognised as a functional component in paint for many years but it is not mentioned in Gooch (1993, p.78-81) in a section dealing with many historically used paint additives.

10.3.3 Quantities of asbestos in paint

A listing of a range of paint formula readily demonstrates the incorporation of asbestos in paints. A red asbestos roofing paint formulation to make 52 gallons is as follows:

Pitch	*50 pounds*	
Naptha (49 degree)	*24 gallons*	
Aluminium Steareate	*2 pounds*	
Bright Red Oxide (yellow tone)	*100 pounds*	
Fibrous Asbestos	*24 pounds*	
Blown Linseed Oil	*8 gallons*	
Kerosene	*4 gallons*	
V.M.&P. Naptha or Gasoline	*10 gallons*	[Atlas Chemical Company, 1896, p.804]

Examples from The Chemical Formulary (1935, p. 101) shows asbestine concentrations at 10% of the pigment fraction and > 6.4% of the dry film weight:

Synthetic Resin House Paint, Formula No. 1:

Pigment: 64%

Leaded Zinc Oxide	*35%*
Cryptone (50% ZnS, 50% $BaSO_4$)	*45%*
Asbestine	*10%*
Silica	*10%*

Vehicle: 36%

Durez Varnish	*40%*
Refined Linseed Oil	*43%*
Turpentine	*15%*
Drier	*2%*

[The Chemical Formulary, 1935, p.101]

The following formula would appear to have the potential to result in some 10-15% asbestos in the final paint film:

Crackle Lacquer (Green)

1/2" R.S. Cotton, Wet	*59*	*parts*
Ethyl Acetate	*68*	*parts*
Butyl Acetate	*99*	*parts*
Toluol	*235.6*	*parts*
Wax-free Dammar	*33.5*	*parts*
Alcohol	*219.9*	*parts*
Benzo	*78*	*parts*
Chrome Green	*226*	*parts*
Asbestine	*85*	*parts*
Magnesium Carbonate	*51*	*parts*

[The Chemical Formulary, 1935, p.91]

Eleven out of twelve paints for steel surfaces tested for durability in Fancut and Hudson (1957, p.43) have a pigment fraction that includes 20% asbestos. Asbestine is contained in paint formulae of Burns and Bradley (1960, p.457) at concentrations of some 9-14% in the pigment fraction of the paint.

A summary of asbestine concentrations in paints (Table 26) from 1950 to 1982 collected from a range of sources include materials from > 4 to 11% asbestos.

***Table 26**: Asbestos levels in a range of paints.*

	Asbestos in paint film or dry ingredients (wt %)	*Paint use/Type*
1)	11%	hull paint
2)	> 4%	red lead primer
3)	> 10%	two pack polyurethane steel primer
4)	> 4%	pink primer for woodwork
5)	approx. 6%	oleoresinous interior primer
6)	>10%	two pack anti-corrosive finish

Data Sources:

1 The Chemical Formulary (1951, p.389)
2 Boxall and von Fraunhoffer (1980, p. 113)
3 Boxall and von Fraunhoffer (1980, p. 123)
4 Boxall and von Fraunhoffer, (1980, p.130)
5 Morgans (1982, p.78)
6 Turner, (1967, p.217)

The amount of asbestos in paint may be some 5-10 wt% in dry paint films, higher concentrations of asbestos are likely to occur in basal priming paint layers on steel than in upper layers on other materials.

Having inspected several hundreds of paint layers and bulk paint samples in polished sections at 400x by reflected light microscope, and conducted limited, incidental SEM inspection and electron microprobe analysis, it appears to the writer that asbestos fibres >5 microns in length are likely to found in older Australian paint layers and samples. More work using techniques such as X-Ray Diffraction, SEM and electron microprobe analysis would be required to establish the status of asbestos in residential paints.

10.3.4 The risk of asbestos in paint

Some early assessments of the occupational risks of asbestos in paint were understated. Hess (1965, p.176) notes that asbestos can *'…cause illness similar to talc, … but more dangerous'*, under talc it is said *'Inhalation of this magnesium silicate as dust can cause illness very similar to pneumoconiosis- "talcosis", and an increased tendency for tuberculosis. Micas, other silicates, are a similar hazard.'* (p.198). In recent decades, asbestos-containing materials have been increasingly regulated. From 1995 (NOHSC, 1995), in the context of the *Control of Workplace Hazardous Substances*, asbestos materials were the subject of strict regulation where Amosite and Crocidolite were listed as prohibited carcinogenic substances and Chrysotile was listed as a notifiable carcinogenic substance.

In the case of asbestos in paint, any risk will relate to the size and morphology of any fibres that may be able to be liberated from the dry film material. There does not appear to have been any assessment of such possible liberation mechanisms of asbestos from paint. It is suggested that a chalking mechanism would be most likely to release larger intact fibres, although the effect of sand-papering probably requires evaluation. Ash from paint incineration may present an asbestos risk, while paint removal by heat gun or chemical stripper may pose a relatively low asbestos risk, at that time. Some investigation would appear to be required to evaluate these risks.

On the basis of literature relating to historical paint formulation there may be widespread asbestos in paint and much of that is overlain by more recent paint layers that may not contain asbestos.

The risk of paint asbestos, where fine powder asbestos is added to the other filler materials and pigments and then ground in oil - as is common, may be low if the fibre length after grinding is less than 5 microns. Meldrum (1996, p.55) in a *Review of Fibre Toxicology* notes the common definition of a regulated fibre for counting purposes as >5-10 microns in length, but less than 100 microns with a width of <1.5 - 2 microns and an aspect ratio of >5:1 to 10:1. The WHO definition is >5microns length and <3 microns diameter with an aspect ratio of >3:1 (Meldrum, 1996, p.4). For an Australian risk assessment of asbestos, Imray and Neville (1993, p.247-259) is suggested.

A sequence of questions to be asked relating to the risk of asbestos in paint may include:

- What is the occurrence of paint layers having fibre lengths that pose a risk (greater than 5 microns)?
- What are the processes for the liberation of any such fibres?
- Would the occurrence of asbestos in basal layers of paint films reduce the likelihood of liberation of fibres in residential settings?
- Are processes for the liberation of any fibres likely to release fibres that present a risk?
- As asbestos fibre is a long-lived highly durable material, have issues related to the present and future risk of asbestos fibre been assessed adequately?

The toxicity of a hypothetical asbestos fibre having adhering residual paint material is unknown.

Asbestos in the upper layers of paints in residential settings is likely to be rare. However given published paint formulae in the paint technology literature, undercoats and priming paints may well have contained asbestos into the 1980s.

The morbidity and mortality of painters and workers in paint manufacturer from asbestos-related disease may warrant epidemiological evaluation. Some areas where quantities of asbestos in paint may be suspected are shipyards and bridge painting or metal/sandblasting situations.

10.4 Driers

10.4.1 Paint driers, old and recent

Driers are used to develop a rapidly drying skin on a paint by oxidation. The benefits are to develop touch hardness sooner, and avoiding problems associated with insects crawling on wet paint surfaces, or water splash.

Examples of early dryer formulations since 1896 are:

(for Varnish Paints)

Cwt	*qrs.*	*lbs.*	
0	*0*	*21*	*White Sugar of Lead.*
0	*2*	*21*	*Powdered Litharge.*
0	*3*	*21*	*White Copperas.*
4	*1*	*0*	*Paris White*
4	*1*	*0*	*Barytes.*
2	*0*	*10*	*Raw Linseed Oil.*

Terebene

Cwt	*qrs.*	*lbs.*	
			24 gallons Raw Oil
0	*1*	*10*	*Flake Litharge.*

Boil 12 hours, and when cool enough mix with 34 gallons of Turpentine.

Patent Dryers.

Special

No.1.

Cwt	*qrs.*	*Lbs.*	
2	*0*	*0*	*Barytes.*
2	*0*	*0*	*Whiting.*
0	*1*	*0*	*White Sugar of Lead.(lead acetate)*
0	*2*	*0*	*White Copperas.*
0	*2*	*0*	*Powdered Litharge.*
0	*2*	*0*	*Dry White Lead.*
1	*0*	*0*	*Boiled Linseed Oil.*

[Atlas Chemical Company, Sunderland. 1896 p.154-155]

Other components of Patent Dryers seen in Atlas Chemical Company (1896) book include:

- carbonate of zinc
- borate of manganese
- sulphate of zinc

The above driers from 1896 are for the dry pigment or pigment paste mixing as opposed to ready made paint sold in a can.

The price of paint driers in 1938, in Sydney, (Mayes, p.303) was 10d per lb. for Ferguson's Driers, patent; and 14/6 per gallon for terebine.

A comment in relation to driers is a valuable insight:

> *Extra Drier Needed.- Under certain weather conditions-on cold, damp winter days and during hot, humid days in the middle of summer-it is sometimes difficult to mix your paint so that it will dry as rapidly as it should. During such weather additional Japan drier to the extent of about ¼ to ½ pint should be added to 100 pounds of lead when raw oil is used. It is not often necessary to add any drier to boiled linseed oil, but there are some extreme conditions where a little is needed.*
>
> *During difficult drying weather a little extra turpentine will accelerate the drying.*
>
> *When using slow drying color pigments such as lamp-black, chrome yellow, chrome green and ordinary yellow ochre in considerable quantities to make dark colored paints additional turpentine and drier are needed.* [Vanderwalker, 1944, p. 124]

More recent use can be described as follows:

> *Action of Pigments.-Whilst pigments do not normally affect the drying of the paint, there are individual ones which assist the binder's drying action. For example, whitelead, redlead and burnt umber are relatively active drying pigments. Others, such as the blacks, tend to retard the action of the binder.*
>
> *Linseed oil paints generally need the addition of driers, when being mixed up, but mixtures based upon the use of varnish or goldsize which have strong drying properties, do not need extra aid. Factory-prepared paints and enamels have driers incorporated in their manufacture, so additions are not necessary.*
>
> *The quantity of driers added can be taken as approximately 2 per cent, of the linseed oil used. Paints on interior surfaces require a little more drier than those for exterior purposes.*
>
> *Solid Driers are used more or less exclusively by the manufacturer.*
>
> *Paste Driers or Patent Driers are prepared by combining drying agents with linseed oil and Barytes. This results in a milder action which is very suitable for light colors and white paints.*
>
> *Terebine. This liquid is by far the most commonly used drier for hand-mixed paints, It is a dark-brown colored liquid, based upon oil and turps in conjunction with drying agents.*
>
> *The major aspect of paint driers lies in the fact that, whilst, in certain instances, driers are very necessary, the use of excess driers will lead to the premature deterioration of the paint, because the accelerating action continues throughout the life of the film.*
>
> *In some instances, excess driers will cause the paint to remain sticky indefinitely.*
>
> *Drying agents are oxides of metals such as litharge, manganese, lead and cobalt. They have a strong oxidating action, and when used in paints draw additional oxygen into the film, from whence it attaches itself to the binder molecules.*
>
> *Complete dispersion of the driers in paints is an extremely important factor in order to gain uniformity of film.* [Brindley, c.a., 1952, p.228]

In addition to the above, orange lead is noted as having a definite drying influence while *'Others notably zinc oxide, lithopone, titanium dioxide, and antimony oxide, are neutral, i.e. they neither hasten nor retard the oxidation of the oil'* (Holloway, 1953, Vol.II p.232).

Crewdson (1943, p.25) refers to two separate types of driers suited to either dark or light coloured paints. Japan driers for dark paints contain *'...linseed oil or tung oil, or both, which are cooked with drying salts from lead and manganese, resins, gums and turpentine or mineral spirits.'*, whereas the driers for white paints *'...are made principally with lead acetate (sugar of lead) and litharge.'*

Vanderwalker (1944) appears to reason that white lead with boiled linseed oil requires no drier, however, where raw linseed oil is used, a Japan drier may be used. The trade off with boiled linseed oil and driers is also mentioned in Holloway, (1953, Vol.I, p.210).

'Zinc oxide has no siccative or drying action on linseed oil, and consequently some form of added drier is usually essential' (Holloway, 1953, Vol.I, p.30), with liquid driers generally being more suitable. Similarly TiO_2, carries with it no drying action. The brittle drying properties of ZnO are likely to not be helped if paint driers are added in excess.

According to Hess (1965, p.6) driers containing lead and manganese accelerate the drying from the inside, while cobalt exerts the reverse effect. The drying effect of cobalt is such that too much added drier is unsuitable in synthetic resin or wood oil based varnishes (p.9-10), causing rapid skinning in the can. It is recommended in Hess (1965, p.66) that drying of wood-oil type varnishes can be improved slightly by small additions of a lead-manganese drier, whereas large additions of a cobalt drier are not recommended.

The catalytic drying agents used are heavy metal salts of organic acids (Table 27), *'...cobalt naphthenate produces surface-drying, whilst lead naphthenate produces through-drying of the film.'* according to Armitage (1967, p.83).

***Table 27**: Typical levels of metal in paints, as percent of liquid paint, from the use of driers (Armitage,1967, p.84)*

Lead	0.01 to 0.1%
Cobalt	0.02 to 0.2%
Manganese	0.02 to 0.2%

A formulation for marine spar varnish included 0.9 wt.% lead naphthenate (at 24% Pb) which would have resulted in a minimum of 2160 mg/kg Pb as lead naphthenate in the dried film (Turner, 1967, p.217).

Some polyurethane coatings contain organo-tin salts as drying catalysts (Armitage, 1967, 85).

For information on the nature of metal driers (curing agents) and metallic soaps such as metal stearates or napthenates the reader is referred to the Kirk-Othmer *Encyclopedia of Chemical Technology* Third Edition Volume 8. pp.34-49; Morgans (1982, p. 181) and Boxall and von Fraunhoffer (1980, p.110). Common metal driers include lead, manganese and cobalt compounds.

In Australia, more recently, driers in liquid form as LMC (lead, manganese, cobalt), from some manufacturers have been referred to as having superseded terebine.

A South Australian paint company once made liquid 'LMC Driers' which were to be used at a rate of up to 1/4 to 1/2 pints per gallon of paint, that was sold in a 500ml can. A more recent product, purchased in December 1993 ($15.92) was a 1 litre container of LMC driers (Line 217) at 26.2% Pb N/Vol. The label on the can did not specify rates of addition to paint; however a product information sheet (also Line 217), dated December 1982 suggested a use of approximately 250ml per 4 litres of paint (equivalent to an additional 1.54% Pb N/Vol.).

10.4.2 Driers: usual practice

The use of additional driers is expected to be higher in outdoor painting situations, and greater in 'wet' climates or when painting in winter. Painters use driers on a discretionary basis, for example, when they need some insurance against the possibility of rain damage. If rain is forecast for late in the day, it was not uncommon for painters to proceed to work in partially sheltered areas under verandahs, and eaves and tell you they add driers to more quickly harden the paint and prevent possible rain splash damage.

According to Hess (1965, p.72*); 'The use of a quicker-drying paint is often recommended for winter conditions, or the manufacturer may supply an "accelerator" in the form of a balanced drier solution to be added to the paint in fixed proportions in order to speed up the initial touch-dry stage.'*

The use of driers (Hess, 1965, p.323) is further justified:

> *There are also cases where by addition of a comparatively great quantity of liquid driers, acceleration of drying (and not delaying) can be achieved, this may be preferable under damp weather conditions.*

In addition to lead pipe as a substrate which promotes paint drying, '*...pigments which normally promote drying will influence the drying of a top coat even if they are contained in an old hard and thoroughly dry film which has been rubbed down for the purpose of being painted over.*' (Daniels in Hess, 1965, p.323).

10.4.3 The misuse of driers

Holloway (1953, Vol.II p.231) notes some of the pitfalls in the use of driers:

> *Abuse of Driers.-In particular, the misuse of driers is frequently to blame.* (for paint failing to dry and harden properly) *These products are added to paint to accelerate the absorption of oxygen and do so effectively, if they are used with discrimination. If too much driers are added, however, oxidation takes place too quickly with the result that a skin is formed on the film and this prevents the process from continuing normally throughout the thickness of the coating, so that the lower part of the latter remains permanently soft. Many painters add driers recklessly because, unfortunately, the strength of these substances varies not only according to their nature but according to the formulation of individual manufacturers, so that it is not possible to say just how much should be incorporated in a paint. In addition, the amount must vary according to the atmospheric conditions; in cold weather, for example, considerably more can be used than on warm days. All that can be said on this point is that they should at all times be employed sparingly and that it is far better to add too little than too much. Any excess may prevent the film from hardening properly and, even if it does not have this effect, it will probably affect the durability of the coating.*

Points of advice given in relation to the use of driers (DLNS , 1955, p.39) are:

> *The accelerating effect of driers is not proportional to their quantity. When added above a certain small proportion, usually not exceeding 2% of the oil, no further increase of drying rate is obtained, and excess is definitely detrimental.*
>
> *The oxidation of an oil does not cease with the completion of the "drying". The elastic film first formed continues to change, becoming harder and less elastic, and ultimately, brittle and disintegrated. The acceleration produced by "driers" hastens these further changes, shortening the life of the oil film.*
>
> *Stimulation of the drying beyond a certain point spoils the quality of the film, causing the oil to dry rapidly on the surface and remain soft underneath, instead of hardening uniformly from top to bottom.*

Incorporation of driers just before application or after a drying problem has been recognised has been common practice. In order to speed up the drying of silicone resin lacquers (Cahn in Hess, 1965, p.63) the '*...addition of 0.5% lead in the form of a drier, calculated on resin solids, one hour before application...*' is recommended.

The addition of too much drier is also noted by Hess (1965), as slowing air drying, for example cobalt drier in a film of greater than 20 microns thickness . In relation to the amount that may be added it is suggested '*Five per cent (depending on its metal content) of the total quantity of paint usually represents very roughly the permissible maximum …In trying out, one should start with adding only 0.5 per cent.*' (p.56-57).

The history of DIY practices such as the mixing of red oxide, car sump oil and lead-based driers to make a fence stain, as found in a newspaper 'handy hints' column require investigation. In this situation there is the added problem of PAHs, petrol-derived organic lead in the sump oil in addition to organic lead in the driers as the more longterm toxic components of such a mixture.

10.5 Risks associated with paint driers

The fate of lead in driers in the dry paint film and subsequent risk implications are not particularly well understood. Cobalt could be expected to be concentrated at the paint surface. Hess (1965, p.237) notes the presence of striations on the paint surface, potentially attributed to *'...precipitation in crystalline form of insoluble lead soaps derived from excessive drier additions.*' This is likely to be a rare cause of striations in paint.

Conventional wisdom suggests that additional paint lead attributable to user added driers may amount to an additional 1 to 2 percent lead in the dry film. The behaviour of individual painters is such that major variability should be expected in the amount of lead in paint that could be attributed to user-added driers. Much information exists regarding the misuse of driers. The proportion of lead attributed to the driers added to a paint by a manufacturer may be more systematic and uniform. At low levels of lead in paint (for example < 1% Pb), little details exist as to the lead compounds found in paint films.

Some questions in relation to the risks of paint lead driers are:

- what are the common concentrations of lead in paint films from lead driers in paint?
- what are the compounds formed by lead driers in paint; before and after paint weathering?
- are there particular characteristics of toxicity of these compounds and is there potential for greater bioavailability of lead or increased dermal absorption for example?
- how mobile are compounds formed by paint lead driers and what is the location of paint lead driers within paint layers before and after paint weathering?
- what is the extent of use of lead driers in situations where there is some likelihood of exposure of children?

10.6 Fungicides

Hess (1965, p.364) notes optimum environmental conditions for mildew growth on and in paint (including fungi and mould) are:

- continuous high humidity, preferably above 75% relative humidity
- high average temperatures - optimum at 25° C
- lack of light and sunshine
- still air
- a substrate suited to the growth requirements of mildew, eg linseed oil, casein, plaster providing nutrients and minerals
- with mildew more readily observed on light coloured paint films
- softer, slower drying paints are more prone to infection by moulds

Risks related to mould growth on paint are those of the degradation of paint films, causing the liberation of toxic paint components such as lead for example, the health risk associated with damp, moulds and spores. Other risks relate to the deliberate addition of fungicidal compounds to paints.

Brindley (circa. 1952, p.99) describes the use of formaldehyde, and the products *Shirlan N.A.* and *Santobrite* as preparations to apply to surfaces already having mould or fungus. Options for an 'antiseptic' wash in Holloway (1953, VII, p.229, and Hess, 1965, p.366-367) include:

1. *A 1 per cent. sodium pentachlorophenate (1lb. to 10 gallons of water). This material is obtainable under the name of "Sanobrite," from the Monsanto Chemicals.*
2. *A 1 per cent. solution of the sodium salt of salicyl anilide.*
3. *As an alternative to either of the above a solution of 6 oz. zinc silicofluoride to a gallon of water can be used*

In addition to the above list, Hess in 1965 listed *'…a solution of an organo mercury compound in white spirit or other suitable solvent'.*

Table 28: *Preservatives and fungicidal agents for paints in the Paint Trade Manual (ca.1960s, p. 75-76).*

Barium Metaborate
Benzoic Acid
Butyl Phenol
Chlorinated Phenols
Chlorinated Xylenols
Cupric Hydroxide
2:4 Dichlor Phenol
Hydroxyl benzoates
Pentachlorophenol
o-Phenylphenol
Salicylic Acid
Salicylic Acid Derivatives
Sodium Benzoate
Sodium Ortho Phenyl Phenate
Sodium Pentachlorophenate
Tributyl Tin Fluoride
Tributyl Tin Hydroxide
Tributyl Tin Oxide
Trichlorphenol 2, 4, 5
Trichlorphenol 2, 4, 6

Table 29: *Bioactive additives and their effective concentrations (Boxall and von Fraunhoffer (1980, pp.31-32)*

Barium metaborate	*15-20%*
Dichlorofluamide	*1.5-2.0%*
Dithiocarbamates	*3-6% of total solids*
Organomercurials	*0.05-0.3%*
Organotin	*1% of solids typically*
Zinc oxide	*30-40%*

The Australian Oil and Colour Chemists Association (1983, p.370) discuss the qualities of the following fungicidal components in house paints (as opposed to marine paints) in relation to their ability to suppress the growth of mould and mildew:

- chlorinated phenols
- pentachlorphenol
- mercurials
- tetramethyl thiuram disulphide
- salicyanilide
- para-toluene sulphonamide
- *n*-trichloromethyl thio-pthalimide
- 2,3,5,6-terachloro-4-(methylsulphonyl) pyridine

Chlorinated rubber, polyvinyl chloride and chlorinated waxes are noted by Hess (1965, p.366) to be resistant to mould growth and bacteria, and that '*…additions of chlorinated paraffins or diphenyls as plasticisers will increase resistance to fungi.*'

Preservatives in water-based construction paints from a survey in the Netherlands are listed by van Faassen and Borm, (1991, p.151).

Emulsion paints, being aqueous suspensions of synthetic acrylic or vinyl polymers, usually contain a small proportion of fungicide and bactericide, as preservatives before or after application (Browne, 1983). Fungicides are a common component of some paints - particularly formulations for humid or tropical settings such as the bathroom, Darwin or PNG.

Interior latex paint containing an additive, 25% bis(tributyltin)oxide, added prior to painting to combat mildew - was thought to be responsible for complaints of nausea, vomiting, sore throat burning nose, watery eyes and wheezing in the case of a family exposed to paint odours in the first days after some indoor painting (Wax, 1995). Six previous cases of illness associated with bis(tributyltin)oxide in indoor paints resulted in regulation in the US State of Washington to forbid the sale of the bis(tributyltin)oxide additive for use in indoor paints. It is noted in Dick (1987, p.267) that levels of organotin compounds in paint solids of up to 1% are required to provide fungicidal protection.

The paint industry's experience has provided them with opportunities for diversification into agricultural pesticides as this comment from Cleary, (c.1956, p.25) suggests, '*...Berger paris green was used to spray crops in Canada and Australia*' and similarly, in the 1940s Taubmans manufactured DDT.

ICI Dulux were promoting a product in Australia in the mid to late 1990s (undated brochure) called Mouldshield that uses zinc oxide in unspecified concentrations as the active ingredient. It is said to prevent mould growth for two years and it is claimed that zinc oxide will not leach from the paint surface.

Mercury use in paint is dealt with in detail in a later section.

10.6.1 Surface disinfection in hospitals

The use of paints having a bactericidal effect at the coat surface on hospital furniture and in operating theatres is noted by Chatfield (1962, p.325). The need for materials that are readily incorporated into the paint at some 2% of total paint weight, yet with *'…enough water solubility to become bactericidally active when the dry paint film is wiped over with a damp cloth'*, are properties of alkyl trimethyl ammonium bromide (Chatfield, 1962, p.325). More recently, Cooney (1995) evaluated the effects of copper in paint and other fungicidal paints in rendering surfaces self-disinfecting.

10.7 Insecticidal paints

The need for and use of insecticidal paints is probably highly varied; the following is from Armitage (1967, p.117), from the UK:

> *Insecticidal paints have also relatively little use in this country, but they may find application in food-storage depots. Here again there is more interest in such coatings in southern climates where insect control is more of a problem. As with fungicidal paints the preparation requires essentially the addition of some agent (in small amounts) which will either repel the insects or actually kill them on contact with the paint. Chlorinated compounds of one sort or another have been recommended. They may act by slow exudation from the surface of the paint, or by actual volatilisation from the paint; after a while it may be found that the activity progressively decreases. Any one paint will not necessarily kill all types of insect.*

Hess (1965, p.369) notes the use of DDT in paint for the control of insect pests such as cockroaches.

Keeping flies from wet paint is of some concern to painters, one solution is the addition of driers so that the paint surface hardens more rapidly. Here is an outline of the problem and solution from Holloway, (1953, Vol. II, pp 220-221):

> *In summertime flies and small insects settling on paintwork while it is still wet often mar the finished effect. Certain essential oils, such as oil of pennyroyal or oil of spike, added to the paint or waterpaint will materially help in keeping them off, but such additions should only be made in very small quantity, and it is a wise precaution to consult the manufacturers of the paint as to whether they are likely to affect the finish adversely.*
>
> *It is said that flies have an antipathy to certain colors, including blue and yellow; in consequence, it has been suggested that pantries, larders, dairies, and other interiors in which the absence of insects is especially desirable, should be decorated in these colors. The evidence on this point is extremely contradictory and it would be unwise to attach too much importance to this theory.*
>
> *The use of finishes which incorporate powerful insecticides, such as D.D.T., has very great possibilities for the decorator since they provide a powerful new argument for having interior painting carried out. Such finishes, however, kill insects which alight on the surface and do not keep them away, so that, from the painter's point of view, the wet film would still be marred.*

Rawlinson and Partners (1969) in *Spon's Architects' and Builders' Price Book for Australia 1969* obtained prices for insecticidal semi-gloss enamel and insecticidal flat PVA latex paint relative to non-insecticidal paints in Australian capital cities, the insecticidal paints were slightly cheaper than other paints in Perth, Melbourne and were progressively more expensive in Adelaide, Sydney and Brisbane.

The addition of organophosphates to TiO_2 so as to have the effect of making the pigment particle surface hydrophobic is described by Buxbaum (1993, p.60). The manufacture, sale, supply or use of a paint containing insecticide is precluded in Australia according to the SUSDP (1996) No.11 24th Sept. 1996 p.246.

10.8 Mercury in paint

10.8.1 Mercury as a pigment

Alternative names for vermilion are Chinese Vermilion, English Vermilion, (Pure Scarlet, Royal Scarlet, Scarlet Vermilion) French Vermilion, Sinopia, Zinnober, (Crown, 1968) while the mineral name for HgS (mercuric sulphide) is Cinnabar.

Kelly (1929, p.147-148) clearly discusses the use of vermilion as a component of (red) paints as if it were a readily available, readily used component for the practical colour mixer of that time. It is also mentioned that red is a colour to be reserved for small prominent objects.

Vermilion was also used in order to achieve red tones in formulations for timber stains, (Hiscox, 1937, p.494).

The pigment vermilion (HgS) was still in production in the USA in 1942 and 1944, with 215 and 323, 76-pound flasks of mercury being consumed for this purpose (Johnston, 1954, p.327), no consumption of mercury for vermilion manufacture is reported for the years 1948 to 1950.

It is noted in Vanderwalker, (1944, p. 23) that Chinese and English Vermilions, from sulphide of mercury, *'…should not be used with white lead, chrome yellows, chrome greens, any of the copper colors or emerald green. Unfavorable chemical reactions result.'* However this rule is broken in his own formulations (p.257, pp.262-264).

10.8.1.1 Substitutions for mercury as a pigment

There are a range of comments relating to the decline and replacement of vermilion, but as will also be shown, vermilion remained prominent in paint colour recipes for some time.

Other pigments such as American Vermilion, a brilliant red consisting of basic chromate of lead (Vanderwalker, 1944, p. 24) were at least available as substitutes, with this material having the benefit of the colour being permanent in strong light.

Crewdson, (1943, p.19-20) calls the mercuric sulphide pigment English Vermilion, and describes it as having been *'…formerly extensively used but because of its cost has been replaced by others and is used today only in relatively small quantities'*. A so called 'American Vermilion' which is a lead chromate is referred to in Crewdson, (1943, p.20).

Cadmium Red was used to replace vermilion where:

> *Reduced quantities however, are coming into extensive use in the replacement of true vermilion, as they have all the permanent qualities, and particularly heat resisting properties, which are not found in the imitations of vermilion prepared by combining dyes with orange lead pigment.'* (DLNS, 1955, p.29).

And also in relation to vermilion:

> *'With the advent of the permanent red dye pigments however, it is becoming obsolete for general painting on account of its high cost and its coarse texture and heaviness. The latter property causes it to settle considerably, whilst the coarse texture makes it somewhat troublesome to work. It is still used as an artists' colour, and to a certain extent, in vehicle painting.'* (DLNS, 1955, p.29).

Vermilion is said to have been in declining use by Crown (1968, p.43). Curiously, Mercadium red and orange pigments ($CdS{\cdot}HgS$) are said to be first offered commercially in or after 1956 (Crown, 1968, p.40 & 42). Mercury was probably not regulated in paints until the 1960s.

10.8.1.2 Lingering use of mercury as a pigment

There are signs of either past or implied future support for vermilion use over the 1940s-1950s. Vermilion is described as being from deep orange to bluish red in colour, being at one time *'the only red of a permanent character which combined brightness of colour with durability.'* (DLNS, 1955, p.28). Whereas according to Hess (1965, p.354) *'Pure vermillion blackens (although to a more pronounced degree when exposed to heat)…'*

Vermilion was available in the USA as listed in Chemical Industries (1942, p.303) through the following sources:

- Baker Chem Co
- Berk and Co, Inc
- Harshaw Chem Co
- Mallinckrodt Chem Wks
- Mann Inc
- Merck & Co Inc
- Phillips & Jacobs

Vermilion was listed as being available through the following agents in the (UK published) Paint Trade Manual (ca.1960s, p. 66):

- Chemische Verfstoffenfabriek NV
- Heinemann, MH, Ltd.
- May and Baker Ltd.
- Tunley, AE, and Son Ltd.

Holloway (1953, Vol. I, pp.201-208), and Vanderwalker, (1944, pp.252-266) define paint colours with the provision of general recipes and paint names. In the list of 246 paint formulas from Vanderwalker covering a wide colour range, 11 specify the use of vermilion as a component, two of these specified vermilion as an option, 4 formulas required a non-specific 'bright red' pigment. In the 89 paints described by Holloway, 21 specify the use of vermilion as a component, and an additional 6 require a non specified bright red pigment. Similarly Holloway (1953 Vol.II, pp.119-120) defines 15 red colours, two contained vermilionette, six contained vermilion and all but one of fifteen paints would contain substantial amounts of lead.

In 1962, the scarcity of selenium is said to be the reason for the use of HgS to replace selenium in CdS pigments with the writer stating that *'Such improved cadmium pigments have many advantages'* (Chatfield, 1962, p.173).

On the basis of the above formulae it may be reasonable to suspect that mercury potentially occurs as a pigment component in paints described as red, reddish purple, apricot, salmon, shrimp pink, dark red purple, scarlet, red brown, pinks and old gold in house paints mixed prior to the 1950s.

The Berger company would tend to have a loyalty at least to the name, colour and symbol associated with Mercury:

> *'Perhaps more than any other colour, vermilion became associated with the name of Berger; and for many years the winged figure of the god Mercury, after whom the basic element of the colour was named, was the trade mark of Lewis Berger and Sons.'* [Cleary, J., circa.1956, p.22]

Perhaps also, some loyalty to mercury use in manufacture, particularly in times pre-1960, could be more likely in some companies than others. The case of the Mercury Paint Company described in the section on biocides is one such example.

Owing to the cost of red paints containing vemilion, and the use of bright red colours not generally being frequent or over extensive areas, mercury in high concentrations, is probably not found in residential settings as a pigment covering large areas or in a large number of properties. Perhaps mercury as a pigment is more readily found in paint sequences having at one time had a salmon pink coloured paint layer for example. Vermilion has a profile as a house paint pigment more likely to be encountered in decreasing quantities through the 1950s, with a lingering use in artists paints. However, by virtue of the above discussion and in view of the toxicity of mercury, more work is demanded in this matter.

More recent use of mercury in house paints is generally understood to be associated with its use as a fungicide.

10.8.2 Mercury as a biocide

'Some emulsion paints containing a nitrogenous colloid such as glue or casein are subject to bacterial attack in the can. The gaseous products formed have been known actually to burst the container; it is therefore common practice to include a bactericide in the paint.' (Armitage, 1967, p.88). Hess (1965, p.18) similarly notes the deterioration of water- based coatings in the can. In tropical conditions, both emulsion and solvent based paints contained additives to prevent mould on painted surfaces.

According to Armitage (1967, p.117) pentachlorophenol or organic mercurials are the usual fungicidal additives in paints for a limited range of situations such as breweries, laundries and greenhouses and in paints for tropical areas, zinc oxide is usually recommended as the main hiding pigment (± additional fungicide).

Use of mercury in paint as a fungicide is likely to be widespread as may be suggested by the following:

> *'Legislation in Australia does not yet eliminate the use of mercury... it is probable that mercury is the most commonly used fungicide for paints. Commercially at a sufficient level, mercury is effective in controlling fungal growth under most conditions*.'
>
> [The Oil and Colour Chemists Association, 1983, p.370]

Hess (1965, p.367) noted the suggested use of mercury sulphate as a wash for the treatment of fungal growth in cellars.

Walker and Hickson (in Hess, 1965, p.369) in US Department of Commerce specifications suggest the use of *'One part of mercuric chloride to every 600 parts by weight of paint properly ground in the paint liquid. The content of mercuric chloride should be stated on the label with the necessary precautions.'*. This added mercury is designed to protect the paint after application.

An emulsion paint based on PVA incorporated phenyl mercury acetate at 0.2% of the wet weight of the paint (Turner, 1967, p.162). At 10% Hg in phenyl mercury acetate and 70% of the paint not being water - a minimum initial mercury concentration for that paint material prior to advanced paint drying and any mercury leaching would have been some 140 mg/kg mercury.

Agocs, Etzel and Parrish *et.al.* (1990) investigated mercury exposure in persons living in houses decorated with paint containing phenylmercuric acetate preservative. A latex paint manufactured by the Mercury Paint Company, contained 4.7 mmol of mercury per litre at a time where the EPA's recommended limit was 1.5 mmol or less per litre. An exposed population of 74 persons from 19 households had a median urinary mercury concentration of 4.7 nmol of mercury per millimole of creatinine; with a range of 1.4 to 66.5, which includes concentrations associated with symptomatic mercury poisoning. An unexposed population of 28 people from 10 households had a median urinary mercury concentration of 1.1 nmol Hg per millimole of creatinine with a range of 0.02 to 3.9.

In what may have been the same incident, (Aronow, et.al. 1990) describe a case of childhood mercury poisoning in a 4 year old boy in the month after the application of 17 gallons of latex paint containing 930-955 ppm of mercury to the house interior. There was no data on the mercury concentration in dry paint films or air Hg concentrations. Paints could contain mercury up to the time of the above incident at levels upto 300 ppm but mercury could not be added to interior latex paint after August 1990 in the USA.

According to Gooch, (1993, p.79) mercury use in the USA is common:

> *'Almost every formulation based on water must have a preservative for can stability. Until recently, most preservatives have been mercurials, but these are being partially replaced by complex organics.'*

and

> *'Most exterior paints experience discoloration due to the growth of fungi or mildew. Until now, this condition has been prevented by including a mercurial in the paint, often in combination with zinc oxide; at present, nonmercurials are also available.'*

Mercury has been variously restricted to 1000 to 5000 ppm in paints in the past in State legislation in Australia. Where mercury occurs in paint at concentrations greater than 0.01% (100 ppm on the basis of the non-volatile component of paint) the warning DANGEROUS POISON is required on a label (NHMRC, 1996, p.172).

In December 1993 a 1 litre container of anti-fungal paint additive was purchased in South Australia by the writer; it had '*Mercury 37 grams/litre as organic mercury'* on the label. This message was partly obscured by black pen ink, however the instructions *'Add to oil or water-based paint at rate of 12.5ml/litre'* were clearly visible. A company information sheet from June 1985, (Line 651) noted the mild and pleasant odour of the additive, and repeated the above details.

If used as recommended, the amount of mercury in the paint can be calculated and an estimation made of the amount of mercury in a layer of dry paint, after application:

mercury in the paint

the additive has 37g/L or 37mg/ml of merury which is added to the paint at the rate of 12.5ml/L resulting in 37 x 12.5 mg of mercury per litre of paint

462.5mg of Hg/L added to the paint.

mercury loading

on the assumption that 1 litre of paint covers 13 m^2

there will be 462.5/13 mgHg/m^2

35.6mg of Hg/m^2 in each coat of paint.

mercury concentration in the paint layer

assume that the paint dries to 30 - 50% of its original volume after application

assume the density of the dry paint is 3 - 4 g/cm^3

then there will be 462.5mg of Hg in 300 - 500cm^3 of dry paint

or 925 to 1542 mg of Hg/1000cm^3

1000cm^3 of dry paint film will have a mass of 3 - 4kg

then there is between 925/4 and 1542/3mg of Hg/kg

231 to 514mg Hg/kg in each layer of dry paint.

an alternative estimate of paint layer mercury concentration

assume 35.6 mg Hg /m^2

assume a paint layer thickness of 20 - 40 microns (2 - 4 x 10^{-3}cm)

assume a dry paint density of 3 -4 g/cm^3

1 cm^2 of paint one layer thick has a volume of 0.002 - 0.004 cm^3

1 cm^2 of paint one layer thick weighs between 3 x 10^3 x 0.002 = 6 mg

and 4 x 10^3 x 0.004 = 16 mg

at 35.6 mg Hg /m^2 the 1 cm^2 of paint one layer thick contains 0.00356 mg of Hg

and the paint layer has a concentration of mercury between:

0.00356/16 and 0.00356/6 kg/kg

222 mg Hg/kg to 593 mg Hg/kg in each layer of dry paint.

The use of the above additive with a content of 37 g Hg/L, added to paint at the recommended rate of 12.5ml/L, is likely to result in an additional 200 to 600 mg of mercury in each kg of dry paint film.

Table 30*: Paint preservatives and fungicidal agents that contained mercury*

(Paint Trade Manual ca.1960s, p.75-76).

Phenyl Mercuric Acetate
Phenyl Mercuric Borate
Phenyl Mercuric Chloride
Phenyl Mercuric Hydroxide
Phenyl Mercuric Nitrate
Phenyl Mercuric Oleate
Phenyl Mercuric Propionate
Phenyl Mercuric Salicylate
Phenyl Mercuric Stearate

Past views of the risks of mercury in paint, are indicated as follows:

> *'Mercury compounds used as fungicides in paints and varnishes are not regarded as potentially dangerous. They must, however, be manipulated with great care.'*

And further, a preference for organo mercurials is stated:

> *'On choosing fungicides, i.e. potential poisons, the contemplated use of the paints has to be considered, thus most inorganic mercury salts have to be excluded from paint designated for food factories, breweries, malt-houses, bakeries, kitchens, etc., but are admissable, e.g. inside optical instruments. Organo mercurials are usually considered satisfactory for decorative or protective paints, due to smaller amounts required, and the lower degree of leaching which these compounds give than the inorganic mercury compounds.'*[Hess, 1965, p.206 and then p.367]

The above is an example of the conventional wisdom of the mid 1960s prior to more critical evaluations of the risks of mercury such as the reviews of Cross *et.al.* (1995) and ATSDR (1994).

A critical review and investigation of mercury use in paint would target paints formulated for use in tropical or humid geographic locations and in laundries and bathrooms. Similarly paints chosen to combat particular mould problems would be worth investigating. Paints having in excess of 300 mg Hg /kg have been encountered in a limited survey of South Australian paints.

Mercury use is also discussed in the section on marine paints and in relation to the use of heat guns for paint removal.

10.9 Plasticisers

Plasticisers are added to resinous materials or polymers to increase their flexibility. The toxicity of plasticisers within paint and paint fragments and the potential for exudation of placticisers from paint and the risks posed within the household setting are poorly understood (Table 31). In the case of paints containing abundant plasticiser the likelihood of brittle failure producing hard paint flakes and chips is not as likely as the formation of large elastic paint blisters.

Chatfield (1962, p.286-287) notes that *'…with emulsion paints, it is common practice to use a relatively volatile plasticiser such as dibutyl phthalate.'*

While plasticisers can be lost due to unforced exudation, the migration of plasticiser can be assisted by high temperature and contact with solvents. Chatfield (1962, p.289) notes the extraction of plasticiser from PVC (the starting material is 60 parts plasticiser to 100 parts PVC) using distilled water and 1% soap solutions at 20% over 240 hours, with 0.05 to 0.5 percent by weight extracted by water and 0.15 to 1% extracted by the 1% soap solution.

Table 31: *Plasticisers used in paints and claims of relative toxicity made in the 1960s.*

Relative toxicity	*Compound*	*Reference*
Not indicated	Tritolyl phosphate	Chatfield,1962, p.297
	Trixylyl phosphate	
	Di-n-butyl phthlate	
	Di-iso-octyl phthalate	
	Phthalate 79 (DAP)	
	Dinonyl phthalate	
	Di-iso-decyl phthalate	
	Di-iso-octyl adipate	
	Di-n-butyl sebacate	
	Di-2-ethylhexyl sebacate	
	Sebacate 79 (DAS)	
	Epoxidised oil (Abrac ‘A’)	
Very toxic	Methoxyethyl oleate and	Hess, 1965, p.195
	Tri tolyl phosphate	
Moderately toxic	2-ethyl hexyl diphenyl phosphate	Hess, 1965, p.195
	Butyl benzyl phthalate	
	Dibutyl phthalate	
	Dioctyl phthalate	
	Tri phenyl phosphate	

Chatfield (1962, p.297) notes how butter will extract tritolyl phosphate from PVC wrapping film and that '*Poisoning has also occurred through contact of the skin for prolonged periods with a plasticised polymer containing tritolyl phosphate, e.g. plastic sandals.*' It is also noted that extracted plasticiser will also transport components such as lead stearate.

Additional details on both the past and present ranges of plasticisers and associated risks are required.

10.10 Stabilisers

The discoloration of polyvinyl chloride paints stoved at high temperature is attributable to hydrogen chloride formation in the paint film. This deterioration may be countered by stabilisers, which may include organic compounds of Ca, Ba, Cd, Zn, or Pb or epoxy compounds (Armitage 1967, p.57), PVC stabilisers are also described as lead compounds, mixed salts of cadmium and barium, and dibutyl tin compounds (Armitage 1967, p.86).

10.11 Thixotropic agents

To prevent pigment settling, one strategy has been to use anti-settling agents, such as asbestos powder, another method is to use thixotropic agents that produce a gel-like consistency. Thixotropy in emulsion paints can be achieved by the addition of 0.2% - 5% (based on the emulsion) of triethanolamine titanate or organic zirconium complexes (Armitage, 1967, p.86). Thixotropic paints that may be used for one coat finishes are sold mainly to the do-it-yourself painter (Armitage, 1967, p.112).

Freedom from sagging or brushmarks are charactistics of a paint having a correct rate of thixotropic recovery (Chatfield, 1962, p.389).

11. Chlorine in paint

11.1 Chlorinated rubber

The availability of chlorinated rubber paints in Australia, is indicated by a reference in DLNS (1955, p.42).

ICI (circa.1995) in their leaflet titled 'Chlorine and You' show a pie chart where some 10 % of chlorine produced in Australia, (as distinct from chlorine used in making PVC) is used in non-specified products in the paint industry.

Chlorinated rubber paints are said to decompose and yellow at temperatures of 60°C unless they contain a heat stabiliser and then are claimed to withstand 100°C for 48 hours (Gay and Hedges in Hess, 1965, p.108).

11.2 Polychlorinated biphenyls in paint

Examples of PCB in house paint are referred to using trade names in The Chemical Formulary (1935) they include Aroclor lacquer # 1 containing Aroclor 1262 at concentrations of 18% in the lacquer fraction resulting in 10% Aroclor 1262 in the dry paint film and some 6% total PCB in paint film. The paint film from lacquer # 3 could potentially contain over 12% PCB:

Aroclor Lacquers

#1

1/2 Sec. Nitrocellulose (Dry Basis)	*100 parts*
Dammar	*80.2 parts*
Aroclor 1262	*20 to 39.5 parts*
Dibutyl Phthalate	*20 to 0 parts*

#3

1/2 Sec. Nitrocellulose (Dry Basis)	*100 parts*
Aroclor 1262	*80 to 70 parts*
Lindol (Tricresyl Phosphate)	*39 to 70 parts*

To each of these paint bases can be added 147 parts by weight of pigment.

[The Chemical Formulary, 1935, p.91-92]

The Chemical Formulary (1951, p.390) notes a TiO_2-based white marine paint that contains 6% Aroclor 1254 in the complete pigment-vehicle-solvent mixture that would appear to be able to produce some 6.4% PCB in dried paint film.

The definition of the trade name "Aroclor" in the 8th edition of the *CRC Handbook of Chemical Synonyms and Trade Names* (Gardner, 1978) notes "Aroclors" 1242, 1248 and 1254 being used as vinyl plasticisers, with 1255 suggested as a substitute for resins.

Commercial production of PCB is said to have began in the 1920s with a significant increase in industrial use in the 1950s (Kimbrough, 1995, p.133-134). In 1971 the sole USA producer, Monsanto, stopped open-ended uses of PCBs (including production of highly chlorinated mixtures as "Aroclor" 1248, 1254, 1260) and ceased production entirely in 1977. Some "Aroclor" 1242 and 1254 which are potentially used in paint were produced up to 1977. The import of PCB into Australia was prohibited in the 1970s (Hinwood and Stasiliunas, 1992). Mandyczewsky (1992) discusses a draft National Model Regulation for the Management of Scheduled Waste which notes the cessation of production of PCB waste producing material in Australia in 1995. The interim definition of a sheduled PCB waste is a concentration of 50mg PCB/kg. A human health soil PCB guideline value of 10 mg/kg has been proposed (Di Marco and Buckett, 1993, p.203) with environmental investigation guideline values being somewhat lower at 0.1 mg/kg in Canada, and 1 mg/kg in Victoria, Australia.

Antimony oxide is mentioned as being *'...a synthetic, inert pigment widely used, in conjunction with chlorine-containing binders, in the formulation of fire retardant paints.'* (Boxall and von Fraunhoffer, 1980, p.16). Morgans (1982, p.62) suggests that this is the principal use of the antimony oxide pigment. The following paint components may expect to be commonly associated in fire resistant paint formulations:

- chlorinated rubber
- PCB plasticisers/fire retardants and
- antimony oxide

The improvement of flame resistant properties of chlorinated diphenyls are likely with increasing chlorine content according to the discussion from Chatfield, (1962, p.294).

Armitage (1967, p.59) notes that '*In chlorinated rubber paints, chlorinated paraffins or chlorinated diphenyls are commonly used plasticisers.'*

It has already been mentioned that chlorinated rubber, polyvinyl chloride and chlorinated waxes are noted by Hess (1965, p.366) to be resistant to mould growth and bacteria, and that '*…additions of chlorinated paraffins or diphenyls as plasticisers will increase resistance to fungi.*'

Chlorinated rubber could be successfully bonded to steel after the development of centrifugal shotblasting. It became widely used in the late 1960s with Holland and Norway early to appreciate its value, in marine situations. Chlorinated rubber needs to be at least 130 microns thick and was formulated into high-build primers. Chlorinated paraffins and PCB's featured in chlorinated rubber coating formulations according to this comment:

> *It is possible to use resins other than the chlorinated hydrocarbons ("Cereclor" and "Aroclor") in order to increase the solids contents of chlorinated rubber paints,* [James, 1975, p.433]

The annual use (pre 1972) of PCB in Sweden, for PVC and other paints was 55 tons; 15 tons for boat paint. Jensen (1972, p.128) also notes, *'PVC and chlorinated rubber paint contained 5-8 per cent of PCB to increase the stability against chemicals and oxidation. Beside this, there is a 3-5 per cent addition to paints used on boats below the waterline. 80-85 per cent of all small boats and 50-60 per cent of the larger ships in Sweden have used such paints.'*

In the mid-1960s PCBs in workplace air (Hess, 1965, p.179) must have been a consideration in the paint industry, the maximum allowable concentration was dependent on the chlorine content of the PCB, with 42% Cl being 1 ppm and 54% Cl being 0.5 ppm.

> *Dairy cattle became contaminated in Ohio from PCB containing paint used to paint the inside of silos between 1941 and 1970. The PCBs leached into the silage fed to dairy cattle and entered the human food chain through milk and cheese.* [Kimbrough, 1995, p.135]

A study of indoor levels of PCBs in two schools in Hagen, Germany revealed indoor air levels of some 4000 ng/m^3, where the source of the PCB was painted surfaces (Bent, 1994).

PCBs are also mentioned in relation to marine paints.

11.3 Chlorinated paraffins in paint

Cereclor™ is described by Gardner (1978) as: *'…a registered trade mark for a series of secondary plasticisers manufactured from chlorinated waxes. The percentage of chlorine is indicated by the number after the name, e.g. Cereclor 70.'*

Some 6.7-7.5% of 'Cereclor' 42 in addition to 11.9-13.2% 'Cereclor' 70 are contained in lead-based marine paint formulations in Ash (1978, p.92).

According to Morgans, (1982, p.169): *A range of liquid plasticizers derived from hydrocarbon waxes is marketed under the trade name "Cereclor" (ICI Ltd.). They are completely non-volatile and are used as plasticizers for chlorinated rubber, vinyls, and cellulose nitrate*. They would appear to have replaced "Aroclors" in paint. According to a letter from D.R. Fellows-Smith (ICI Toxicology Information Officer, 14th May 1993) 'Cereclors' have been marketed in Australia for about 40 years and are still used in paints as plasticisers or fire retardants at levels of less than 10%. The use of chlorinated paraffin in association with antimony oxide is mentioned by Armitage (1967, p. 117). ICI have extensive trade information relating to the use of 'Cereclors' and compounds with which they are compatible (Table 32).

***Table 32**: Compounds which may be used in paints and are compatible with 'Cereclors'*

Acrylic Resins	"Alloprene" (chlorinated rubber)
Alkyd resins	Bitumen
Cellulose acetate butyrate	Coumarone - indene resins
Drying Oils eg Linseed/Tung	Natural Rubber
Nitrile, butyl and most synthetic rubbers	Nitrocellulose ('Cereclor 50LV only)
'Neoprene'	Polyester resins
Polystyrene	Polyvinyl acetate and copolymers
Polyvinyl chloride and copolymers	Rosin
Rosin esters	Styrene butadiene resins

ICI have published a wide variety of paint formulations that contain 'Cereclor'. Typical commercial 'Cereclor' grades may range from 40 to 70% Cl and from carbon chain length C_{10}-C_{13}, C_{14}-C_{17}, C_{18}-C_{20} to >C_{20} carbon chain. A fire resistant emulsion paint for example contains 4.18% % w/w 'Cereclor' 65L (carbon chain length C_{10}-C_{13} , at 64% Cl) as well as antimony oxide at 10.8% w/w. A lustre finish flame resistant alkyd paint contained 6.9% 'Cereclor' 70 (carbon chain length >C_{20}, at 69-71% Cl) and 2.2% 'Cereclor' 65L , as well as the typical addition of antimony oxide, this time at 15.7%.

According to a Material Safety Data Sheet for 'Cereclor', (ICI, 1993, p.2) *'Some animal test data suggests a carcinogenic potential for this material.'* In the case of specific chlorinated paraffin chain lengths and specific Cl contents, IARC (1990a, p.68) considers that...*'There is sufficient evidence for the carcinogenicity of a commercial chlorinated paraffin product of average carbon-chain length* C_{12} *and average degree of chlorination 60% in experimental animals.'* And as an overall evaluation, in the absence of human data,*'Chlorinated paraffins of average carbon-chain length* C_{12} *and average degreee of chlorination approximately 60% are possibly carcinogenic to humans (Group 2B)'* (IARC, 1990a p.70).

Existing toxicological appraisals are not based on dust from paint films containing chlorinated paraffins. More needs to be known about the characteristics of chlorinated paraffins distributed in a range of paint materials in the past and also in currently manufactured paints. There are no known studies of exposure of humans to chlorinated paraffins via paint films as the source of exposure. Chlorinated paraffins do not readily biodegrade.

12. Metal primers: General

The mechanisms of protection of anti-corrosive primers are a function of both the paint binder and the pigment. The anti-corrosive pigments are divided into three in Buxbaum (1993, p.187):

- *pigments with a physical protective action*, these are inactive or passive physical means of providing a protective barrier such as with micaceous iron oxide flakes lengthening the pathways and obstructing the penetration of ions
- *pigments with chemical protective action*, soluble components in the pigment actively maintain a constant pH value in the coating. In red lead, redox reactions can occur to form protective compounds such as oxides or oxide hydrates. The paint binder may also contribute to maintaining pH.

- *pigments with an electrochemical protective action*, the protective coating provided by phosphate pigments is an example of anodic protection, where phosphate ions may be transported to the metal surface and react to iron phosphate complexes and stop corrosion. Pigments such as chromates prevent rust formation by their high oxidation potential and provide cathodic protection.

Buxbaum (1993, p.189-194) notes the following anticorrosive pigments:

Phosphates

zinc phosphate, basic zinc phosphate, chromium phosphate, aluminium triphosphate, barium phosphate, aluminium zinc phosphate, and zinc/iron phosphate.

Chromates

zinc chromate, zinc tetraoxychromate, basic zinc potassium chromate, zinc potassium chromate, strontium chromate and lead silicochromate.

Molybdates

basic zinc molybdates, sodium zinc molybdates, basic calcium carbonate zinc molybdate and basic calcium carbonate zinc phosphate molybdate.

The lemon yellow lead cyanamide ($PbCN_2$) and white to beige zinc cyanamide ($ZnCN_2$) have a passivating action under alkaline conditions and contain some 83 and 60 % Pb and Zn respectively (Buxbaum, 1993, p.199). Buxbaum (1993, p.200) states *'Zinc cyanamide is nontoxic, but the toxicological classification of lead cyanamide has to take the lead content into account.'* This is one generalised expression of opinion from a potential range of views on the toxicity of the cyanamide products.

Boxall and von Fraunhoffer (1980, p.108) describe red iron oxide and zinc chromate-based primers that vary from 100% red iron oxide to 100% zinc chromate. These paints have a pigment volume concentration of 35% for the high zinc chromate concentration paints and up to 55% for low zinc chromate concentrations relative to red iron oxide.

Zinc-rich primers on steel prevent the passage of ferrous ions into the aqueous phase as the zinc becomes the anode and the iron surface the cathode, the higher reactivity of the zinc providing cathodic protection by sacrificial corrosion for a limited time (Armitage 1967, p.147). Paints containing, lead metal, red lead, calcium plumbate, basic lead carbonate and sulphate, and zinc oxide offer varying degrees of anodic protection or anodic passivation to steel surfaces (Armitage 1967, p.148-149).

The use of surfactants of the long chain amine oleate type in priming paints such as red lead, iron oxide and aluminium at 0.5 to 1% on the pigment weight, is said to improve the weathering characteristics of these materials (Chatfield, 1962, p.325).

13. Metallic materials in paint

Vanderwalker (1944, p. 75), notes the use of metal powders of copper, brass, zinc and aluminium, where the original metallic lustre of the pigment is preserved by sealing the paint under a thin varnish or lacquer.

13.1 Metallic lead as a primer

Metallic lead as a primer was considered to have been of limited use by Holloway, (1953, Vol.I, p.144).

Armitage (1967, p.70-71) refers to the use of 1 micron particles of metallic lead incorporated as part of anticorrosive primer formulations. Such material is made from molten lead atomised in a steam jet. Lead metal in the presence of linseed oil forms lead salts which with water and oxygen inhibit corrosion by adsorption at anodic areas suppressing electrochemical action (Armitage 1967, p.148-149).

Buxbaum (1993, p.204) describes the particle size of lead powder as being from 1-15 microns diameter, and the uses of it for protection against aggressive chemicals and in radiological protection, properties of high UV reflection and good elasticity are also noted.

Mixtures of metallic lead and lead oxide are listed by Hess (1965, p.215-216) and are named, Arcanol, Grey lead oxide and Subox.

13.2 Zinc dust metal paints

Metallic zinc powder makes up 94% of the zinc in zinc dust pigment, with the remaining zinc being as zinc oxide; specifications in Johnstone, (1954, p.648) would potentially permit between 0.01% and 1.5% lead. It is also noted that, *'This product is finding an increasing use in paints for the protection of metallic surfaces, particularly in conjunction with zinc oxide, or 35 per cent. leaded zinc oxide, and with a colouring pigment, such as red oxide of iron. Suitable mixtures can be used for either priming or finishing.'*

According to Holloway (1953, Vol.I, p.144) zinc dust is said to provide good protection against corrosion and to be an excellent pigment for priming new galvanised iron. It is also noted that zinc dust was not used on an extensive scale at that time.

In a more recent description, zinc dust is a blue grey powder in some 3 to 4 micron diameter particles (Buxbaum,1993, p.203) it is useful in providing cathodic protection and has pigment of >99 wt.% total zinc and 94-96% metallic zinc content.

14. Luminous and fluorescent paints

The following is an example of a luminous paint formulation:

strontium thiosulphate	60 parts by weight	
acidified alcoholic solution of 0.5% bismuth nitrate	12 parts by weight	
alcoholic solution of 0.5% uranium nitrate	6 parts by weight	[Hiscox, 1937, p.495]

Table 33: *Compounds used in luminous and fluorescent paints (*Hiscox, 1937, p.494 and The Chemical formulary 1943, vol. VI p.290-292)*

Strontium Carbonate*	Beryllium Oxide
Cadmium Borate	Cadmium Chloride
Cadmium Phosphate	Cadmium Silicate
Cadmium Sulphate	Cadmium Tungstate
Calcium Molybdate	Magnesium Tungstate
Molybdenum Oxide	Samarium Oxide
Zinc Beryllium Silicate	Zinc Sulphate

Hess (1965, p.206) considered:

> *'Radioactive pigments used in luminescent paints (radium or thorium compounds) have caused the death of at least one woman who licked the brush with which she was painting watch dials.'*

Hunter (1957, p.827-828) refers to the death of 38 such dial painters in the US and notes the use of radioactive materials in a zinc sulphide base from 1908.

Caution is warranted with fluorescent paints, particularly old ones. Somewhat rare, unusual and potentially toxic compounds could well be found in such materials.

15. Some non-household paints

Cars, boats, trailers, trucks, trains, bridges, cranes, military equipment, pipelines and industrial plant and buildings are and have frequently been coated with paint products that would not be suitable for household use. Such painted products may pose risks to children and, in some circumstances, farm animals and routinely pose risks of occupational exposure and of distribution to the wider environment.

15.1 Vehicle paints

Motor car paint binders (vehicles) include alkyd-melamine formaldehyde, acrylic lacquers, modified thermosetting acrylics, nitrocellulose finishes and two-pack polyurethane finishes (Browne, 1983). Some early organic and inorganic pigments used in motor vehicle paint are listed in Burns and Bradley (1960, p.395).

Lead pigments have been used in the top coats of car paints in the search for newer and brighter colours according to Browne (1983). Hunter (1957) notes a decrease in the incidence of lead poisoning among vehicle spray painters (perhaps in the 1920s and 1930s) due to the absence of lead (perhaps more particularly white lead) in sprays. Lead concentrations in car paints are not well documented. Lead chromate paints at 10-30% lead could be expected to have been widely used on cars. In the past, in Australia, there was no motor vehicle specific regulation of lead-based paints. Changes in use of paint for motor vehicles that may have considered lead as an issue have been driven by occupational health considerations. Robotic spraying, and immersion methods of paint application may result in paint components, which have previously posed occupational risks, returning to use in motor vehicle paints.

The child lead exposure issues associated with vehicle paints are not well understood. Fading, chalking car paints could pose risks. The bright green, red, orange and yellow colours typical of lead chromates were popular in the 1970s and early 1980s but are no longer common.

It has already been mentioned that bismuth and cadmium based pigments have been used in lead free brilliant yellow car finishes and it is only recently that cadmium free yellow automotive paints have been widely used (pers. comm. A. Langley, Hazardous Substances Section, SAHC).

Industrial equipment and vehicles are often painted with bright lead-pigments.

There is no Australian legislation controlling the levels of antimony, barium, cadmium, chromium or lead in paint films on motor vehicles.

15.2 Marine paints

This section is based mostly on James (1975), whose focus in relation to marine paints appears to be the research and adoption of paint systems by the British and US Navies.

The painting system for iron ship bottoms up to World War I used a red lead in linseed oil primer, which gave good results provided it was dried for a long time and was coated by alkali permeable acidic resins. The long drying period needed for red lead became a limiting factor in the use of this primer. '*The anti corrosive painting of ship bottoms was an unsatisfactory affair right up to World War II*' according to James (1975, p.429).

Shortly before WW II an aluminium-bituminous primer was developed commercially followed by the recognition of oleoresinous primers, vinylite schemes, epoxies, coal-tar epoxies and chlorinated rubber, along with the use of cathodic protection in the 1950s. At the end of the 1950s the use of centrifugal shotblasting is considered by James (1975) as being responsible for increased performance of all types of coating. Airless spraying arrived in the 1960s. A report from the Royal Australian Navy indicates that '*...an aluminium/bituminous system would last about six years with cathodic protection, after which it must be blasted off.*' (James 1975, p.431).

Oleoresinous primers appeared not to use red lead and favoured pigments containing basic lead sulphate, white lead, iron oxide and barytes. Several oil varnishes were used; a 2:1 mix of linseed stand oil/rosin modified phenolic varnish was used in relation to pigment formulations containing white lead. Where white lead (#173) was replaced by aluminium flake (#185), a 1:1:1 mixture of tung oil/linseed stand oil/rosin-modified phenolic was used.

"Vinylite" resins by Union Carbide were used in ship coating systems beginning with wash primer, continuing with red lead primer and finishing with cuprous oxide based antifouling. Vinyl systems were used by the US and Canadian Navies in the 1950s.

15.2.1 *Antifouling*

The buildup of barnacles on a ship’s hull is such that the antifouling needs to be recoated every 6-12 months, and it is said that the effect of barnacles after 200 days of sailing is to require an increased power consumption of 30% to maintain boat speed (Armitage 1967, p.145-146), while another account, (Starbird, 1973, p.623) suggests that a six-month accumulation can force a vessel to burn 40% more fuel to maintain normal cruising speed.

At one time it was thought that organotin poison in kerosene, dispensed through perforated tubes along the hull of a boat, while the boat was not moving, would prevent hull fouling - however such methods failed (James, 1975, p.441).

The most important antifouling agent is cuprous oxide, which has been traditionally boosted by the use of mercury. According to James (1975, p.448) the cost of mercury has more recently limited its application although where used it is more effective in the form of phenylmercury rather than inorganic mercury. Extensive mercury use is suggested; *'Mercuric oxide was used for many years (possibly as long as a century)'* (Browne, 1983, p.1585). Inorganic arsenic was widely used in the early days but was ineffective; however, James (1975, p.449) considers that organic arsenicals, phenarsazine and phenoxarsine are very effective.

The recorded annual consumption of mercury in anti-fouling paints in the USA in the years 1942 to 1950 in units of 76-pound flasks was from 996 to 3133 flasks (Johnston, 1954, p.327).

One early antifouling ship-bottom paint recipe for steel ships (The Chemical Formulary, 1951, p. 389) would have resulted in a dry film cuprous oxide content of some 16% and some 4% mercurous arsenite.

The use of vermilion as a ship bottom paint is also described in (Atlas Chemical Company, 1896, p.141 and Hiscox, 1937, p.498), where a pink paint was formulated as follows:

Pale Rosin	25 pounds
D.L. zinc	16 pounds
Deep vermilion	7 pounds
Mineral naphtha	1 gallon
Petroleum Spirit	1 ½ gallons

The mercury concentration in the dry film of such a paint may be expected to be some 12.5% by weight; another formula (Atlas Chemical Company, 1896, p.141) used oxide of mercury at some 2% of the pigment fraction with arsenic comprising 13.7%. Another formulation (p.346) required some 4% by weight of red oxide of mercury in the pigment fraction which was to be increased to 6.7% if the vessel was going 'East'.

Other antifouling paint components mentioned by James included comments on the effectiveness of DDT on barnacles and tetramethyl thiuram-disulphide which was low cost and with a general toxicity similar to copper. DDT was incorporated into a marine paint formula at 1.9% DDT according to Ash (1978, p.91).

According to Armitage (1967, p.146) the mechanism of cuprous oxide and mercury salts in anitfouling compositions is to '...*leach out and poison the water immediately in contact with the ships' sides.'*

Tri-butyltin and triphenyl tin have been widely used in antifouling paints. According to Fent (1996, p.7) bans on the use of TBT on boats less than 25 metres long occurred in France, (1982), UK (1987), USA (in relation to non-aluminium boats in 1988), Canada (1989), with Switzerland and Germany implementing sales bans in 1990. TBT occurrs on larger ships but subject to regulation. It should be noted that the consumption of TBT was not diminished by restrictions on use (Fent, 1996, p.8).

In relation to the toxicology of tri-butyltin the reader is referred to Turczynowicz (1991) and Fent (1996) for a review of ecotoxicology.

For further information on antifouling preparations the references in James (1975) are a valuable starting point, as well as, Pettis *et al.* (1977), *Antifouling activity of phytotoxic compounds and experimental polymeric algicides.*

Table 34: *Antifouling agents for paints (Paint Trade Manual, ca.1960s, p.13)*

Copper Oxychloride
Copper 8 hydroxy-quinolinolate
Cupric Hydroxide
Cuprous Oxide
Cuprous Oxide - Electrolytic
Mercury Compounds General
Mercury Oxide
Tributyl Tin Oxide
Zinc Oxide

16. Paint failure

16.1 Paint chalking descriptions

The early stages of paint chalking is often noticed as a dulling of the gloss of paint or the wiping off of pigment materials. The breakdown of the paint film can be a fault of the materials such as the binder or the pigment, a function of the reaction between binder and pigment or a function of the relative volume of the embedding medium and pigment.

> *"A smooth, glossy paint film, in which the pigment particles are completely covered by a layer of embedding medium reflects incident light at the surface in a mirror-like way; any departure from perfect smoothness blurs the reflected image*." [Tilleard and Bullett in Hess,1965, p.219]
>
> *'Gradual loss of gloss of outdoor paints is the consequence of at first very small surface defects on ageing due to slow oxidation, etc., possibly followed by chalking and destruction of the film surface. This is a natural phenomenon and cannot therefore be considered a defect…'*[Hess,1965, p.219]

Loss of gloss may be a good indication of incipient breakdown of paint. In many accounts, particularly pre-1970s situations, in publications by 'painters' as opposed to 'paint formulators' it appears that the 'cause' of chalking is attributed mostly to the pigments and not to reactions in and with the binder.

16.2 Paint chalking causes

Buxbaum (1993, p.33) citing Völz *et.al.*, notes:

> '*The shorter wavelength radiation of sunlight acts on rainwater and atmospheric oxygen to form extremely reactive radicals ($^{\cdot}OH$, $HO_2^{\cdot}$) that cause deterioration of the coating matrix by oxidative attack. Titanium dioxide pigments may be stabilized by reducing the number of radical-producing hydroxy groups on the surface of the TiO_2 particles (e.g., by doping with zinc oxide). Alternatively, coatings of oxide hydrates are produced by aftertreatment of the pigment surface to give "reaction walls" on which the radicals are destroyed.*'

also:

> *'If breakdown of the binder is so extensive that the pigment may be loosened, chalking takes place. Chalking is defined as loosening of pigment or extender particles following destruction of the binder at the surface.'*
>
> *'The reason for the chalking is the superficial erosion of the vehicle caused by simultaneous action of light and oxygen on, and washing-away of, the thin weathered out layer of the film by rain and efflorescence of water-soluble pigment particles, which remain on the surface of the film in the form of a fine dust.*' [Hallet in Hess, 1965, p.309]

While chalking is described as being an innate property of pigment compounds, it may also be attributable to the paint formulation. Chalking can be as a function of degradation of the pigment, and lack of binder. Failure of the binder also is a potential cause of chalking. Surface conditions such as high levels of suction on porous surfaces can absorb much of the binder leaving poorly bound pigment at the paint surface (DLNS, 1955, p.103).

16.3 Chalking of white lead paint

Mayes (1938, p.301) stated, in the context of white lead paints, that: *'The life of paint depends largely upon the quality of linseed oil used in the making.'*

Crewdson (1943, p.14) suggests that white lead *'...holds up under ordinary weather conditions for about two years. It then begins to chalk, and when it has become sufficiently worn to need repainting, it requires sanding down to remove the fine powder and is then in perfect condition to receive a new coating.'*

Vanderwalker (1944, p.68) notes that white lead makes a paint that is:

> *'...a little too soft, one which chalks or dusts off the surface after a couple of years when white paint is used. This peculiarity can, however, be easily overcome by the addition of from 10 to 15 per cent of zinc oxide to the paint to make it a little harder film. In some localities, notably along the sea coast, the tendency of white lead paint to chalk is greater, and the addition of from 20 to 25 per cent of zinc oxide is made by some painters.'*

Vanderwalker (1944, p.77) also notes:

> *'The weakness of white lead used alone as paint is commonly stated as that of chalking. After two or three years of service white lead paint begins to powder or dust off of the surface. In other words, it wears out in that manner. It does, however, leave a surface in perfect condition for repainting.'*

An Australian publication, DLNS (1955, p.24), notes the deterioration of white lead thus *'After prolonged exposure it deteriorates by chalking. Repainting of such a surface is much more convenient and economical than if it were cracked, or flaking, as the expense involved in removing the latter is considerable.'* The chalking of white lead is said to be *'accelerated in salty atmospheres in proximity to the sea'* (DLNS , 1955, p.24).

It is important to note that while there is comment in the literature regarding the development of chalk free rutile and chromate pigments due to pigment particle coating, no such reference is made in the case of carbonate lead.

16.4 Susceptible pigments and modifications of pigments to address chalking

Anatase TiO_2 on its own, and anatase mixed with barium sulphate is described as free chalking, while anatase mixed with barium carbonate is described as chalk resisting (Johnstone, 1954, p.563). It is perhaps the solubility of the barium carbonate in the weak acids generated from the degradation of the paint vehicle (eg linseed oil) and perhaps a sacrificial role that provides apparent chalk resisting properties.

While it was considered perfectly acceptable and even natural for paints to chalk, great efforts were made by the pigment industry from the 1940s with particle coating technology to minimise that mode of failure.

According to Johnston (1954, p.562) while rutile has a lesser tendency than anatase to chalk, there are specifications for an aluminium treated semi-chalking rutile as well as a chalk-resisting silicon-aluminium-zinc treated rutile (p.564).

Brindley (ca.1952, p.220) notes the common mixing of white lead with zinc oxide and titanium white with zinc oxide and that *'For some time after the war, there were a number of grades of zinc white which had the weakness of "chalking" excessively'.* This it is an unexpected observation, the more common observation is the brittle non chalking nature of zinc oxide material.

16.5 Properties of chalked paint surfaces

Fancut and Hudson (1957, p.65) describe chalking as *'...the formation at the surface of the paint film of a loose powder, produced from the substance of the paint itself,...'* and also note the possibility that excessive chalking may make paint act as a sponge and absorb excessive quantities of water.

The excess of pigment relative to the volume of and ability of the binder to retain pigment particles renders '*films susceptible to wiping off or powdering'* in a similar manner to chalking (Hess, 1965, p.312). An indication of an adequate formulation pigment-volume-concentration may be the observation of '*...the presence of some of the medium, e.g. by a faint sheen'* (Hess, 1965, p.312).

The dependance of chalking on the composition of the binder is underlined by Hess (1965, p.312), and the suitability of particular binders to indoor or outdoor use appears to have substantial implications for chalking. Further, the *'…conditions of underbinding may be created if a well-formulated paint is applied on a porous absorbing substrate'. 'Binder can be lost as the result of the effects of heat...*' and again, '*...highly humid conditions at tropical temperatures'* are cited by Hess (1965, p.312) to suggest these conditions accelerate chalking.

Hess (1965, p.308) suggests that some pigment combinations may retain chalk on the surface and other combinations exert a self cleaning action. The degree to which paint binder and pigment combinations interact under a range of ambient settings in the production of chalking particles is not likely to be simple.

In the case of white paints which do not chalk, Hess (1965, p.308) notes that discolouration due to dirt accumulation can be a problem. His remedies are to suggest the use of a chalking white paint and accept a lower gloss finish or to select a darker paint to begin with.

'Excessive chalking leads to the formation of a milky liquid during rain, which reduces the lifetime and decorative value of the paint' Hess (1965, p.308).

16.6 The risks of chalking paint

Chalking paints pose particular risks to children since fingers wiped on such paint inevitably and naturally will deliver some of that adhered paint to the mouth for subsequent ingestion. Details relating to child behaviour and the amount of lead on a finger for example obtained from a fixed length of finger wipe on chalking paint are the details required to assess the health risk of chalking paints. Chalking paints also liberate materials more generally to house dust and soils but the wiping of fingers on paint as well as direct sucking of paints require special consideration.

Explicit evaluations of some of the variables relating to exposure to chalking paint are required to backup the regulations for toxic components in paint in order to minimise risks to children.

Tests of the amount of chalking on paint surfaces used in the paint industry noted by Buxbaum (1993, p.35 & 2) include:

- The Kempf method; (ASTM D4214, DIN 53 159),
- Photographic method, (ASTM D659)and the
- Adhesive tape method (ISO 4628-6 and DIN 53 223)

These are assessments of the relative amount of chalking for general assessment of fitness for a decorative or protective purpose as opposed to methods of quantifying risk from paint components and child exposure via finger wipes and hand to mouth transfer.

One apparent method of testing potential paint exposure is a test of:

> *'Resistance to Spittle and Sweat. This test indicates whether a pigment on a child's colored toy is likely to be transferred to the mouth, mucous membranes, or skin during use. Strips of filter paper are wetted with NaHCO, and NaC1 solutions and pressed against the test samples. The discoloration of the paper is judged visually.'* [Buxbaum, 1993, p.37]

That this test is adequate to guard against 'toxic' paint components is questioned. This test requires only visual inspection of the filter paper and not chemical analysis. This test may not be useful for predicting the intake of toxic paint components by way of sucking and mouthing of painted surfaces by children if the test is applied to relatively unweathered new and glossy paint materials - that will later chalk and weather. Such a test using white filters could not be used well on white paints. Used for screening, the above or similar tests could be used to detect grossly unacceptable paints and exclude such positive samples from more detailed compound or element specific analysis, but absence of visual discolouration should not be a measure of absence of toxic components.

16.7 The durability and weathering of paint films

Chalking is a somewhat universal and expected property of paints. The following discussion of paint film durability and weathering relates to aspects of paint degradation that are not desirable or necessarily inevitable and often result from paint formulation problems, the use of the wrong paint for particular purposes, exposure of paint to harsh weather conditions or problems resulting from the material being painted.

Just as with chalking, incipient degradation can be recognised through variation in the appearance of a paint. A range of factors, not necessarily just weathering have an impact on paint appearance.

The variation of appearance and colour of applied paints can be due variously to:

- separation of pigments in the can and inadequate stirring
- any movement of materials of differing particle sizes or compounds within the film soon after application
- variations in the porosity of the substrate or seal of the priming coats may produce patchy fading, by local over pigmentation due to absorbtion of paint binder by the substrate
- the presence of deleterious impurities in raw materials eg water soluble salts
- incompatibility of paint film components
- photochemical and thermal modifications of pigment compounds
- exposure to SO_2, hydrogen sulphide, (darkening due to the formation of sulphides) acid fumes, ammonia, alkaline conditions, dirt collection, microbiological attack and tobacco fumes
- separation of organic pigment coatings from extender particles after application

- tendencies to yellow with age, or yellow in the dark interacting with tendencies to bleach or whiten when exposed to sunlight (thick films yellow more rapidly). Some colour changes such as slight yellowing are reversible.
- the dulling of the gloss of paint over time
- the incorporation of dirt in the paint surface over time
- weathering effects of water and oxygen affecting at least one pigment component or the paint binder (eg chalking)

The observation of colour change with the location are useful data. Locations exposed and not exposed to sunlight, air or rain may give indications as to the mechanism and degree of breakdown of exposed paint films.

Paint weathering on an iron surface can readily be described as if it were advanced chalking:

> *'Loss of matter in a paint film first induces hazing and dulling, followed by chalking. The pigments are thus gradually freed from the surrounding and protecting vehicles and increasingly exposed to the influence of the atmosphere. Some of them are washed away by rain, and the repetition of this process renders the film more and more permeable to the humidity of the atmosphere, inducing corrosion and destruction of the coated objects unless the protective films are renewed in time.'* [Hess, 1965, p.274]

Advances in weather resistance of paint over the years from the 1920s to the 1960s are such that frequency of repainting attributable to weathering is likely to have reduced:

> *Specially suited as weather-resistant materials are paints, etc., based on long-oil varnishes, or stand oil or certain long-oil synthetic resin varnishes whose high weather resistance is due chiefly to the large molecules formed during the manufacturing, e.g. boiling. The retention of gloss, ability to shed dirt, and general integrity of gloss paints based on alkyds far surpasses that of the best products based on linseed stand oil or long-oil varnish; e.g. for dark shades durability has been extended 50 per cent, and for light shades up to 100 per cent. A life of five years can be expected of a good exterior paint under normal conditions of exposure.* [Hess, 1965, p.269]

The decomposition products of a linseed oil film include, formic, propionic, caproic, palargonic, azelaic, and acetic acids; aldehydes, CO, CO_2 and H_2O_2 (Merzbacher, Eibner and Wing, in Hess (1965, p.60). These products have a potential role in the further breakdown of paint film and susceptible pigment particles.

Weather resistance of paints in the tropics would appear to have been minimal in the past, with many coatings giving:

> *'...lives of five to six years in conditions such as prevail in central Europe and Great Britain. Generally, the greater the sunshine falling upon a coating, the shorter its life. Thus alkyd finishes giving six years' life in Great Britain may fail in less than two years in tropical areas.'*
>
> [Hess, 1965, p.274]

Again comments on the longevity of paint films:

> *Oil paints are bound to deteriorate gradually if exposed to the outside atmosphere. In the temperate zone in the case of one priming coat and two top coats, oil paint films will last from two to five years, depending on conditions, while in the hotter and humid zones decay of these films takes place more quickly. For such conditions the application of two priming and two finishing coats will certainly pay.* [Hess, 1965, p.278]

In another opinion of the factors associated with weathering, comment has been made in relation to colour as opposed to the stability of pigments; *'Apart from colour changes and loss of gloss, green paints are reasonably durable (in the tropics) and like black and red oxide paints take much longer than whites to fail.' (from Hess, 1965, p.354).* It is suspected that it may be too simple to imply that colour is a substantial determinant of weathering. The degree to which particular 'colours' have assumed differential use in varying climatic zones due to their durability is unknown.

At a particular time, the desire for particular colours, or availability of particular paints or colours from a single manufacturer in a region may mean that entire communities have the same paint layer in the same relative position within the sequences of paint layers on their houses. Where that paint has a susceptibility to failure due to cracking or has particular hazardous properties, there may be cause for drawing attention to paint colours.

The degree to which solar radiation is reflected from white paints and the temperature of a painted surface is minimised may be a trade-off against having a somewhat darker surface that heats up more but which prevents the UV destruction of the oil base. However, Gardner in Hess (1965, p.271) considered *'...that primers tinted slightly pearl-grey (with a few per cent of graphite or carbon black, or of aluminium bronze) and applied on wood are more permanent than white primers, because the darker pigments absorb the ultra-violet rays, protecting the oil-base vehicle against their destructive influence.*'

Hess (1965, p.272) is critical of the weather resistance of lithopone used in the absence of *'...50% zinc oxide and white lead*' and of paints containing chalk (mostly calcium carbonate material composed of the skeletons of marine microorganisms).

Current paints, baked paint finishes and powder coatings all have potentially longer resistance to weathering than the 2-5 year period frequently referred to in Hess. It appears that older paint formulations, in high UV locations, in tropical or coastal locations have in the past had much reduced lives, and perhaps in these climates, particularly where there is also a large utilisation of timber weatherboards, there would be greater problems with lead derived from paint simply due to the increased frequency of paint maintenance work.

The discussion of the inhibitive properties of pigments by Chatfield (1962, p.434-436) indicates that a range of lead compounds may be seen in the weathering products of lead-based paints depending on the nature of the setting in which corrosion takes place.

16.8 Gross failure

16.8.1 Alligatoring and cracking

The pattern of alligatoring which has the appearance of regularly sized and spaced cells as in alligator hide or mud cracks is quite distinctive.

One reason for the mode of failure known as alligatoring as well as cracking is the application of a short oil paint over a long oil material (Hess, 1965, p.85). In the case of alligatoring due to paint layer incompatibility, as described by Hess (on multilayer painted surfaces), the paint failure may not continue down to the substrate.

It is not only the relative expansion and contraction of films but the shrinkage and expansion of the substrate that can cause gross failure through cracking of the paint film. When conducting paint renovation, it may be helpful to differentiate failure as a result of forces in the paint film from external forces such as the substrate.

In the case of painted timber exposed to the weather, linear cracking and curling of the paint film may mimic a regular underlying pattern of the timber grain. Some also describe this type of failure as alligatoring. Perhaps a more rigorous or descriptive language for characterising paint failure to as to deal with the technical and risk assessment issues is required.

'*Embrittlement, when coupled with film shrinkage leads to cracking'* as noted in Hess (1965, p.317).

Checking, is described as V-shaped cracks in the paint film which relieve tension but which may not extend to the base of the paint layer or base of the paint film. Such tension relief in moderation can be an acceptable feature as opposed to gross failure through cracking of the film. Checking can progress to complete cracks.

In terms of the ability of checking to open up V-shaped crack tips that extent into a lead-based paint layer, these features are potential explanations for lead appearing at the surface of 'lead free' paints, when paint is tested with colorimetric test kits like the sodium sulphide or sodium rhodizonate-based kits.

The section on paint plasticisers notes the migration of plasticiser in paint films. In addition to this it is noted in Hess (1965, p.362) that:

> *'When lead-free paints are applied over old paints containing lead, sufficient lead compounds can often migrate into the top coat for sulphide discolouration to ensue if the environment is suitable, eg in chemical laboratories. Water paints are more susceptible to such migration than solvent-based materials.'*

It is further stated that:

> *'Staining has followed heavy condensation or other damp conditions which have been responsible for the migration to the surface of soluble lead compounds subsequently darkened by a hydrogen sulphide content of the atmosphere.'*

These statements must be treated with caution, and direct evidence of the elevation of lead concentration in layers overlying a lead-based paint is required.   Movements of lead may be via cracks or at the margins of coarse grit particles incorporated at paint layer boundaries as opposed to soluble lead migration.

Cracking of paints can occur in brushmark grooves, and can occur on metals due to *'...variations of temperature'*, or in timber due to the '*…variations of the moisture content'* (Hess 1965, p.317).

Highly permeable paints in tropical conditions that take up and lose water daily '*...tend to chalk, craze and peel at a much higher rate than they do in temperate climates*' according to Footner and Murray (in Hess, 1965, p.320).

> *Should the atmosphere contain a comparatively high contamination of sulphur dioxide emanating from gases of combustion, crystalline zinc sulphate may be found on surface of zinc white paint coatings. In some cases this was believed to be responsible for the subsequent cracking of the film. Such cracks are described as star-shaped with a zinc sulphate crystal as nucleus. Alkaline influences, such as ammonia, also tend to destroy some films. The cracking caused by external effects usually is much more pronounced than that by "internal" causes (i.e., due to properties of vehicles, pigments, driers, etc.), as the changes may commence while the films are still fairly wet, increasing with the degree of drying. Where cracking is induced by "internal" causes the cracks are mainly of longitudinal type of small ,width, while "external" influences, especially direct sunlight, alternating, e.g. moist and dry weather, etc., cause, e.g. the paint film to contract to give in the worst cases the appearance of tree bark.*

16.8.2 Blistering

> *'Blistering, in the majority of cases, is due to air, liquids and their vapours, e.g. from moisture being trapped in or underneath a film. In such cases the paint film should be permeable long enough to let the vapours escape. If it is not possible at least to a certain extent, the gas-pressure between the base and paint film may either produce blisters or may cause peeling of the paint. The thicker the film layer the more is it prone to the possibility of blistering.'* [Hess, 1965, p.102]

The moisture content of timber that would preclude blistering is probably dependent on the likely rates of change of temperature and the local climate and may be some 10-12 % in some countries such as Great Britain and different for others. There are indications of accelerated blistering in springtime in Europe; and tropical settings will present problems owing to the potential for timber to contain in excess of 30% moisture (Hess, 1965, p.105).

17. Renovating

Lead poisoning of persons carrying out renovation does not only date back to the pre-1950s when white lead was more common. Recent poisonings are documented by Hart (1996) and Marino (1990).

17.1 Sandpaper abrasion of paint

The particle size of paint material abraded with the action of sandpapers may be influenced by the grade of paper used, the state of 'sharpness' of the sandpaper, and the mechanism of sanding ie manual sanding or mechanical (orbital, circular and belt) sanding. Detailed studies of sandpaper abraded paint particle size are not currently available. Weyand (1991), in a study of sandblasting residues, found no particular size fractionation with respect to lead in sieved particle sizes <6300 to <53 microns although it would be critical to know if fractionation occurs below 53 microns.

Disturbance of lead by power sanding in a Canadian study by Pinchin (1995) generated lead in air readings of 1,000 to 4320 µg Pb/m^3, where by comparison, the 8 hour occupational exposure level for Australia is 150 µg Pb/m^3.

17.2 Paint removal using heat

If choosing to burn off paint, the initial consideration is that of the heat gun temperature and whether lead will be volatilised from the paint. The *'Lead Alert Painting your Home'* booklet (EPA, 1995) recommends that the temperature used with the 'electric hot air gun' type device should be below 370°C.

The use of a flame or high temperature will readily liberate volatile lead and other toxic products. For example, Acrolein may be encountered in fumes when using a blow lamp to remove paint (Hess, 1965, p.175).

Phosgene gas can be derived from painted surfaces treated by paint strippers such as methylene chloride where these surfaces later come in contact with a heat gun (Snyder, Mishel and Christensen, 1992). Cases of phosgene poisoning associated with use of methylene chloride paint stripper were reported in the 1960s. Metabolism of methylene chloride in the body produces carboxyhaemoglobin as is the case with the inhalation of carbon monoxide (pers.comm. A. Langley).

The heating of 1m^2 of tar epoxy resin paint coated steel at 1000° C produced 2.4g of hydrogen cyanide, 9.6g of benzene, 1.2g of naphthelene, while at 700° C produced 3.7g of phenol and 0.57g of p-isopropylphenol. This example of the gas generated from paint pyrolysis was based on a case of acute intoxication of two workers estimated to be in a work atmosphere of 16 mg/m^3 hydrogen cyanide, 64 mg/m^3 benzene and 24 mg/m^3 of phenol (Sakai, Araki, Nakano, Sata & Araki, 1994).

A wide variety of pyrolysis products can be expected from paints as a result of use of a heat gun due to:

- the extreme variety of numbers of volatile compounds added to individual paints and the potential variation in the levels of addition of these compounds
- the variety of potential reactions between volatile paint compounds, post paint formulation and post application as well as reaction between volatile compounds during pyrolysis
- the wide variety of potential paint types in layers in a multi-layer paint film being burnt off
- the temperature at which paints are heated
- the age of the paint film and the conditions under which volatiles may have already been lost over time

It is suggested that knowledge of pyrolysis products of paint is limited. A review '*Toxic Pyrolysis Products of Solvents, Paints and Polymer Films'*, by Peterson (1993) is a welcome introduction to this matter, but the available data on the topic is still limited. There is the potential for a wide range of organic gas products to be formed - organic pigments, polymers and chlorinated components of paint are of concern as are the organic and inorganic fungicidal components of paints, mercury in particular.

In the hypothetical case of a $40m^2$ wall surface area in an old laundry, where organic mercury anti-fungal additives were used in paints, a multilayer paint film at 0.4 mm thick, and at 30 mg/kg mercury and density of 4.0 g/cm^3, will have 16,000 $cm^3$of paint weighing 64 kg. The contained mercury in that 64kg of laundry paint would have been some 1.9 grams. The proportion of mercury liberated from the paint when heated is unknown, as is the likely mercury uptake of a heat gun operator or any other potential subsequent exposure scenarios.

A survey of mercury in some 90 dried paint samples collected from Adelaide and Port Pirie commonly found some 5 to 30 mg/kg mercury. While values in excess of 300 mg/kg were encountered in two paints, and such concentrations may occur in individual paint layers, such average concentrations through a thick paint layer sequence may be rare. With the use of a hot-air-gun for stripping paints containing mercury, the following questions are raised:

- what is the association between paint mercury content and mercury lost to air?
- is the loss of mercury from a paint film, just from surface layers, or the whole film thickness?
- at what temperature of heat gun; and Hg concentration, Hg loading and Hg distribution in paint, is there likely to be a significant health risk?

The upper legal limits for mercury in paint at 1000 to 5000 mg/kg - as regulations in Tasmania and New South Wales once required, suggest that very high levels of mercury in paint films may be possible. Toxic effects on home occupants were discovered in the USA simply from the passive release of mercury paints containing some 930-955 mg/kg of mercury (Aronow *et.al.*, 1990). The presence of mercury additives in paint and hardware stores right through to the early 1990s for painters to add to paints where additional anti-fungal protection was required, give cause for added awareness in the assessment of mercury in paint. In the earlier section on mercury in paint, it is roughly estimated that the use of one particular product would result in some 370 to 1100 mg/kg of mercury in a paint layer. In an extreme situation where 370 to 1100 mg Hg/kg paint occurred in the same hypothetical laundry setting as above, there would be some 24 to 70g of mercury in the paint. Little is known regarding the rates of losses of mercury from within the paint can into the air space in the can and from a painted surface to the air.

18. Paint solvents

Studies of the neurological symptoms associated with use of solvents by paint sprayers and paint manufacture workers readily demonstrate the ease with which over-exposure occurs (Wang & Chen, 1993).

For a summary of the impacts particularly of solvents, the following are useful references:

IARC (1989) *Some organic solvents, resin monomers and related compounds, pigments and occupational exposures in paint manufacture and painting*. IARC Monograph, on the evaluation of carcinogenic risks to humans. Volume 47 WHO IARC Lyon.

ECETOC (1996) *Chronic Neurotoxicity of Solvents* Technical Report No. 70. February 1996 European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels

19. Paint Substrates

Any analysis of paint materials applied to surfaces must be wary of possible confounding due to the composition of, and reactions with, the substrate. Heavy metals and toxic compounds can be found in paint substrates and a number of examples are listed.

19.1 Putty

Materials for filling cracks in timber, knots and nail holes as well as for sealing glass to window frames has frequently contained lead. Examples of recipes for putty are:

50 pounds Whiting
4 pounds White Lead
1 gallon Raw Linseed Oil

40 pounds Whiting
4 pounds Litharge
2 pounds Patent Dryers
1 gallon Raw Linseed Oil

50 pounds Whiting
8 pounds Litharge
2 pounds Dryers No.1 [Atlas Chemical Company, Sunderland, 1896, p.154-155]

Vanderwalker (1944, p.181) notes the need for soft porous putty to be used in soft porous materials and the putty to be used on hard dense surfaces should have similar properties. Hard plaster finishes and metal window frames are therefore likely sites where putties hardened with white lead may be found. A common putty made from marble dust is described as becoming hard and brittle and (p.182) as being made better with the addition of '*...a little white lead, paste or dry white lead...*'. Vanderwalker (1944, p.181-184) describes a range of putty mixtures that contain white lead, including Knifing Putty, Quick-Setting Putty and First Class Putty. In addition a putty made from paint mixed with whiting is described as being good for fillings on the next to last coat of flat wall paint, the paint used in such a putty would generally have been a lead-based paint (p.182a).

In relation to cracks in timber weatherboards, Brindley, (c. 1952, p.54) suggests the use of a *'...linseed oil putty or a mixture of this putty and a little paste white lead.'* and in relation to picket fences suggests *'...A mixture of white lead and linseed oil putty will make a more durable stopping to fill up the open joints'*. (p.59).

In describing the use of putty for glazing work, Holloway, (1953, Vol.I, p.69) notes that*:*

> *'...Ordinary linseed-oil putty is not particularly satisfactory for metal sashes, for which it is generally too soft. There are a number of proprietary brands of putty for this purpose or ordinary linseed-oil putty can be adapted for it by adding approximately 1 oz. red lead to every 1lb. of putty; the red lead should be of the "jointing," not the "non-setting," type.'.*

And when describing puttying in surface filling (page 158):

> *'For nailholes and similar defects in everyday work, the form of putty most popular among painters is ordinary linseed-oil putty. It is cheap, easy to use, and sufficiently plastic to accommodate itself to subsequent movements of the wood, but it cannot compare with hard putty, made from paste white lead, whiting japan, gold size, and turpentine or mineral spirits. …...If desired, a little red lead can be added to the mixture to harden it and speed up the drying.'*

And as part of the putty recipe, (Vol.II, p.57) a ratio of two thirds ordinary putty to one third white lead in oil is specified.

An Australian source (DLNS , 1955, p.28) notes the use of red lead *'...as the principal ingredient in putties, when considerable tenacity and durability are required.'*

The history of use of white lead and red lead in putty to fix window glass in place is poorly documented. It is likely to have been the material of choice at some time and in some situations by some individuals in residential glazing work. Ingestion of lumps of failed old 'window' putty, containing white lead or similar chipped-out putty from glazing repair would be a source of severe child lead exposure. Glazing putty, being on the outside of window frames, may contribute lead to the soil around the house when it fails. The contribution of lead from putty, to the window well, internal window sill and house dust should also be considered.

PCB has been used in caulking compounds, and as sealants in buildings (Mandyczewsky, 1992) amongst other products.

19.2 Wood preservatives

Timber preservatives include, creosote, coal-tar derivatives, pentachlorophenol, copper chrome arsenate, copper chromate, copper sulphate, zinc chloride, zinc sulphate, mercuric chloride and copper naphthenate (Soong, 1993, Holloway, 1953). An example of a former white ant spray formulation is: 1lb arsenate of soda to 4 gallons of warm water (Mayes, 1938, p.310).

Such compounds could occur in timber being sampled for paint investigations.

19.3 Wood

Some timbers shed paint more rapidly than others and paint failure can be attributable to the timber substrate.

The durability of painted timber is described in Hess (1965, p.303) as follows:

> *The woods which hold paint longest and suffer least when repainting is neglected are:*
>
> (i) *cedar, redwood and cypress;*
> (ii) *next in order are northern white pine, western white pine and sugar-pine;*
> (iii) *the third group in order is Ponderosa pine, spruce and hemlock;*
> (iv) *the last group consists of woods which have the poorest paintholding properties: Douglas fir, western larch and southern yellow pine.*

and Five factors significantly affect the serviceableness of exterior paints on wood:

> *(1) the kind and quality of the wood;*
> *(2) the effectiveness of the design of the building or structure in keeping the wood dry enough to hold paint;*
> *(3) the composition and quality of the paint;*
> *(4) the technique of application and programme of maintenance; and*
> *(5) the severity of the climate and local conditions of exposure.*

Resin exudation, knots and differential physical properties of soft wood and hard wood are some of the intrinsic problems with timbers and their paint holding abilities. British Columbian pine (Oregon and Californian pine or Douglas Fir) is noted as having resin exudation problems and poor paint holding properties (Hess, 1965, p.303). For more local knowledge, a bibliography, '*The paint holding of Australian woods'* by Rischbieth, J.R., (1957), available from the National Library of Australia, is suggested.

German standards (Hess, 1965, p.304) DIN 18363 & 55925 stipulated that timber being painted should not contain above 15% water, a condition that may be difficult to achieve in tropical settings or in winter.

19.4 Corrugated iron

Galvanised iron is a source of zinc oxides, zinc chlorides, basic zinc carbonate and perhaps finally iron oxides when weathering takes place. The degree to which cadmium and perhaps traces of lead may be associated with older galvanising, should be considered. The association between cadmium and zinc in ceiling dust from houses with galvanised iron roof materials is demonstrated in van Alphen (1992, p.66).

New sheets of iron have in the past been left to weather to a dull surface before painting owing to difficulties of adhesion resulting in extensive paint flaking.

> *The difficult adhesion of coatings on new galvanised iron sheets is believed to be due to the formation of a very fine skin of basic zinc chloride, remaining from the use of ammonium chloride, etc., in the galvanising process. (Edwards and Buschlinger.) Also other residues of chemicals and greasy impurities, e.g. palm oil, form a thin layer on hot galvanised zinc sheets and may impair the adhesion of coatings. Other chemicals e.g. trisodium phosphate and solutions of caustic soda, are used for cleaning the sheets, also acid fluxes.* [Hess, 1965, p.257]

Calcium plumbate was a common primer for galvanised iron, and red lead is often used to paint between overlapping segments of adjacent sheets.

Hess (1965, p.257) notes the corrosion of zinc as 10-15 times less than for steel, at 0.2oz (avoirdupois)/sq.ft./year in industrial atmospheres, this being some 61 grams/m^2/year. In rural locations the rate of corrosion is interpreted as being of the order of 15 to 30 grams/m^2/year. It is stated that in enclosed and polluted locations such as railway tunnels, zinc may corrode as fast as steel.

Reactions between zinc and other materials are noted; *'If on account of extraordinary chemical or electrolytic influences, e.g. by contact with nobler metals, a strong corrosion of the zinc has taken place, the layer of white zinc salts formed is sometimes called "white rust". It consists mainly of basic zinc carbonate.'* (Hess, 1965, p.258). White salts are commonly seen on the overlapping join areas of sheets of corrugated iron, particularly in coastal settings.

19.5 Paint failure on cement

The compatibility of some paints with particular substrates may be a guide in relation to paint failure or likely presence or absence of pigment. Salt damp related paint failure should be able to be readily discriminated from paint incompatibility with the substrate owing to the localisation and visible salt in the case of salt damp. The compatibility of pigments with Caustic alkali or lime in substrates such as cement, plaster and brickwork, are shown in Table 35.

***Table 35:** Effect on pigments applied to cement, plaster and brickwork. (Hess, 1965, p.336)*

Affected	*Generally compatible*
Inorganic	***Inorganic***
Chrome Yellows Chrome and Molybdate Chrome Oranges and Reds (there may be some grades unaffected). Chrome (Brunswick) Greens. Prussian (Milori) blues. Go-precipitated Greens containing Chrome Yellows.	Chromium Oxide. Hydrated Chromium Oxide (Guignets Green). Zinc Yellow (Zinc Chromate). Ultramarine Blue and Violet. Carbon Blacks, Iron Oxide Blacks and Graphite Iron Oxides (Reds, Browns, Yellows), Earth Colours (Ochres, Umbers, Sienna, etc.). Cadmium Yellows, Oranges and Reds (Cadmium/Selenium colours). Antimony, Titanium and Zinc Whites, Lithopones. Extenders: Asbestine, Barytes and Blanc fire, Kieselguhr, Silica.
Organic*	***Organic****
Azoic Toners, e.g. Manganese, Calcium and Barium toners of Azo Reds B, 2B and 4B. Manganese Calcium and Barium B.O.N. Toners. Maroon Toners (e.g. Manganese).	Nickel Azo Yellow.

**organic pigments containing elements which may be used in characterisation of other organic pigments are not listed here.*

19.6 Miscellaneous

Timber glues have been known to include lead (Atlas Chemical Company, 1896, p.189-190).

The use of lead fillers and molten lead for car panelbeating resurfacing (Browne, 1983) is likely to have been a source of lead contamination in relation to car finishing in addition to any lead in paint. It would appear that in Detroit at least in the 1930s that some 80lb of lead was used in the bodywork of a new car (Hunter, 1957), later reduced to 5lb.

On occasion paint embrittlement can be attributed to the substrate:

> *Many oil varnishes and paints exhibit insufficient adhesion to lead and leaded surfaces, particularly cold- and hot-water pipes, leading to flaking because of the catalytic action of the lead and lead oxides (intentionally made use of in driers) on the drying of oils. This favours the drying of the films, but as the action continues after the drying, the ageing of the film is accelerated and the films embrittle within a comparatively short time. This is certainly not the only reason. For instance bad adhesion to cold-water pipes made of lead or other metals can often be attributed to a film of condensed moisture usually encountered on such surfaces.*
>
> [Hess, 1965, p.262]

20. Lead in paint on Australian houses

Paint lead concentrations based on a range of sampling methodologies are available from houses in Port Pirie, Broken Hill, Boolaroo, Mort Bay and in Queensland. A small but systematic study of paint lead, representing the whole of Australia, was part of the National Survey of Lead in Children carried out through the Australian Institute of Health and Welfare (Donovan *et al.*, 1996) and is summarised here.

20.1 Queensland

Queensland data is summarised by Edwards-Bert, Maynard and Calder (1993, p.15) as follows:

> *The analysis of 282 paint samples for lead content by Queensland Health from July 1988 to June 1992 provided the following results (w/w dry); 51% of the samples had a concentration over 1% and the average lead concentration was 6.5%. The range of results was between 0.02 and 53%; 24% had concentrations greater than 10% lead.*

20.2 Mort Bay, Sydney

Paint samples were collected as flakes and removed by forceps and/or a paint scraper. Lead analysis by Atomic Absoption Specroscopy used a 300mg aliquot of paint digested in a mixture of nitric and perchloric acids.

The results of this survey are summarised in Table 36 and are further described by Smith (1992, p.63);

> *"The majority* (70%) *of interior paints contained less than 1% lead and approximately half of the exterior paints contained in excess of 10% lead. With one exception, all the premises had interior paints less than 10% lead and only 8 houses had a lead concentration of greater than 2%. In contrast, 21 of the 25 premises with flaking exterior paint had greater than 2% lead, with 16* (64%) *having concentrations greater than 10%.*

Table 36: *Mort Bay study results [wt % Pb; LQ - lower quartile; UQ - upper quartile] (Smith, 1992, p.37)*

	n	*Arithmetic Mean*	*Std. dev.*	*Min.*	*LQ*	*Median*	*UQ*	*Max.*
Exterior Paint	53	13%	13%	0.09%	1.7%	9.5%	18%	61%
Interior Paint	59	1.5%	2.9%	0.02%	0.1%	0.35%	1.6%	15%

20.3 Boolaroo, Newcastle

Paint analysis from external and internal surfaces of houses (Galvin, Stephenson, Waller, *et.al.* 1992, p.93) was directed at peeling or flaking paint from houses of children having blood lead levels > 25µg/dl or houses in First Street Boolaroo. Peeling paint was found in 12 of 22 houses, 8 houses had peeling external paint analysed and 8 houses had peeling internal paint analysed.

A range of concentrations from 0.014 to 36 % Pb were encountered over all samples. Average lead concentration from external paints was 13.4 % from 12 samples, with 5 paints less than 3.4 % Pb and 6 paints greater than 19 % Pb. For external paints, 58 % of samples had lead concentrations in excess of 10 wt.%. Internal paints consisted of 10 samples less than or equal to 0.34 wt.% Pb, having an average of 0.16 % Pb and one sample at 17.1 % Pb.

The relative lack of elevated lead in internal paints suggests that most of the painted surfaces sampled may have not been in place before the 1950s and show a distribution of lead on surfaces perhaps more typical of the early 1960s if not later. The lead concentrations on external surfaces appear to be elevated, given the age of the local housing.

20.4 Port Pirie

Qualitative paint analysis from Port Pirie, using a sodium rhodizonate-based test (modified from Body, Dolan and Manning, 1985 pp.86-87) was used to distinguish paints having a lead concentration in excess of a threshold of some 2%. Detailed description of the methodology relating to the determination of the threshold value and validation of the technique was not reported. Some commercially available tests (Luk, *et al.*, 1993) have been tested as to sensitivity.

The sodium rhodizonate method was favoured because of the non-destructive nature of the tests. It was used over cracked, peeling or flaking sections of paint, where possible, so as to get an indication of whether lead-based primers or older, partly hidden layers of lead paints existed. Because the test was targeted for use on paint-failure-areas, a high rate of detection of lead paints, could be expected.

A number of compilations of paint analysis results are readily available. Out of 2,400 interior paints tested, 46.6% tested positive and of 4,144 exterior paint samples 71.1% tested positive. Bias in the selection of sample locations means that no inference as to the relative surface area of Pb-based paint can be made from the above information. More precise chemical analysis of some 171 interior paint samples (as inferred from Body, 1986, Figure 3) revealed that 43% of samples exceeded 2% lead and 24% exceeded 10% lead. In the case of 598 exterior paint samples 63% had in excess of 2% lead, 31% contained in excess of 10% lead and 10% of samples contained in excess of 20% lead (also inferred from Body, 1986, Figure 3). A recent evaluation of results of >20,000 indoor and outdoor paint tests using sodium rhodizonate, over 8 years to 1994 reveals that positive paint lead tests were obtained for some 52% of samples collected from mostly Pirie West and Solomontown. It is estimated that more than 95% of all houses in these areas were built before 1960. Industrial paints had been used on homes for many years in Port Pirie - even after they were generally less available from retail supplies.

20.5 Broken Hill

The Broken Hill Environmental Lead Centre, a joint NSW EPA and NSW Health organisation has reported on quantitative paint lead analysis carried out since January 1995 (pers. comm. Boddington, 1997). Paint samples collected are from homes that have or care for children under 5 years of age where such assessment is recommended. Only unstable paint surfaces, those that are peeling and chalking for example are sampled. Samples are collected by scraper into a plastic bag where necessary and analysed by AAS at the Mineral Resources Development Laboratory in Sydney after a perchloric/nitric acid digestion.

In Broken Hill, at or above a level of 1% lead, it is recommended that paint is removed or covered. There is some discretion depending on the location and degree of instability of the paint; paint on a child's cot may be acted on at lower lead concentrations for example.

Out of 1703 samples collected to May 1997, 61% were outdoor samples. The minimum paint lead content was 0.01%, the average was 4.1% lead and the maximum was 58%.

40%	had greater than or equal to 1% lead,
33.6%	had greater than or equal to 2% lead and
14.7%	had greater than or equal to 10% lead.

20.6 Paint lead in residential settings in Australia

Table 37: *Locations of failing paint samples taken from Australian residences (Donovan et al, 1996)*

	Number	*Per Cent*
Window	201	30.3
Skirting Board	18	2.7
Wall	244	36.8
Other	183	27.6
Source not stated	17	2.6

The National Survey of Lead in Children carried out through the Australian Institute of Health and Welfare (Donovan *et al.*, 1996) included the first national survey of paint lead in residential settings. This survey was designed primarily to obtain a national random sample, and results for individual states need to be treated with caution. The selection of households sampled is documented by Donovan *et al.*, (1996, pp.8-11) and the selection of paint sampling sites (Table 37) described as follows:

> *...if badly peeling paint was noted, a paint flake was scraped into a clean container using a plastic knife. A window sill was suggested as the most suitable place to sample, because it was a site very likely to show peeling, and because the paint used on window sills was considered more likely than other paint to contain lead.* [Donovan *et al.*, 1996, p.14]

and further:

> *Paint samples were collected from 663 households, with the interviewer noting that they were not required from 1376 households where there was no peeling paint.* [ibid p.15]

***Table 38:** Paint lead analysis data by state (pers. comm. Phil Anderson, 1997)*

	# of *Houses**	*# of Paint* *Samples*	*Low Decile*	*Low Quartile*	*Median*	*Geo-metric Mean*	*Upper Quartile*	*Upper Decile*	*High*
			(% weight of lead in paint chips)						
New South Wales	136	40	0.04	0.12	0.32	0.37	0.85	6.2	29.4
Victoria	113	24	0.02	0.11	0.62	0.67	8.2	20.0	22.5
Queensland	219	62	0.00	0.02	0.20	0.12	0.36	1.81	12.6
Western Australia	60	12	0.03	0.14	0.65	0.66	5.3	19.2	24.9
South Australia	97	31	0.00	0.04	0.26	0.29	2.50	7.1	29.7
All SA	146	46	0.00	0.06	0.38	0.31	2.10	7.0	29.7
Northern Territory	15	6	-	-	0.05	0.06	-	-	0.40
All NT	22	8	-	-	0.10	0.08	-	-	0.40
Australian Capital Territory	44	3	-	-	0.27	0.06	-	-	0.32
All ACT	99	7	-	-	0.32	0.19	-	-	0.64
Tasmania	102	42	0.01	0.17	0.34	0.30	0.99	2.46	12.7
All TAS	150	53	0.01	0.16	0.32	0.26	0.72	1.65	12.7

*(*for SA, NT, ACT, TAS; use the upper line of data to compare with NSW, VIC, QLD and WA*

The survey is based on only one sample per house. Paint samples were analysed by ICPMS after concentrated nitric acid digestion at the Trace and Toxic Element Unit of the Clinical Biochemistry Department at the Royal Prince Alfred Hospital, Sydney.

All houses in the survey had children under 4 years. Tabulations of paint lead analysis data by State (Table 38) are such that paint lead data from Queensland, New South Wales, Western Australia and Victoria are from houses with flaking paint where blood samples were also obtained. Paint lead data from Northern Territory, Australian Capital Territory, Tasmania and South Australia were available for all locations where flaking paint was collected.

Paint lead results were available for 252 households. For all children in the survey (where the condition of some houses is counted more than once due to more than one child in the household), 2.8% were said to have severe chalking and or peeling paint, 25.9% had some peeling paint and 69.2% had no chalking and/or peeling paint.

Keeping in mind the earlier note of caution regarding the survey being a national random sample as opposed to a State by State survey, indications are that paint lead may be more of an issue in Victoria, followed by Western Australia. The upper quartile lead concentrations in these States were 8.2% and 5.3% wt.% Pb respectively.

The maximum lead content of 252 paint samples collected and analysed in this survey does not exceed 29.7% lead. This is perhaps because the paint flakes may not include all older and commonly high-lead basal paint layers. If the samples collected in this survey were mostly interior paint samples this would, in part, explain the relatively low paint lead concentrations returned.

20.7 Summary: The analysis of lead in paint in Australia

A model used for the evaluation of lead risk in Australia assumes that at any point in time, 8% of houses are undergoing renovation, 65% have lead paint and therefore 5.2 % of children are exposed to high lead concentrations (Wlodarczyk *et.al.*, 1993). Assembled data here does not account in detail for the age of painted surfaces and is also somewhat generalised.

As a general summary statement, it would appear that paint lead concentrations from peeling paint chips or complete multilayer paint sequences, in excess of 2-10 wt.% Pb, would be encountered relatively frequently on the exterior of older Australian houses.

Locations having:

- a high proportion of pre 1950s housing
- a high proportion of older housing with weatherboard walls
- housing with painted galvanised iron wall cladding
- high rainfall or coastal settings where frequent repainting is required
- locations that were prosperous when the more costly lead-rich paints were available
- housing for the workforce of major industrial plants where industrial paints may have been used for residential purposes

are various settings where the amount of lead in paint may be expected to be high.

Individual older paint layers can contain some 50 to 75%+ lead. These are generally overlain by many layers of material with substantially lower lead concentration such that there is a substantial reduction of 'average' paint lead through typical multilayer paint films on old surfaces. Such averaging of the lead content of multi-layer paint films as above may result in paint bulk sample lead concentrations of 10 to 60%, where individual layers at 50-75% Pb exist. The risk posed by a multilayer paint-flake that is at 0.4% Pb on the top side and 75% Pb on the oldest, basal layer may not be well reflected by an average bulk sample paint lead value of 8 wt.% Pb for example. There is limited understanding of the risk posed by lead compounds derived from the use of lead naphthenates, lead stearates, lead linoleate, lead acetate and other organic lead compounds in paint. Similarly, the degree to which particle coatings and paint particle size may mediate or add to risk. Sampling and analysis methods that represent the particular or site specific paint lead risk of multilayer paint materials containing a range of possible lead compounds are not yet developed.

21. Paint covering and paint thickness, lead loadings and lead concentrations

21.1 Upper limits for lead content

Area-based analyses within dry red-lead paint layers by electron microprobe, suggest that while the lead content of the Pb_3O_4 pigment material itself is some 90.7%, high lead analyses are around some 70 to 75 weight % lead. In the case of white lead [$Pb(OH)_2 \cdot 2PbCO_3$], where lead comprises 80.1% by weight of the pigment, in practice, somewhat pure layers of 'white lead' paint film are only 60 to 65% lead. Examples of films of peeling paint at high lead concentration from Freeman (1970, p.643) include material at 48%, 65% and 84% lead. The presence of extenders, the nature of the paint vehicle (binder component) and the pigment particle size distribution, will tend to dictate these upper practical bounds to the lead content in individual dry paint layers.

21.2 Paint film thickness

Paint film thickness can vary from a single layer to several millimetres of paint layers built up with successive re-coatings. The number of paint layers applied to 'first class new enamelling work' (Kelly, 1929, p.115) may amount to 12 coats, with four or five coats being common.

In a physical examination of Australian paints, it appears that the more recent paint coat thicknesses are about 20 microns, while older paints are more variable in thickness at 30-40 microns, but more descriptive work is required on this matter.

Table 39: *Paint film thickness for a single coat of paint on steel, applied by four different painters (Fancut and Hudson, 1957, p.61).*

	Average Paint Film Thickness (microns)*			
Painter	*Paint 1*	*Paint 2*	*Paint 3*	*Paint 4*
A	43.25	47.0	59.0	39.5
B	31.0	36.5	39.25	32.25
C	34.8	35.3	45.25	22.75
D	44.5	43.5	44.0	15.75[†]

**converted from Mils - 1Mil = 25 microns)*

[†] *paint 4 applied more 'freely' by the other painters*

In a test of a single coat of paint, applied by different painters (Table 39) the variability in paint film thickness applied by brush, was attributable to the painted surface temperature, air temperature, and the rate of application by different painters (Fancut and Hudson,1957, p.61).

'*The amount of paint used for the same job can vary with different operators by as much as 50 per cent.*' according to Wampler (in Hess, 1965, p.41).

The thickness of a single paint film is said to vary from 25 to 75 microns (1/1000 to 3/1000 of an inch), with the thickness of decorative or protective multilayer paint system being some 125 microns. Hess, (1965, p.40) also notes; *'The coverage of properly brushed on priming paints of the white lead or zinc oxide type on large, normal, plain and dry wood surfaces is approximately 60-70 sq.yd. per gal.'*

The duration of protection provided by paint layers on steel in a study of 100 different priming paints in Fancut and Hudson (1957, p.59) is increased from 3.5 years at 2.8 Mils (70µm) thickness to some years at 4.2 Mils (105µm), and in another example, increased from under two years at a paint thickness of 2.5 Mils (62.5µm) to some 4.5 years at 3.7 Mils (92.5µm).

According to (Vanderwalker, 1944, p. 118), an experienced brush painter will spread paint over 15-25% more surface than a lesser experienced person. It is also noted that thin coats of paint are more durable than thick coats.

Hess (1965, p.109) describes paint layer thickness as follows:

> *The average thickness of a thin single coat of paint is of the order of 1mil. (25µm). Oil-based primers and undercoats may vary in thickness from 1.5 mil. (37.5µm) to 3 mil. (75µm) according to type and application. Decorative enamels may be from 1 mil. (25µm) to 1.5 mil. (37µm) in thickness, industrial stoving lacquers may form films of up to approx. 2.5mil. (62µm).*

The thickness of the paint film has to be much greater than the diameter of individual paint pigment particles, and there would ideally be a film of paint binder material and finer pigment encapsulating the coarser pigment/extender materials (Hess, 1965, p.47). If the volume of pigment relative to the volume of binder is too great, paints have dull surfaces and poor durability.

21.3 Painted surface lead loadings

In an Australian builders' guide book a hundredweight (1/20th of a ton) of red lead paste is said to cover 377 square yards and weigh 36½ lbs per gallon when thinned with 30lbs. of pure linseed oil per cwt. of paste (Mayes, 1938, p.305) ie. 50.8 kg of red lead paste is spread over 315.2 m^2. Given that red lead is 90.7% Pb, and making an assumption of 1-3 kg of linseed oil in the paste some 43.4 to 45.2 kg of elemental lead may expected to be distributed over 315.2 m^2 . This suggests a paint lead for a single coat of some 13.8 to 14.3 mg Pb/cm^2. This is a lead loading value that, as will be seen later, would be at the high end of the range for white lead paint layers. More detail is needed on the covering ability of red lead.

Table 40: *Components and total volume of paint made up using 100 lb. of white lead-based paste with 92% pigment, and coverage of a single coat. (Vanderwalker,1944, p.121 & 124-130)*

Paint function	*Linseed oil (gallons)*	*Turpentine (gallons)*	*Paint volume (gallons)*	*Paint Coverage (Sq feet/gallon)*
New outside (wood ?) surfaces				
First Coat	4	1 ¾	9	600
Second Coat	1 ½	1 ¼	6	700
Finish Coat	3	- *	6	700
Repainting old outside wood surfaces				
First Coat	2	1 ¾	7	700
Finish Coat	3	- *	6	700
New Interior Wood Surfaces				
First Coat	3	1 ¾	8	700
Second Coat	-	2 ½	5 ½	800
Third Coat, Flat	-	2 ¼ (or flatting oil)	5 ¼	800
Cement, brick stucco, stone surfaces				
First Coat	3 (+1gal. spar varnish)	1	8	300
Second Coat	2	1	6	400
Third Coat, Flat	- (¾ gal. spar varnish)	1 ¼	5	400
Third Coat, Gloss	3	-	6	600

Another recipe in Mayes (1938, p.303) for a paint to cover 100 square yards on average timber comprised, 15lb. white lead, ½ gallon linseed oil, ¼ gallon turps, ¼ lb. driers.

Extracts of paint coverage data (Table 40) from Vanderwalker in 1944 (p.121) are based on formulas using 100 lb. of white lead soft paste at 92% pigment in paste by weight.

With some additional details and a few assumptions, lead loadings on painted surfaces can be calculated.

In the case of the new outside surfaces (Table 40) the first coat of paint will spread 41.7 kg of white lead over 501.7 m^2, and assuming 80% Pb in white lead, producing a film at 8.3 mg of white lead per square centimetre being 6.7 mg of lead per square centimetre. For the above three coat painting sequence the surface will be covered by 23.9 mg Pb/cm^2.

Formulations for paint mixed using white lead paste (Table 41) give some insight into the weight of a gallon of such paint; about 13 kilograms.

Table 41: *Ingredients for paints using white lead paste (Holloway, 1953, Vol.1, p210)*

	*Ingredients to make 1 gallon of white paint**		
	Priming paint	*Second coat on new work, and first coat on old work*	*Finishing coat*
White lead, stiff paste	21 lb.	23 lb.	23 lb.
Red lead, dry	1 lb.	-	-
Raw Linseed oil	3 ½ pints	¼ gallons	3 pints
Turpentine (pure gum spirits)	1 pint	¼ gallons	½ pint
Patent driers	12 oz.	10 oz.	1 lb.

** in outside work, raw & boiled linseed oil used in the ratio of 2:1, in which case, a one-fourth part less of driers will be sufficient*

An example of the weight of a paint in pounds per gallon is given by Rawlinson (1969, p.280), as follows:

standard undercoat	16.75 lb./gal.	(1.7 kg per litre)
gloss enamel	11.80 lb./gal.	(1.2 kg per litre)

from Vanderwalker, (1944, p. 118)

white lead paint	20-22 lb./US gal.	(2.4 - 2.6 kg per litre)
ready mixed paints	14 lb./US gal. average	(1.7 kg per litre)

and from Holloway (above)

white lead paint	~13kg/gal	(~2.9 kg per litre)

A table from Holloway (1953, Vol.I, p.78) suggests that 35 square yards (29.26 m^2) of paint coverage on plaster or stone would consume 8 lb. (3.97 kg) of white lead, while on a smooth surface of 40 square yards, (33.45 m^2) some 6 lb. 10 ½ oz. (3.02 kg) of white lead would be consumed. Given that there is 80.1 wt.% Pb in white lead, the amount of lead on these two surfaces amounts to 10.9mg Pb/cm^2 and 7.2 mg Pb/cm^2, respectively.

While a paint formulation based on white lead, to cover 40 square yards of rough plaster or stone would contain 10 lb. of white lead, 1 lb. 1 ¼ oz. of patent driers, 1 quart 1 ½ gills. of linseed oil and 2 ½ gills of turpentine, a third layer or coat of paint formulated to cover 40 square yards would only contain some 6 lb. 10 ½ oz. of white lead, 9 ½ oz. of patent driers, 3 gills. of linseed oil and 1 gill of turpentine (Holloway, 1953, Vol.I, p.78). These paints layers will again result in some 10.8 and 7.2 mg Pb/cm^2, excluding the lead contribution from the patent driers. The additional use of extenders such as asbestine and barytes and tinting pigments will tend to reduce the surface lead loadings.

Table 42: *Covering capacity (ft^2 per gallon) of paints on different surfaces (Holloway, 1953, Vol.1 p.80)*

		Covering capacity per gallon (ft^2)		
Paint Material	*Surface Type*	*Primer or 1st Coat*	*2nd Coat*	*3rd Coat*
Exterior Paint	Brick	200	400	420
Exterior Paint	Sheet Metal	550	600	-
Flat Finish	Smooth Plaster	720	630	700
Gloss or semigloss	Smooth Plaster	720	540	540
Flat Finish	Sand-finished Plaster	297	450	486

1 ft^2 = 0.0929m^2

Table 43: *Coverage of a variety of white lead paints (adapted from Holloway, 1953, Vol.I, p.81)*

Square Yards	*Coat*	*Lead*		*Paste driers*		*Oil*		*Turpentine*	
Paint on Iron, Tin or Zinc ...									
		lb.	*oz.*	*lb*	*oz.*	*gal.*	*gills.*	*gal.*	*gills.*
400	1st	66	10	4	3	½	1	1½	-
	2nd	66	10	4	3	1	1½	1	1½
	3rd	66	10	6	4	2	3	½	¾
Paint on Wood, Plaster... (oil increased with absorbance of surface)									
400	1st	100	-	6 ¼	-	4	22	-	25
	2nd	66	10	4	3	1	1 ½	1	1 ½
	3rd	66	10	6 ¼	-	2	3	½	-

Typical covering capacities of paints in Table 42 are likely to be based on white lead paint.

The weight of lead in Table 43 could be lead paste or dry white lead powder, or even a mix of white lead and red lead (in the case of the priming coat). Assuming it is dry white lead, the formulae for wood will result in 105.8kg white lead/334.4m^2 (25.3 mg Pb/cm^2), for three coats of paint. More lead could be expected if red lead is used, and less lead if lead pigment pastes are used.

The summary of approximate paint covering capabilities (Table 44) in square yards covered per gallon (square metres per litre), relates to more recent paint materials.

Table 44: *Paint coverage, in square yards per gallon (m^2/l), on a variety of surfaces (Rawlinson & Partners, 1969, p.280)*

	Metal	*Wood or Smooth Plaster*		*Brick or Rough Plaster*	
	All Coats	*First Coat*	*Subsequent Coats*	*First Coat*	*Subsequent Coats*
Red or white lead and oil	55 (10.1)	40 (7.3)	-	35 (6.4)	-
Wood primer	-	55 (10.1)	-	-	-
Zinc chromate primer	70 (12.9)	-	-	-	-
Gloss enamel paint	85 (15.63)	-	85 (15.63)	-	65 (12.0)
Flat enamel paint	75 (13.8)	-	75 (13.8)	-	60
Plastic or latex base paint	-	50 (9.2)	65 (12.0)	65 (12.0)	75 (13.8)

A one litre first coat application of white lead covering 7.3 m^2 (Table 44), having an assumed pigment volume concentration in that one litre of 15-20% (Boxall and von Frauhoffer,1980, p.38) will contain 150 cm^3 to 200 cm^3 of white lead pigment. In this case, if all of the pigment volume is white lead $[Pb(OH)_2 \cdot 2PbCO_3]$, (no particle packing assumption is required), this compound being 80% lead by weight and having a density of 6.14 g/cm^3 (CRC Handbook of Chemistry and Physics, 1989-1990); basic lead carbonate is present in the paint layer at 921 to 1228 grams per 7.3 m^2 or 100.9 - 134.6 grams of lead per square metre; or 10.1 to 13.5 mg Pb/cm^2.

21.3.1 Summary

Individual white lead paint layers have a lead loading in the range from 7 to 14 mg Pb/cm^2 and 10 mg Pb/cm^2 may be a common level, but these values do not take account of any later abrasion or lead loss by chalking. Paint lead analysis, using X-ray fluorescence, routinely reports results as mg Pb/cm^2.

22. How much paint lead on a house?

In the case of paint films from buildings built between 1900 and the 1920s, it is common to see multiple high lead layers at the base of the paint sequence. Among the basal layers, it is rare to have unbroken sequences of lead-based paint layers. This general observation and the sequence chosen for the following calculations of lead loading is based on some electron microscopy inspection of some 50 paint layer sequences by the writer.

The following points are the basis of a hypothetical model for estimating the amount of lead on the weatherboards of a house built in 1900:

- the surface is first painted with three coats of white lead @ 10 mg Pb/cm^2 each coat
- no loss of lead by sandpapering or weathering is assumed
- the surface is repainted with two coats at 6 year intervals to 1930
  - two of the 5 repaintings to 1930 were 2 coats of white lead, @ 10 mg Pb/cm^2 /coat each, one repainting was 50:50 white lead/zinc oxide @ 4 mg Pb/cm^2/coat
  - the remaining two paintings to 1930 were at 2% lead (2x30 µm layers, density = 4.5 g/cm^3) = 0.54 mg Pb/cm^2
- the surface is repainted with two coats at intervals of 10 years from 1930 to 1990
  - one of the paints used between 1930 and 1960 was white lead, @ 10 mg Pb/cm^2 /coat, one other contained lead chromate @ 2 mg/cm^2 /coat there was one re-coating at 2% lead (2x30 µm layers, density = 4.5 g/cm^3) = 0.54 mg Pb/cm^2
  - the surface is repainted in 1970, paint = 1% lead (2x20µm layers, density = 4.0g/cm^3) 0.16 mg Pb/cm^2
  - the surface is repainted in 1980, paint = 0.5% lead (2x20µm layers, density = 3.0g/cm^3) 0.06 mg Pb/cm^2
  - the surface is repainted in 1990, paint = 0.2% lead (2x20µm layers, density = 3.0g/cm^3) 0.02 mg Pb/cm^2

The lead loading is estimated from the above as follows:

$$30+40+8+1.08+20+4+0.16+0.06+0.02 = \sim 103 \text{ mg Pb/cm}^2.$$

If the outside weatherboard walls of a house were generalised to be of the following size:

$$[(20 \text{ x } 4\text{m}) + (20 \text{ x } 4\text{m}) + (15 \text{ x } 4\text{m}) + (15 \text{ x } 4\text{m})] = 280 \text{ m}^2$$

with 103 mg Pb/cm^2 these exterior wall surfaces would be covered by some 288 kg of lead.

If, due to chalking and sandpapering, some 10% of each paint layer pair is lost from the surface prior subsequent repaintings some 29 kilograms of lead would have been lost to the surrounding soils and environment. Considering the above example, the 280 m^2 wall having a nominal paint lead loading at 103 mg Pb/cm^2 where these exterior wall surfaces would have contained about 288 kg Pb; there is still about 259 kilograms of lead on the wall if 29 kilograms are lost over time by abrasion and weathering.

A worst case scenario for a house built in 1900 may be repainting at 5-10 year intervals -up to 1950 with white lead producing paint film lead loadings in the range from 130 to 230 mg Pb/cm^2. This worst case scenario would result in some 364 to 644 kg of lead on house walls with the above dimensions.

Depending on the building age, size, building materials and painting history, older houses will have had some some tens to hundreds of kilograms of lead applied to building surfaces. The rate of weathering of paint and human intervention may determine what proportion of applied paint remains.

23. The amount of lead in a chip of paint

The ingestion of paint chips by children has been a cause of many severe lead poisonings. Chalking paint and dust from paint also pose significant risks for children, but only the matter of paint chips is addressed here. While it is difficult to assess the amount of daily lead intake and uptake from soils, dusts or paint chips ingested by children, it is possible in the case of paint chips to represent the relative risk of paint chips of various dimensions and lead content.

Table 45 takes into account the fact that older paint layers are thicker than modern paint layers and makes an estimation of the increase in density of paint with increasing lead content. The table demonstrates that for a 1 cm^2 area of paint, one paint application layer thick, the amount of lead in the case of a 0.5 wt.% Pb paint is 30 micrograms, and in the case of a 50wt.% old lead-rich layer, 7175 micrograms of lead.

In practice, the minimum thickness of paint likely to peel from a surface is a sequence of 2 or three or more layers of paint. To take that into account all the numbers should be multiplied by at least two. Similar lead loading values for a multi-layer paint sequence could be 'constructed' from the values here.

Table 45: *The lead content of individual paint layers (per cm^2) for a range of lead concentrations, paint layer thickness and paint density.*

Concentration of Lead in Paint (% by wt.)	*Thickness of Individual Layer (microns)*	*Specific Gravity of Paint Flake (g/cm^3)*	*Lead Content of Flake with 1 cm^2 Area*
0.2	20	3	0.002 cm^3 x 3g/cm^3 x 0.002 **= 12 µg Pb**
0.5	20	3	0.002 cm^3 x 3g/cm^3 x 0.005 **= 30 µg Pb**
1	20	3.1	0.002 cm^3 x 3.1g/cm^3 x 0.01 **= 62 µg Pb**
2	25	3.2	0.0025 cm^3 x 3.2g/cm^3 x 0.02 **= 160 µg Pb**
10	30	3.6	0.0030 cm^3 x 3.6g/cm^3 x 0.1 **= 1080 µg Pb**
30	35	3.9	0.0035 cm^3 x 3.9g/cm^3 x 0.3 **= 4095 µg Pb**
50	35	4.1	0.0035 cm^3 x 4.1g/cm^3 x 0.5 **= 7175 µg Pb**

X-ray images of the gut of a child with pica (Freeman, 1970) and almost intact paint chips seen in faecal material are evidence that paint flakes are not totally dissolved in the gut of a child. Some estimation of the amount of lead solubilised during ingestion, taking account of lead phases, appears to be required. It has been demonstrated that a multilayer paint flake from an old house could contain 103 mg Pb/cm^2, (103,000 µg Pb/cm^2) but there may be little point in developing an understanding of the amount of lead in multilayer paint chips if the lead uptake from paint chips is mostly from the surface of the chip.

Table 45 provides the ability to determine multilayer paint flake lead contents if required but the problem with this approach is that the proportion of lead dissolved in the gut from a paint flake is unknown. The situation when a paint flake is chewed thoroughly perhaps creates the scenario where the above tabulation is able to be more realistically used.

Models of lead uptake from paint chip ingestion could assume:

- the complete dissolution of lead from paint chips, the scenario of concern for assessing a case of child lead poisoning by paint chips (Table 45)

or

- lead solubilised mostly from the flake surface, (surface area limited) perhaps the scenario of concern for setting "safe" levels of lead in paint (Table 46).

Table 46 is a 'what if' model, to challenge issues related to the dissolution of lead in the gut from paint flake external surfaces. While the thickness and 'bioavailability' data are arbitrary values, the tabulation is valuable in demonstrating the need for information on the kinetics of dissolution, in the human gut, of lead in paint chips.

Table 46: *A model of possible lead dissolution from paint chips in the human gut for ranges of lead levels in the paints and 'bioavailability' in the gut.*

Concentration of lead in paint (% wt.)	*Amount of paint surface dissolved in the gut*	*Specific gravity of the paint flake (g/cm^3)*	*Lead dissolved from both surfaces of a 1 cm^2 flake**
0.2	50% of the lead dissolved in a 5 micron thickness	3	2^a x 0.0005 cm^3 x 0.5^b x 3g/cm^3 x 0.002^c **= 3 µg Pb**
0.5	50% of the lead dissolved in a 5 micron thickness	3	2 x 0.0005 cm^3 x 0.5 x 3g/cm^3 x 0.005 **= 7.6 µg Pb**
1	50% of the lead dissolved in a 5 micron thickness	3.1	2 x 0.0005 cm^3 x 0.5 x 3.1g/cm^3 x 0.01 **= 15.6 µg Pb**
2	50% of the lead dissolved in a 5 micron thickness	3.2	2 x 0.0005 cm^3 x 0.5 x 3.2g/cm^3 x 0.02 **= 32 µg Pb**
10	80% of the lead dissolved in a 10 micron thickness	3.6	2 x 0.001 cm^3 x 0.8 x 3.6g/cm^3 x 0.1 **= 576µg Pb**
30	80% of the lead dissolved in a 10 micron thickness	3.9	2 x 0.001 cm^3 x 0.8 x 3.9g/cm^3 x 0.3 **= 1872µg Pb**
50	80% of the lead dissolved in a 10 micron thickness	4.1	2 x 0.001 cm^3 x 0.8 x 4.1g/cm^3 x 0.5 **= 3280 µg Pb**

** the flake edges are assumed to be of negligible area compared to the faces.*

a the flake has two faces

b fraction dissolved in the gut

c fraction of lead in paint

The simplicity of table 46 would be drastically affected if a modern paint at 0.2% Pb was only leached to a depth of 2 microns and a white lead-based paint at 50% Pb was leached to a depth of 60 microns within the transit of a childs gut. More field data is required. The point of interest is whether paint at 0.1% lead, as legislated in Australia, from December 1 1997, is 'safe' and will a 100-year sequence of paint layers at 0.1% Pb be 'safe'?

To place the above discussion into perspective, a 'safe' daily level of intake of lead for a 2 year old child has been estimated at 47 micrograms of lead per day (Maynard, 1991, p.117). It should not be implied from the above discussion that the lead level setting for paint should be determined solely on the basis of a paint chip ingestion scenario, but the many other exposure pathways for paint lead should also be considered. Other sources of lead exposure should also be included in the account.

The following questions (among others) are raised:

- Will a 5-layer paint chip at 2% lead, ingested by a child, deliver 800µg of lead per cm^2 of flake if well chewed (Table 45) or will a more passive digestion (Table 46) result in the absoption of 32µg of lead per cm^2 of flake?

- What proportion of children ingest particular quantities of paint chips, at particular lead concentrations etc, and what proportion of children will be protected by particular 'safe' levels of lead in paint?

24. Lead added to soils

The addition of paint lead to soil and house dust can result in pronounced elevations in lead concentrations. The prediction of lead concentrations in soil or the proportion of lead lost from an external wall surface is explored in the following modelling.

The scenarios being evaluated are that of a painted wall 4 metres high, carrying lead in paint film at 40, 80 or 120 milligrams of lead per square centimetre. Options in the modeling of the amount of paint lead lost from the wall and added to the soil compartments are: 5 per cent, 10 per cent, 20 per cent and 50 per cent of the paint lead. Scenarios of 5-10 % paint loss may represent various degrees of paint chalking and minor chipping, whereas levels of 20 to 50 % paint loss represent scenarios of gross failure or mechanical abrasion of paint films.

Given a 4m wall height and a 1m unit width of wall, Table 47 represents the amounts of lead (in grams) that may be lost onto the surface of an adjoining 1m unit width of soil.

Table 47: *The amount of lead (g) lost to adjacent soils from a given wall area in terms of lead loading on the wall and the percent lost from the wall*

Lead loading on 4m high wall surface	*Amount of lead on 4m x 1m wall*	*Amount of paint LEAD lost (grams) to adjoining soil at four percentages of loss*			
(mg Pb/cm^2)	(g)	**5%**	**10%**	**20%**	**50%**
40	1600	80	160	320	800
80	3200	160	320	640	1600
120	4800	240	480	960	2400

The next step in assessing the soil lead elevation is to apportion the lead from paint to particular soil components, or volumes of soil so as to calculate the effective lead concentrations of those soils. The manner of distribution of such lead with localised concentration or dilution is critical to soil lead concentrations.

Three geometries of soil volumes are evaluated, as are three alternative ratios of paint lead addition to each soil volume. A soil density of 1.7 g/cm^3 is used for all soils and a unit length of wall and soil of 1 metre is used.

Model one assumes a 0.9m width of soil adjacent to the house wall where soil has been tilled to a depth of 0.3m, and an adjoining 2.0m wide strip where paint lead is distributed in soil to a depth of 0.1m. Such might be a garden bed against the wall then a lawn on sandy soil.

Model two assumes incorporation of paint lead into soil close to the dripline at the base of a house wall 0.3m wide and 0.3m deep with lateral dilution of paint lead into 0.6 x 0.15m and 2.0 x 0.05m soil sections. The latter soil volumes, at the reduced depths used, may represent a more clay-rich soil.

Model three assumes a concrete path immediately adjacent to the house wall and a narrow section of soil, 0.3 m wide and 0.1m deep, adjacent to the path is a soil volume collecting much of the paint lead debris swept, hosed or washed by rain or wind off the concrete path.

Modification of the model can be easily made in the case of:

- wall height
- paint lead loading
- proportion of lead lost

- volumes of soil compartments incorporating lead lost
- the relative amounts of paint lead assigned to each soil compartment

To improve the validity of the model; consider these matters:

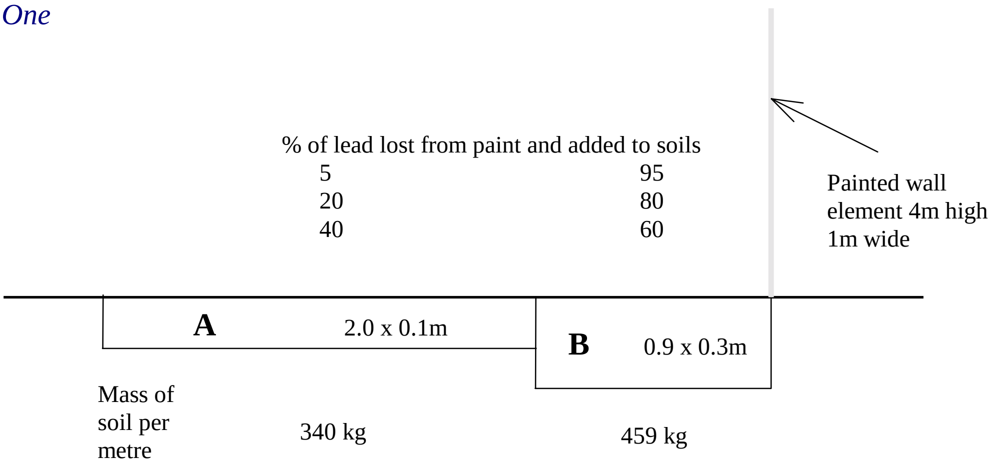
- the proportion of paint flake and chalked paint lead that are carried well beyond the immediate vicinity of a wall.
- the proportion of flaked paint lead that may be removed from the soil surface and not incorporated in soil volumes due to sweeping and removal of flakes or paint flakes being picked up when a lawn is mown and removed with grass clippings
- methods of sampling soils that remove the >2mm soil material prior to soil lead analysis
- the degree to which paint flakes are retained at or near the soil surface, or among the stems and roots of grasses
- the degree of physical tillage of soil, trampling of the ground or mowing of grass which could incorporate paint flakes in greater soil volumes after reducing the size of flakes.
- when has new soil been added or old soil removed

To work through an example from the model; where a house wall 4m high containing 40 mg paint lead per square centimetre is weathered, abraded by sandpaper action or flaked to the extent that 10% of the lead is lost, some 160 grams of lead is lost to soil (assuming 100% paint lead loss to adjacent soil; refer table 47) for each linear metre of wall. Where 40% of the lead from the wall is incorporated in a volume of soil of 2m x 1m x 0.05m (model 3, soil volume F, line 2, next to last column in table 50) the soil lead concentration attributable to paint lead is 380 mg/kg.

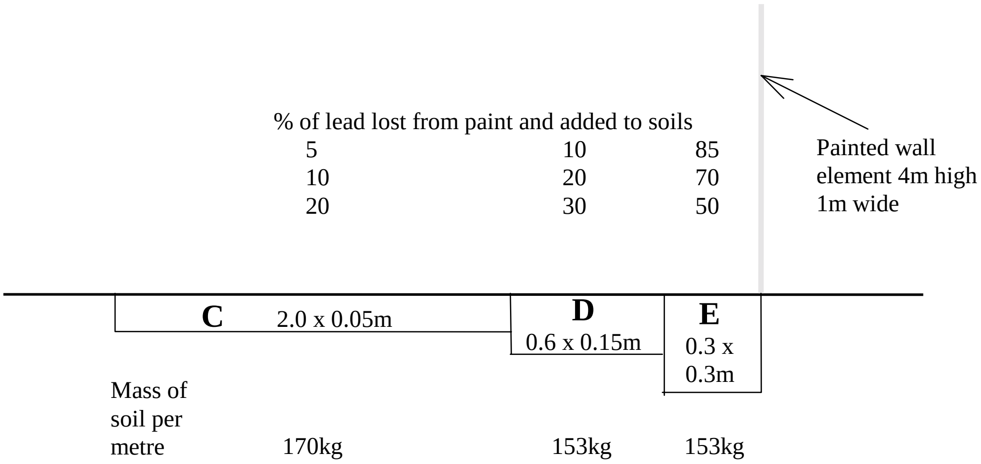
The paint lead model outlined demonstrates how tilling the soil will dilute lead concentrations and that restricting the volume in which paint lead accumulates, greatly increases soil lead concentrations. Locations such as an alley or narrow strips of soil between two painted walls or fences (as are common on the sides of many houses) are locations where paint lead can drive soil lead concentrations to high levels. That is where soil lead, attributable to paint may be more than double levels for adjoining sites due to the close proximity of walls. High walls, for example on two story houses or on the downslope wall of a house on a hillside are settings where additional soil lead may be atttributed to paint.

The model here is not a substitute for testing but is useful in the interpretation of soil lead and paint lead data. While this model only accounts for paint lead, it is likely that lead dust from other sources (for example motor vehicles or industrial emissions) is also concentrated in close proximity to walls.

Model One



Model Two



Model Three

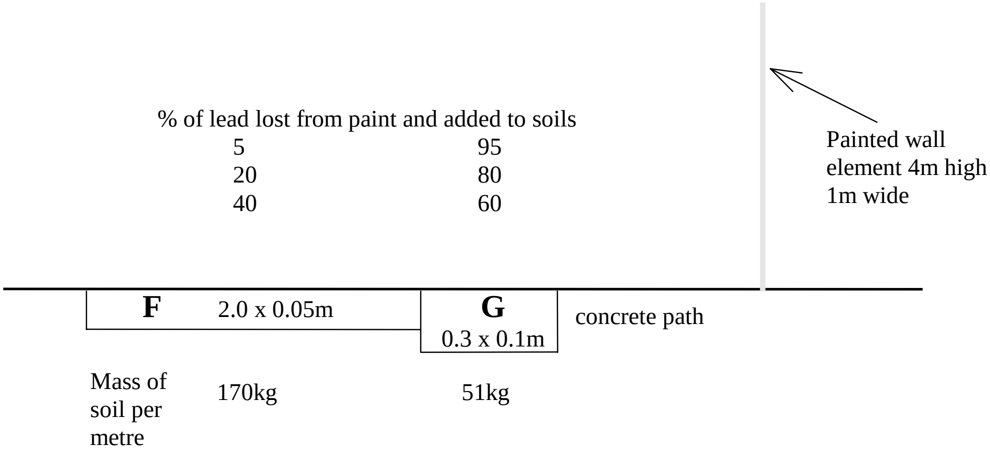


Table 48: *Additional lead in soil volumes A and B (Model One)*

LEAD added to the soil	*Soil lead concentrations for a range of partition ratios of paint lead to soil volumes*					
	5% A	*95% B*	*20% A*	*80% B*	*40% A*	*60% B*
(g)	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*
80	12	170	47	140	94	110
160	24	330	94	280	190	210
240	35	500	140	420	280	310
320	47	660	190	560	380	420
480	71	990	280	840	570	630
640	94	1330	380	1120	750	840
800	120	1660	470	1400	940	1050
960	140	1990	570	1670	1130	1260
1600	240	3310	940	2790	1880	2090
2400	350	4970	1410	4180	2820	3140

Table 49: *Additional lead in soil volumes C, D and E (Model Two)*

LEAD added to the soil	*Soil lead concentrations for a range of partition ratios of paint lead to soil volumes*								
	5% C	*10% D*	*85% E*	*10% C*	*20% D*	*70% E*	*20% C*	*30% D*	*50% E*
(g)	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*
80	24	52	440	47	110	370	94	160	260
160	47	110	890	94	210	730	190	310	520
240	71	160	1330	140	310	1100	280	470	780
320	94	210	1780	190	420	1460	380	630	1050
480	140	310	2670	280	630	2200	570	940	1570
640	190	420	3560	380	840	2930	750	1260	2090
800	240	520	4440	470	1050	3660	940	1570	2610
960	280	630	5330	570	1260	4390	1130	1880	3140
1600	470	1050	8890	940	2090	7320	1880	3140	5230
2400	710	1570	13330	1410	3140	10980	2820	4710	7840

Table 50: *Additional lead in soil volumes F and G (Model Three)*

LEAD added to the Soil (g)	*Soil lead concentrations for a range of partition ratios of paint lead to soil volumes*					
	5% F (mg/kg)	*95% G (mg/kg)*	*20% F (mg/kg)*	*80% G (mg/kg)*	*40% F (mg/kg)*	*60% G (mg/kg)*
80	24	1490	94	1260	190	940
160	47	2980	190	2510	380	1880
240	71	4470	280	3770	570	2820
320	94	5960	380	5020	750	3770
480	140	8940	570	7530	1130	5650
640	190	11920	750	10040	1510	7530
800	240	14900	940	12550	1880	9410
960	280	17880	1130	15060	2260	11290
1600	470	29800	1880	25100	3770	18820
2400	710	44710	2820	37650	5650	28240

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Appendix 1 ~ Inorganic pigments

From Crown (1968) *The Forensic Examination of Paints and Pigments* Table II, Courtesy of Charles C Thomas, Publisher, Ltd., Springfield, Illinois.

Name	*Formula*	*Comments*	*Pigment*
Alumino-silicates		Muscovite Mica Phlogopite Mica Pyrophyllite Talc Lepidolite Biotite	
Antimony Black	Sb_2Sb_3	Some use in camouflage paints.	C I # 77050
Antimony Vermillion	Sb_2S_3 or Sb_2S_5 or Sb_2Sb_3 Sb_2O_3	Discovered 1842, produced after 1847, minor use as an artists colour	Pigment Red 107 C I # 77060
Antimony White	Sb_2O_3	Introduced 1919, widely used between 1930 and 1942 for buildings and vehicles	Pigment White 11 C I # 77052
Azurite	$2CuCO_6 \cdot Cu(OH)_2$	Minor use	Pigment Blue 30 C I # 77420
Barium Carbonate	$BaCO_3$		Pigment White 10 C I # 77099
Barium Potassium Chromate	$BaK_2\ (CrO_4)_2$	Used as a metal primer. Produced after 1945.	Pigment Yellow 31 C I # 77103
Barium White mixtures of $BaSO_4$ & White Lead	$Ba\ SO_4$ Dutch White 80:20 Hamburg White 65:35 Venetian White 50:50		Pigment White 21, 22
Basic Lead Silicate	SiO_2 core with rind of $PbSiO_3$ and $2PbSO_4 \cdot PbO$	First available 1947.	
Basic Lead Silico Chromate	$PbO \cdot SiO_2 \cdot CrO_3$ 47:47:6	Used for primer and finishing coat for steel	
Basic Lead Sulphate	$5PbSO_4 \cdot PbO$ or $2PbSO_4 \cdot PbO$ or $PbSO_4 \cdot PbO$	Widely used as a primer and in building finishes. First introduced between 1855 and 1866, leaded zinc oxide form introduced in 1896.	Pigment White 2 C I # 77633
Black Iron Oxide	$FeO\ Fe_2O_3$ or $Fe(OH)_2\ Fe_2O_3$	Traces of SiO_2 and Al_2O_3 in natural forms	Pigment Black 11 C I # 77499
Brunswick Green	Chrome Yellow, Iron Blue and Barium White		
Cadmium Green	Cadmium Yellow and Cobalt Blue		Pigment Green 14 C I # 77199, 77436
Cadmium Orange	CdS	Commercially available in 1846	Pigment Orange 20 C I # 77199
Cadmium Orange Lithopone	$CdS \cdot CdSe$ and $BaSO_4$ plus ZnS possibly	First used around 1926	
Cadmium Red	$3CdS \cdot 2CdSe$	First produced commercially ca. 1910	Pigment Red 108, Pigment Yellow 37 C I #s 77196, 77199
Cadmium Red Selenide	CdSe	Became available ca. 1925	Pigment Red 108 C I # 77196
Cadmium	$CdS \cdot CdSe$	First commercial production after 1910	Pigment Yellow 37,

Name	*Formula*	*Comments*	*Pigment*
Selenide Orange			108
Cadmium Yellow	CdS plus ZnS usually	Discovered 1817, commercially available after 1846.	Pigment Yellow 37 C I # 77199
Cadmium Yellow Lithopone	Cadmium yellow, barium white and zinc sulphide or cadmium yellow and barium white	First used in 1926.	Pigment Yellow 35 C I # 77117
Calcium Plumbate	Ca_2PbO_4	Minor current use in primers.	Pigment Brown 10 C I # 77227
Carbon Black	80-95% carbon	Traces of S and organic matter.	Pigment Black, 6, 7, 8 C I # 77266, 77268.
Cerulean Blue	$CoO \cdot nSnO_2$ plus $CaSO_4$	Introduced in 1860. Used as an artists colour.	Pigment Blue 35 C I # 77368.
Chrome Green	$PbCrO_4$ and $Fe_4(Fe(CN)_6)_3$ coprecipitated	Probably first used ca. 1825	Pigment Green 15 C I # 77520 + 77600 77601 or 77603
Chrome Orange	$PbCrO_4$ and $Pb(OH)_2$ or $PbCrO_4 \cdot PbO$ and $PbSO_4$ sometimes	Discovered 1809, commercial production began in 1818	Pigment Orange 21 C I # 77601
Chrome Red	$PbCrO_4 \cdot Pb(OH)_2$ and $PbSO_4$ possibly	Discovered 1809	Pigment Red 103 C I # 77601
Chrome Yellow	$PbCrO_4 + PbSO_4$ with $Al(OH)_3$ sometimes	Discovered 1809, commercially available after 1818.	Pigment Yellow 34 C I # 77600, 77603
Chromium Green	Cr_2O_3	Discovered 1797, first appeared as an artists colour 1862	Pigment Green 17 C I # 77288
Cobalt Blue	$CoO \cdot Al_2O_3$ or $Co_3O_4 \cdot 2Al_2O_3$	Discovered 1802.	Pigment Blue 28 C I # 77346
Cobalt Green	$CoO \cdot ZnO$	Discovered in 1780, first mentioned in the literature in 1835	Pigment Green 19 C I # 77335
Copper Blue	CuS	Minor current use	Pigment Blue 34 C I # 77450
Copper Maroon	$CuKFe(CN)_6$	Relatively recent product	
Copper Red	Cu_2O	Now obsolete	C I # 77402
Cuprous Sulphide	Cu_2S	Used in antifouling paints.	C I # 77449
English Vermillion	HgI_2	Now obsolete	
Florentine Brown	$Cu_2Fe(CN)_6 \cdot xH_2O$	First mentioned in literature 1849.	Pigment Brown 9 C I # 77430
Gypsum	$CaSO_4 \cdot 2H_2O$ or $CaSO_4$	Not used on iron and steel surfaces	Pigment White 25 C I # 77231
Hydrated Cupric Oxide	$4CuO \cdot H_2O$	Some current use as a primer.	
Iron Blue	$Fe_4(Fe(CN)_6)_3$ plus K, Na and NH_4 salts.	Discovered 1704. Widely used. Also known as *Prussian Blue*	Pigment Blue 27 C I # 77510, 77520
Iron Titanate	$FeTiO_3$	First introduced 1865.	Pigment Black 12 C I # 77543
Lead Cyanamide	$Pb(CN)_2$	Currently used in primer coatings. First produced in Germany ca. 1928.	Pigment Yellow 48 C I # 77610

Name	*Formula*	*Comments*	*Pigment*
Lead Sulphate	$PbSO_4$		Pigment White 3 C I # 77630
Lead Titanate	$PbTiO_3$ or $PbTiO_3$ plus $PbSO_4 \cdot PbO$	Commonly used in the Netherlands as a primer and in architectural finishes. Minor use in USA. First mentioned in the literature in 1936	Pigment Yellow 47 C I # 77645
Lithopone	ZnS plus $BaSO_4$	First discovered 1847, commercially produced 1874, lightfast varieties since the 1920s.	Pigment White 5 C I # 77115
Magnesite	$MgCO_3$	Some use in some English flat finish paints.	Pigment White 18 C I # 77713
Magnesium Ferrite	$Fe_2O_3 \cdot MgO$	A recent development.	
Manganese Black	MnO_2		Pigment Black 14 C I # 77728
Manganese Blue	$BaMnO_4:BaSO_4$ 11:89	Fist mentioned in literature 1935. Minor use as an artists colour.	Pigment Blue 33 C I # 77112
Manganese White	$MnCO_3$	Minor use	C I # 77723
Mercadium Orange	CdS plus HgS	First offered commercially January 1956	Pigment Orange 23 C I # 77201
Mercadium Red	$HgS \cdot CdS$	First offered commercially after 1956	Pigment Red 113 C I # 77201
Mercuric Arsenate	$HgHAsO_4$	Minor use in waterproofing and anti-fouling paints	C I # 77762
Mineral Black	$AlHSi_2O_6 \cdot C$		Pigment Black 18 C I # 77011
Mineral Grey	$AlHSi_2O_6$		Pigment Black 19 C I # 77017
Mineral Orange	Pb_4O_5 or Pb_3O_4	Minor use	
Mineral Yellow	$PbCl_2 \cdot 5\text{-}7PbO$	Patented in 1871. Some use as an artists colour.	Pigment Yellow 30 C I # 77592
Molybdate Orange	$PbCrO_4$, $PbMoO_4$ and $PbSO_4$	First produced commercially after 1935	Pigment Red 104 C I # 77605
Naples Yellow	$PbSb_2O_6$ or $Pb_3(SbO_4)_2$ or $PbO \cdot Sb_2O_5$ sometmes with ZnO and BiO	Some use as an artists colour.	Pigment Yellow 41 C I # 77588,77589
Nickle Iron Blue	$Ni_2Fe_2(Fe(CN)_6)_3$	Available after ca. 1938	
Orpiment	As_2S_3 or As_2S_2	In use as an artist's colour to the end of the 18th century.	Pigment Yellow 39 C I # 77085, 77086
Paris Green	$CuOAs_2O_3 \cdot Cu(C_2H_3O_2)_2$ or $Cu(C_2H_3O_2)_2 \cdot 3CuAs_2O_4$	Still used in anti-fouling paints. First produced 1814, once used in architectural finishes	Pigment Green 21 C I #77410
Plessy's Green	$CrPO_4 \cdot 4H_2O$	Common in primer coatings and vehicle finishes. Formerly used as an artist's colour, now obsolete.	Pigment Green 17 C I # 77298
Prussian Green	$FeCo_2\ (CN)_6 \cdot xH_2O$	Minor use, now obsolete	
Realgar	As_2S_2 or AsS	An artists pigment	
Red Iron Oxide	$Fe_2O_3 \cdot Al_2O_3 \cdot SiO_2$, $CaSO_4$ and $MgCO_3$ possibility	Artificial forms available since 1850's	Pigment Red 101, 102 C I # 77015, 77491,

Name	*Formula*	*Comments*	*Pigment*
			77538
Red Lead	Pb_3O_4 or $PbO_2 \cdot 2PbO$	Primer coating	Pigment Red 105 C I # 77578
Scarlet Chrome	$PbCrO_4 \cdot PbSO_4 \cdot PbMoO_4$	First produced commercially 1935	
Scheele's Green	$CuHAsO_3$ or $3CuAs_2O_3 \cdot xH_2O$	First prepared 1778, now obsolete in architectural finishes, some use in anti-fouling paints.	Pigment Green 22 C I # 77412
Sienna	$Fe_2O_3 \cdot Al_2O_3 \cdot SiO_2 \cdot 2H_2O$		
Umber	$Fe_2O_3 \cdot Al_2O_3 \cdot SiO_2 \cdot 2H_2O$ MnO_2		
Silicon Nitride	$Si_3 N_4$		C I # 77811
Strontium White	$SrSO_4$	Only minor use prior to 1927	C I # 77845
Strontium Yellow	$SrCrO_4$	Declining use in primers and building paints.	Pigment Yellow 32 C I # 77839
Sublimed Blue Lead	$PbSO_4 \cdot PbO \cdot PbS \cdot PbSO_3 \cdot ZnO \cdot C$	Used in primer coatings. Was in use around turn of the 20th century	
Titanated Barytes	$TiO_2 + BaSO_4$	First produced between 1918 and 1920	
Titanated Gypsum	$TiO_2 + CaSO_4$	Commonly used. 50%:50% mixtures marketed after 1952	
Titanium Green	Co_2TiO_4	Discovered in 1934, minor use.	
Verdigris	$Cu(C_2H_3O_2)_2 \cdot H_2O$ or $Cu_3(OH)_2 (C_2H_3O_2)_4$	Used in anti-fouling paints. Former use in artists paints.	
Vermilion	HgS	Use declining	Pigment Red 106 C I # 77766
Viridian	$Cr_2O_3 \cdot 2H_2O$	Introduced 1838, patented 1859, marketed as an artist’s colour 1862	Pigment Green 18 C I # 77289
White Lead	$3\text{-}6PbCO_3 \cdot Pb(OH)_2$ $2Pb CO_3 \cdot Pb(OH)_2$ or $4Pb CO_3 \cdot 2Pb(OH)_2$ – –PbO		Pigment White 1 C I # 77597
Yellow Ochre	$Fe(OH)_2$ (and $Al_2O_3 \cdot SiO_2$ plus trace $CaSO_4$ and Mg occasionally. Artificial form $Fe_2O_3 \cdot H_2O$		Pigment Yellow 42 & 43 C I # 77492
Zinc Green	$ZnCrO_4$ plus $Fe_4(Fe(CN)_6)_3$		Pigment Green 16 C I # 77955 plus 77525 or 77607
Zinc Sulphide	ZnS or $ZnS \cdot H_2O$	First used ca 1852, major use after 1927.	Pigment White 7 C I # 77975
Zinc White	ZnO	First produced on a commercial scale around 1835	Pigment White 4 C I # 77947
Zinc-Iron Blue	$Zn_2Fe_2 (Fe(CN)_6)_3$	Minor use	C I # 77530

Appendix 2 ~ Paint pigments

(Jennings,1926, 7th edition, 1st edition 1902 and Hess 1965, p.215-216)*

American Vermillion*	chrome red
Antimony yellow	Lead antimonate.
Antwerp Blue*	prussian blue plus alumina
Arcanol	Partly metallic lead (grey oxide of lead with about 70 per cent of lead).
Aureolin or Cobalt Yellow*	a double nitrate of cobalt and potassium
Aurora Yellow*	a cadmium yellow, introduced 1889
Azure Blue*	mixture zinc oxide and ultramarine
Azurite*	a basic copper carbonate
Basic lead silico chromate	An active surface layer of basic lead chromate over an inert core of silica.
Basic sulphate white lead	Basic lead sulphate.*
Basic lead sulphate	Basic lead sulphate.
Berlin Blue*	another name for prussian blue
Berlin white	See White lead.
Berzelius mineral white	Zinc oxide containing lead sulphate.
Black Lead*	graphite
Bloom pigment	Powdered lead-base alloy.
Blue lead	Basic lead sulphate.*
Brunswick green	Lead chromate and Prussian blue.
Calcium plumbate	Calcium plumbate.
Canary yellow and Carmin imitation	Lead chromate.
Cassel yellow	Oxychloride of lead.
Cerulean Blue *	a variety of cobalt blue
Ceruse*	french name for white lead (Cerrusite = $PbCO_3$)
Charcoal Black*	wood ash/carbon reduced with zinc oxide
Charlton White*	original name of lithopone ($ZnS + BaSO_4$)
Chinese Blue*	ferric ferrocyanide
Chinese Red*	another name for red chrome
Chinese White*	a special type of zinc oxide
Chrome Green*	mixture of prussian blue and chrome yellow also sometimes with zinc greens = Brunswick Green
Chrome ochre	Lead chromate and ochre.
Chrome orange	Lead chromate and lead hydroxide.
Chrome red	Lead chromate and lead hydroxide.
Chrome yellow	Lead chromate.
Chrome*	lead chromes, orange and red, primrose and lemon mixture of chromate and sulphate of lead, orange chrome shown to be the best protective for iron and steel. will not mix with pigments containing Sulphur eg.cadmium yellow and ultramarine

Chromium mixed green	Lead chromate and Prussian blue.
Cinnabar green	Lead chromate and Prussian blue (not to be mistaken for the lead-free chromium oxide green).
Cinnabar Greens*	similar composition to chrome greens
Cinnabar imitation or substitute	Dyestuff precipitated on or mixed with red lead.
Cinnabar*	natural mineral used to make vermillion (HgS)
Citron Yellow*	variety of zinc chrome
Cobalt Blue*	oxide of cobalt & other ingredient (partly obscured on copy)
Cobalt Green*	oxide of cobalt and zinc oxide
Cremnitz white	See White lead.
Crystal minium	See Red lead.
English green	Prussian blue and lead chromate.
English yellow	Oxychloride of lead.
Gold Litharge	See Litharge.
Grey lead oxide	Partly metallic lead.
Hookers Green*	either prussian blue and gamboge or zinc yellow, lake in cadmium yellow with prussian blue
Iodine lead yellow	Lead iodide.
King's yellow	See Litharge.
Kings Yellow*	formerly prepared from orpiment (As_2S_3) now usually mix of chrome yellow and zinc oxide in oil or cadmium yellow and zinc oxide in water
Kremser white	See White lead.
Lakes	some
Lead chromate	Chromate of lead.
Lead cyanamide	Lead cyanamide.
Lead phthalocyanine	Lead phthalocyanine or Lead chromate and phthalocyanine blue.
Lead sulphate	Sulphate of lead.*
Lead superoxide	Lead dioxide.
Lead titanate	Lead titanate.
Lemon chrome	See Chrome yellow.
Lemon Yellow*	chrome yellow plus lead sulphate. Also the name for chromate of barium
Litharge	Oxide of lead.
Lithopone*	33.3 % zinc sulphide 66.6% barium sulphate
M50	See Basic lead silico chromate.
Malachite Green*	manufactured from malachite rock ? $Cu_2CO_3(OH)_2$
Massicot	Oxide of lead.
Metallic lead	Metallic lead of practically colloidal particle size.
Middle chrome	Chromate of lead.
Milori green	Prussian blue and lead chromate.
Mineral Grey*	ultramarine or a mix of lamp black, ultramarine and oxide
Mineral yellow	Oxychloride of lead.
Minium	See Red lead.

Minium*	another name for red lead
Mixed chrome green	Lead chromate and Prussian blue.
Molybdate red	See Scarlet chrome.
Montpellier yellow	Oxychloride of lead.
Naples yellow	Basic antimonate of lead.
Naples Yellow*	formerly antimony and lead pigment now either a mix of zinc oxide, yellow ochre and venetian red or French ochre, Venetian red and white lead
New yellow	Extended lead chromate.
Nottingham White*	white lead with barytes
Orange chrome	See Chrome orange.
Orange minium	See Red lead.
Oxide of Chromium*	a chromium sesquioxide also called viridian
Paris red	See Red lead.
Paris yellow	Extended lead chromate.
Patent yellow	Oxychloride of lead.
Pattinson white lead	Basic chloride of lead.
Plumbago*	graphite
Primrose Yellow*	strontian yellow or a light zinc chrome shade
Prussian Blue*	ferric-cyanide of iron
Red Lead*	lead oxide (Pb_3O_4)
Red lead	Oxide of lead or more exactly lead salt of orthoplumbic acid.
Royal yellow	See Litharge.
Saturn cinnabar	See Red lead.
Scarlet chrome	Lead chromate and lead molybdate.
Signal red	Dyestuffs (lightfast) often together with red lead.
Silk green	Prussian blue and lead chromate.
Silver litharge	SeeLitharge.
Slate white	See White lead.
Sliver white	See Whitelead.
Smalt*	powdered glass, coloured with cobalt
Strontium White*	white earth similar in properties to barytes
Sublimed blue lead*	from smelting lead sulphide (galena). A slate grey colour and of very fine grainsize
Subox	Partly metallic lead (grey oxide of lead containing about 55 per cent of lead).
Sulpho-white lead	Basic sulphate of lead.*
Terra alba*	sulphate of calcium or gypsum
Terra verte*	bluish grey tint (composition not stated)
Titanox L	Lead titanate.
Turner's yellow	Oxychloride of lead.
Tuscan red*	from alizarine precipitated on to a base of iron oxide
Ultramarine*	original was lapis lazuli

Vandyke brown*	80% organic matter 20% mineral matter imitated by mix of black pigment, red or oxide, yellow chrome.
Venetian red*	light red iron oxide
Verdigris*	a basic acid of copper, replaced by aniline greens
Vermilion*	ancient pigment was a mercury sulphur compound manufactured from cinnabar. Bright scarlet, turns black in sunlight
Vermilionette and Vermilion substitute	Eosin or similar dyestuff on red lead.
Vermilionette*	a mixture containing red lead
Virdian*	hydrate oxide of chromium (also Guignet's Green)
White lead	Basic carbonate of lead.
White Lead*	basic carbonate of lead
Whiting*	calcium carbonate used with dry white lead in painters putty
Yellow iodide	Lead iodide.
Zinc Oxide (grey) usually 5 to 7 per cent lead sulphate.*	Variable percentage of lead compounds contained
Zinc Oxide*	ZnO (prone to cracking)
Zinc White*	lithopone often called zinc white
Zinc Yellow*	a zinc chrome which is free from lead. Sometimes preferred to lead chromes

Data from: Jennings,1926, 7th edition, 1st edition 1902 and Hess 1965, p.215-216*

Appendix 3 ~ Synthetic organic pigments

From Crown (1968) *The Forensic Examination of Paints and Pigments* Table II, Courtesy of Charles C Thomas, Publisher, Ltd., Springfield, Illinois.

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Acylamino Yellow	Di-1aminoanthraquinonephthalate		-	some current usage	recent origin		
Alizarin Yellow	m-nitroaniline coupled with salicylic acid	Mordant Yellow 1	14025	used	patented 1887		
Anthrapyrimidine Yellow	carboxyanthrapyrimidine condensed with 1-aminoanthraquinone	Vat Yellow 20	68420	used	produced after 1951		
Auramine Yellow	HCl salt of aminated Michler's ketone	Basic Yellow 2	41000	minor	patented in 1883		
Benzidine Yellow AAA	3,3'dichlorobenzidine coupled with acetoacetanilide	Pigment Yellow 12	21090	minor	known since 1911	minor	
Benzidine Yellow AAMX	3,3'dichlorobenzidine coupled with 2,4-acetoacetoxylide	Pigment Yellow 13	21100	minor		minor	
Benzidine Yellow AAOA	3,3'dichlorobenzidine coupled with acetoaceto-o-anisidine			used	introduced around 1949	used	
Benzidine Yellow AAOT	3,3'dichlorobenzidine coupled with o-acetoacetotoluidine	Pigment Yellow 14	21095	commonly used	known since 1911	commonly used	
Fast Light Yellow G	aniline coupled with 3-methyl-1-(p-sulphophenyl)-5-pyrazolone	Acid Yellow 11	18820	minor use	discovered 1892		
Fast Yellow GRL New	2-nitro-p-toluidine coupled with o-acetoacetotoluidide	Pigment Yellow 9	11720	currently used	first referred to 1926		
Flavanthrone Yellow	Flavanthrene	Vat Yellow 1	70600	some usage, declining	discovered 1901		declining usage
Hansa Yellow G	2-nitro-p-toluidine coupled with acetoacetoanilide	Pigment Yellow 1	11680	commonly used	introduced 1909		commonly used
Hansa Yellow GR	4-chloro-2-nitroaniline coupled with 2,4-acetoacetoxylidide	Pigment Yellow 2	11730	commonly used	discovered 1909		
Hansa Yellow 3G	4-chloro-2-nitroaniline coupled with acetoacetoanilide	Pigment Yellow 6	11670	commonly used	discovered 1909		
Hansa Yellow 5G	o-nitroaniline coupled with acetoacetoanilide	Pigment Yellow 5	11660	commonly used	discovered 1909		

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Hansa Yellow 10G	4-chloro-2-nitroaniline coupled with o-chloroacetoacetanilide	Pigment Yellow 3	11710	commonly used	discovered 1911		commonly used
Hansa Yellow 13G	p-nitroaniline coupled with acetoacetoanilide	Pigment Yellow 4	11665	commonly used	discovered 1909		
Hansa Yellow R	2,5-dichloroaniline coupled with 3-methyl-1-phenyl-5-pyrazolone	Pigment Yellow 10	12710	currently used	first referred to in 1928		
Hansa Yellow RN	2-nitro-p-anisidine coupled with o-acetoacetanisidide		11740	some current use			
Helio Fast Yellow	1-aminoanthraquinone condensed with salicylic acid	Pigment Yellow 23	60520	some minor current use	Patented 1909		
Lithol Fast Yellow GC Extra	5-chloro-2-nitroaniline condensed with formaldehyde	Pigment Yellow 11	10325	used	discovered 1909		
Lithol Fast Yellow NCR	o-nitroaniline coupled with 2,4-quinolinediol	Pigment Yellow 7	12780	used in Europe			used in Europe
Napthol Yellow S	Disodium salt of 2,4-dinitro-1-naphthol-8-sulphonic acid ppt. on Alumina; sometimes as a Ba lake.	Acid Yellow 1	10316	some minor use	patented in 1879		
Nickel Monazo Yellow	Nickel complex of p-chloroaniline coulped with 2,4-quinolinediol	Pigment Green 10	12775	currently used	discovered in 1946		
Permanent Yellow HR	3,3' dichlorobenzidine coupled with acetoacet-4-methoxy-5-chloro-o-anisidide	Pigment Yellow 83		currently used	produced after 1956		
Permanent Yellow NCG	2,4-dichloroaniline coupled with 4-4'-Bi-o-acetoacetotoluidide	Pigment Yellow 16	20040	some minor current use	discovered 1921		
Pigment Chrome Yellow L	o-toluidine coupled with 1-phenyl-3-methyl-5-pyrazolone		12720	formerly some minor usage, now obsolete	patented 1904		
Quinoline Yellow	Mono and disulphonic acids of quinophthalone	Acid Yellow 3	47005	some current use	patented 1882		
Tartrazine Yellow	Phenylhydrazine-p-sulphonic acid and dioxytartaric acid ppt. on Alumina or Barium White	Acid Yellow 23	19140		patented 1884		
Thioflavin Yellow	Phosphomolybdic-tungstic acid (PMTA) lake of methylated dihydrothio-p-toluidine	Pigment Yellow 18	49005	used with green toners	patented 1888, PMTA from 1914		

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Benzidine Orange	3-3'dichlorobenzidine coupled with 1-phenyl-3-methyl-5-pyrazolone	Pigment Orange 13	2110	commonly used	discovered 1910		
Brilliant Orange	Ba lake of aniline coupled with Shaeffer's acid	Pigment Orange 18	15970	some minor current use	patented 1878		
Dianisidine Orange	o-dianisidine coupled with acetoacetanilide	Pigment Orange 16	21160	some minor current use			
Dibrompyranthrone Orange	Dibromopyranthrone	Vat Orange 2	59705		discovered 1905		some use
Dinitroaniline Orange	2,4-dinitroaniline coupled with 2-naphthol	Pigment Orange 5	12075	commonly used	discovered 1907		commonly used
Fast Orange L	5-nitro-o-toluidine coupled with 2-naphthol	Pigment Orange 3	12105	some minor use	patented 1904		
Fast Orange O	o-nitroaniline-p-sulphonic acid coupled with 2-naphthol			formerly used now obsolete	patented 1901		
Hansa Yellow 3R	2-nitro-p-anisidine coupled with o-acetoacetotoluidide	Pigment Orange 1	11725		discovered 1926		
Helio Orange TD	Ba lake of o-chloraniline coupled with Shaeffer's acid	Pigment Orange 19	15990				
Lithol Red 3GS	2-amino-4,5-dichlorobenzene-sulphonic acid coupled with 2-naphthol	Pigment Orange 7	15530	some minor current usage			
Metanitraniline Orange	m-nitroaniline coupled with 2-naphthol		12065	formerly used now obsolete	discovered 1885 patented 1894		
Orange 4R	Brominated pyranthrone	Vat Orange 4	59710	current use	discovered 1909		current use
Orthonitraniline Orange	o-nitroaniline coupled with 2-naphthol	Pigment Orange 2	12060	commonly used	discovered 1895		commonly used
Persian Orange	Ba lake of sulphanilic acid coupled with 2-naphthol	Pigment Orange 17	15510	commonly used	patented 1876		
Pigment Fast Orange 4G	2-nitro-p-toluidine coupled with 3-methyl-1-phenyl-5-pyrazolone	Pigment Orange 6	12730	some minor current use			
Vat Orange GR	Trans isomer of N,N'-diaryl-1,4,5,8-naphthalenetetracarboxylic diimides treated with o-phenylene diamine	Vat Orange 7	71105	used	discovered 1924		

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Alizarin	1,2 dihydroxyanthraquinone ppt. on Alumina and sometimes on earths containing Sn, Ca, Fe, Co, Cu, Mn, Al	Pigment Red 83	58000	formerly used	discovered between 1868 and 1876		formerly used
Amaranth	Ba lake of naphthionic acid coupled with R acid	Acid Red 27	16185	some minor current use	discovered 1878		
Ananthrone Red	Brominated ananthrone	Vat Orange 3	59300		discovered 1913		used
Arylide Maroon	4-nitro-o-anisidine coupled with 3-hydroxy-2-naphtho-o-toluidide	Pigment Red 19	12400	currently used	? after 1945		currently used
Azo Brilliant Red	m-chloraniline coupled with 2,4-dichlorobenzoyl-1-amino-8-naphthol-4,6-disulphonic acid			some minor use	patented 1914		
BON Maroon Dark	Ca, Mn salts of 2-amino-1-naphthalene sulphonic acid coupled with 2-oxynaphthoic acid	Pigment Red 63	15880	commonly used	patented 1907		commonly used
Bordeaux F3R	4-nitro-o-anisidine coupled with 3-hydroxy-N-1-naphthyl-2-naphthamide	Pigment Red 16	12500	used	discovered 1911		
Bordeaux Lake	Ba lake of alphanaphthylamine coupled with 2-naphthol-3,6-disulphonic acid ppt. on alumina or barium white	Acid Red 17	16180	some minor current use	patented 1907		
Bordeaux Red	Mn lake of 4-chloroanthranilic acid coupled with 2-oxy-naphthoic acid	Pigment Red 55	15820	some minor use	of rel. recent origin		some minor use
Bordeaux Red RR	Cis isomer of Indanthrene Red F2B	Vat Red 15	71100	currently used	discovered 1924		
Brilliant Lake Red	Ca lake of aniline coupled with 2-oxy-naphthoic acid	Pigment Red 64	15800	used	discovered 1893		
Brilliant Lake Scarlet	Ba lake of 6-amino-m-toluene-sulphonic acid coupled with 2-naphthol	Pigment 70	15590	some minor current use			
Chlorinated Para Red	4-chloro-2-nitroaniline coupled with 2-naphthol	Pigment Red 6	12090	commonly used	discovered 1906		commonly used
Erythrosine B	Al and Pb lakes of tetraiodo-fluorescein	Acid Red 51	45430	some minor former use now obsolete	discovered 1876		
Fanal Pink G Supra	Rhodamine Y and Auramine Yellow 93:7	Red mixture					

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Fanal Red 6B	Esterified Rhodamine B, PMTA	Pigment Violet 2	45175	used	discovered 1891, PMTA forms after 1914		
Fast Red FR	o-chloraniline coupled with 3-hydroxy-2-naphthanilide	Pigment Red 21	12300	some minor current use	discovered 1911		
Fast Red F2R	2,5-dichloroaniline coupled with 3-hydroxy-2-naphthanilide	Pigment Red 2	12310	used	discovered 1911		
Fire Red	2-chloro-4-nitroaniline coupled with 2-naphthol	Pigment Red 4	12085	used	patented in 1905		used
Hansa Rubine G	2,4-dinitroaniline-6-sulphonic acid coupled with 2-oxy-naphthoic acid			used	patented 1911		
Helio Bordeaux	Ba, Ca, Mn lakes of 1-naphthylamine coupled with 1-naphthol-5-sulphonic acid	Pigment Red 54	14830	used	discovered 1910		
Helio Purpurin	2-naphthylamine-1,6-disulphonic acid coupled with 2-naphthol-3,6-disulphonic acid			used	patented 1904		
Helio Red RMT	Ba lake of 4-amino-o-toluene-sulphonic acid coupled with 2-naphthol	Pigment Red 51	15580	used	discovered 1920		
Helio Rubine	Al and Cr lakes of trihydroxyl-sulphonic anthraquinone	Pigment Red 84	58210	some minor current use	discovered ca. 1895		
Indanthrene Red RK	Anthraquinone condensed and cyclized with anthranilic acid	Vat Red 35	68000	current use	discovered 1910 only recently commercialised		
Indanthrene Red F2B	1-nitro-2-anthraquinone-carbonyl chloride condensed and cyclized with 2-amino-3-hydroxyanthraquinone	Vat Red 10	67000	currently used	discovered 1926		
Indo Red	oxidised 1,5-dibenzamidoanthraquinone	Pigment Red 85	63350	some minor current use	discovered 1909		
Lake Caramine L	Ba lake of 4,4'dibenzyline-di-2,5-xylidine coupled with 2-naphthol-3,6-di-sulphonic acid, ppt. on alumina and barium white or Zn white and Ba white	Pigment Red 61	24830	currently used	discovered 1887		
Lithol Bordeaux RN	Ba lake of the Na salt of 4-amino 5-methoxy-	Pigment Red 56	15870	some minor current			

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Extra	o-toluene-sulphonic acid coupled with 2-oxy-naphthoic acid			use			
Lithol Fast Scarlet G	4,5-dichlor-2-nitroaniline coupled with 2-naphthol			used			
Lithol Red	Na, Sr, Ba, or Mn lakes of 2-amino-1-naphthalene sulphonic acid coupled with 2-naphthol	Pigment Red 49	15630	commonly used	patented 1899	commonly used	
Lithol Red GGS	Ca, Pb, Ba, Al salts of 6-amino-4-chloro-m-toluene-sulphonic acid coupled with 2-naphthol	Pigment Red 69	15595	some minor current use	discovered 1904		
Lithol Red 2G	Ca, Mn lakes of 2-chloro-5-toluidine-4-sulphonic acid coupled with 2-oxy-naphthoic acid	Pigment Red 52	15860	currently used	discovered 1910, commercially important after 1954		
Lithol Rubine	Ca and Mn lakes of the Na salt of 6-amino-m-toluene-sulphonic acid coupled with 2-oxy-naphthoic acid. May contain Al and heavy metal rosinates	Pigment Red 57	15850	commonly used	discovered in 1903	commonly used	
Naphthol Maroon Dark	4-chloro-2-nitroaniline coupled with 3-hydroxy-2-naphtho-o-anisidide	Pigment Red 15	12465	commonly used	discovered 1922		
Naphthol Maroon Light	4-chloro-2-nitroaniline coupled with 3-hydroxy-2-naphtho-o-toluidide	Pigment Red 14	12380	commonly used	available after 1945		
Naphthol Red Medium	4-nitro-o-toluidine coupled with 3-hydroxy-2-naphtho-o-toluidide	Pigment Red 12	12390	commonly used	available after 1945		
Para Red Dark	p-nitroaniline coupled with 2-naphthol and 2-naphthol-7-sulphonic acid	Pigment Red 1	12070	commonly used	patented 1885		commonly used
Para Red Light	p-nitroaniline coupled with 2-naphthol and 2-naphthol	Pigment Red 1	12070	commonly used	patented 1885		commonly used
Permanent Red F4R	5-nitro-o-toluidine coupled with 4-chloro-3-hydroxy-2-naphthanilide	Pigment Red 8	12335	used	discovered 1911		
Permanent Red F4RH	4-chloro-o-toluidine coupled with 4-chloro-3-hydroxy-2-naphtho-o-toluidide	Pigment Red 7	12420	used	discovered 1921		
Permanent Red FGR	2,4,5-trichloraniline coupled with 3-hydroxy-2-naphtho-o-toluidide (?)		12370	some minor current use			

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Permanent Red FRLL	2,5-dichloraniline coupled with 3-hydroxy-2-naphtho-o-anisidide	Pigment Red 9	12460	commonly used	discovered 1922		
Permanent Red ITR	N,N-diethyl-4-methoxy-metanilamide coupled with 5-chloro-3-hydroxy-2,4-dimethoxy-2-naphthanilide	Pigment Red 5	12490	commonly used	discovered 1931, avail. In US after 1945		
Permanent Red 2B	Ba, Ca, Mn lakes of Na salt of 6-amino-4-chloro-m-toluene sulphonic acid coupled with 2-oxynaphthoic acid. May contain Al or heavy metal resinates	Pigment Red 48	15865	commonly used	introduced in Germany in 1928 commercially available in US after 1940		
Permanent Rubine FBH	5-chloro-o-toluidine coupled with 5-chloro-3-hydroxy-2-naphtho-o-toluidide	Pigment Red 11	12430	commonly used	discovered 1921		
Perylene Maroon	Methylated 3,4,9,10-perylene-tetracarboxylic acid diimide	Vat Red 23	71130	currently used	discovered 1913, commercial use only recent		currently used
Perylene Red	3,4,9,10-perylene-tetracarboxylic acid condensed with p-anisidine	Vat Red 29	71140		discovered in 1919, commercial use only recent		currently used
Perylene Scarlet	3,4,9,10-perylene-tetracarboxylic acid condensed with p-chloraniline	Vat Red 32	71138	currently used	discovered in 1919, commercial use only recent		currently used
Phloxine	Pb lake of tetrabromofluorescein, also as K salt alone	Pigment Red 90	45380	still used	discovered 1871		
Pigment Bordeaux R	1-naphthylamine coupled with 2-naphthol	Pigment Red 40	12170	some minor current use	discovered 1878		
Pigment Carmine 3B	Ba lake of m-tolidine coupled with 2-naphthol-3,6-disulphonic acid	Pigment Red 62	23295	some minor current use			
Pigment Purple A	o-anisidine coupled with 2-naphthol ppt. on substrate	Solvent Red 1	12150	some minor current use	discovered 1899		
Pigment Red FRL	2,5-dichloroaniline coupled with 3-hydroxy-2-naphtho-p-toluidide	Pigment Red 10	12440	commonly used	discovered 1921		
Pigment Rubine 3G	Ca, Sr, Ba, Mn lakes of p-chlor-aniline-m-sulphonic acid coupled with 2-oxynaphthoic	Pigment Red 58	15825	current use			

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
	acid. May contain Al and heavy metal rosinates						
Pigment Scarlet 3B	Ba lake of anthranilic acid coupled with 2-naphthol-3,6-disulphonic acid ppt. on alumina or zinc white	Pigment Red 60	16105	current use	discovered 1902		
Ponceau G	aniline coupled with R acid	Acid Orange 14	16100	formerly some minor use	discovered 1878 now obsolete		
Ponceau 3R	pseudocumadine coupled with R acid	Food Red 6	16155	formerly some minor use	discovered 1878 now obsolete		
Ponceau 5R	aminoazobenzene coupled with 2-naphthol-3,6,8-trisulphonic acid			formerly some minor use	now obsolete		
Pyrazolone Maroon	benzidine coupled with 3-carbethoxy-1-phenyl-5-pyrazolone	Pigment Red 39	21080	some current use			
Pyrazolone Red	3,3'-dichlorobenzidine coupled with 3-carbethoxy-1-phenyl-5-pyrazolone	Pigment Red 38	21120	common use			
Quinacridone Magenta	dimethyl quinacridone			currently used	produced after 1958		currently used
Quinacridone Maroon	quinacridone			currently used	discovered 1935 produced commercially after 1958		currently used
Quinacridone Red	quinacridone			currently used	discovered 1935 produced commercially after 1958		currently used
Quinacridone Scarlet	dichloroquinacridone			currently used	produced after 1958		currently used
Red Lake C	Ba salt of o-chlor-m-toluidine-p-sulphonic acid coupled with 2-naphthol	Pigment Red 53	15582	some current use, use declining	patented 1902		
Red Lake D	Ba salt of anthranilic acid coupled with 2-naphthol	Pigment Red 50	15500	some minor use in past now obsolete	patented 1905		
Red Lake P	Ba lake of 2-amino-5-nitrobenzene sulphonic acid coupled with 2-naphthol		15550	some minor use in past now obsolete	patented 1901		

Common pigment name	*Chemical compound*	*Pigment name*	*Colour Index Number*	*Pigment use in architectural finishes Mid - Late 1960s*	*Date of discovery or first use*	*Use on toys (1968)*	*Use in vehicle paints (1968)*
Rhodamine B	phosphomolybdic-tungstic acid lake of m-diethylaminophenol condensed with phthalic anhydride, ppt on alumina	Pigment Violet 1	45170	commonly used	rhodamine B patented 1887, PMTA forms patented 1915		
Rhodamine 6G	phosphomolybdic-tungstic acid lakes of monoethyl-m-aminophenol condensed with phthalic anhydride	Pigment Red 82	45150	common use	rhodamine 6G discovered 1891, PMTA toner patented after 1914		
Rhodamine Y	phosphomolybdic-tungstic acid lake of esterified ethylamino-p-cresol condensed with phthalic anhydride	Pigment Red 81	45160	used	rhodamine Y discovered 1892, PMTA forms introduced after 1925		
Rose Bengal	tetrachloro-tetraiodofluorescein	Acid Red 94	45440	some minor former use now obsolete	patented 1882		
Scarlet Lake 2R	Ba salt of 2,4-xylidine coupled with 2-naphthol-3,6-disulphonic acid, ppt on alumina or barium white	Acid Red 26	16150	some minor use in the past now obsolete	discovered 1878		
Solfast Scarlet	5-nitro-o-toluidine coupled with 3-hydroxy-2-naphthanilide	Pigment Red 22	12315	current use	discovered 1911		
Solfast Scarlet Dark	5-nitro-o-anisidine coupled with 3-hydroxy-2-naphthanilide	Pigment Red 23	12355	current use	discovered 1911		
Thioindigo Maroon	(5-chlor-o-tolylmercapto)acetic acid cyclised and oxidised with chlorosulphonic acid		73390	used	discovered 1906		used
Thioindigo Red	oxidised 7-chloro-3(2H)-thia-naphthenone	Pigment Red 87	73310	currently used	discovered 1907		
Thioindigo Red Violet RH	(4-chloro-o-tolylmercapto) acetic acid cyclised and oxidised with chlorosulphonic acid	Vat Violet 2	73385	currently used	discovered 1907		currently used
Toluidine Maroon Dark	2-nitro-p-toluidine coupled with 3-hydroxy-3'-nitro-2-naphthanilide	Pigment Red 18	12350	used	discovered 1911		used
Toluidine Maroon Light	2-nitro-p-toluidine coupled with 3-hydroxy-2-naphtho-o-toluidide	Pigment Red 13	12395	commonly used			commonly used
Toluidine Red	o-nitro-p-toluidine coupled with 2-naphthol	Pigment Red 3	12120	very commonly used	patented ca. 1905		very commonly used

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Virginia Red	o-chlor-m-toluidine-p-sulphonic acid coupled with 2-oxy-naphthoic acid			used			
Acid Green	Ba lake of Na salt of a - (N-ethylanilino) - m-toluene-sulphonic acid, ppt on alumina or alumina plus barium white	Acid Green 3	42085	formerly used now obsolete	introduced 1883		
Brilliant Green	phosphomolybdic-tungstic acid lake of N-N-diethylaniline coupled with benzaldehyde	Pigment Green 1	42040	currently used	dyestuff intrduced 1879, PMTA forms after 1925		
Brilliant Green	Brilliant Green plus Auramine	Green Mixture					
China Green	Synthetic Malachite Green ppt on Terre Verte	Green Mixture					
Green Toner Y	Brilliant Green plus Thioflavin Yellow	Green Mixture		used			
Hansa Green	Ba lake of Fe salt of 5,6-diamino-1-naphthalenesulphonic acid or 5,6-diamino-4-chloro-1-naphthelene-sulphonic acid	Pigment Green 9	49415	formerly some minor use, now obsolete	discovered 1909		
Metal - free Phthalo Green	polychlorinated metal-free phthalocyanine	-	74120	some current use	discovered 1935		
Naphthol Green B	Fe, Na salt of nitrosated 1-naphthol-4-sulphonic acid	Acid Green 4	10025	some minor current use	discovered 1885		
Phthalocyanine Green	chlorinated Cu tetrabenzo-tetraazo-porphin	Pigment Green 7	74260	used	discovered 1935, made available 1938		used
Nickel Green	Ni complex of p-chloraniline coupled with 2,4-quinolinediol	Pigment Green 10	12775	some minor current use	discovered 1946		
Pigment Green B	Fe complex of 1-nitroso-2-naphthol and 1-nitroso-2-naphthol-3-carboxylic acid	Pigment Green 8	10006	currently used	discovered 1921		
Synthetic Malachite Green	phosphomolybdic-tungstic acid lake of dimethylaniline coupled with benzaldehyde	Pigment Green 4	42000	currently used	dyestuff patented 1877, PMTA forms after 1914		
Alizarin Cyanine	Na salt of 1,3,5,7-tetrahydroxy-2,6-disulphonic anthraquinone	Mordant Blue 23	58610	some minor current use	discovered 1891		
Alkali Blue	Na salt of di-n-triphenyl-tri-amino-triphenylcarbinol-sulphonic acid	Pigment Blue 19	42750A	some current use	introduced 1861		

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Chromophyl Blue	o-dianisidine coupled with 3-hydroxy-2-naphtho-o-anisidine	Pigment Blue 26	21185	some minor current use	of rel. recent origin		
Congo Blue	o-dianisidine coupled with 3-hydroxy-2-naphthanilide	Pigment Blue 25	21180	some minor current use	of rel. recent origin		
Erioglaucine	Ba lake of Benzyl-ethylaniline-sulphonic acid condensed with benzaldehyde-o-sulphonic acid	Pigment Blue 24	42090	some current use	discovered between 1888 and 1896		
Indanthrone Blue	trichloroindanthrone	Pigment Blue 21	69835	commonly used	discovered in 1905		commonly used
Indanthrone Blue B	dichloroindanthrone	Vat Blue 6	69825	currently used	discovered in 1903		currently used
Indanthrone Blue GCD	monochloroindanthrone	Vat Blue 14	69810	currently used	discovered in 1903		currently used
Indanthrone Blue R	indanthrone	Vat Blue 4	69800	currently used	discovered 1901		currently used
Indigo, Synthetic	2,2'-bis-indole-indigo	Vat Blue 1	73000	some minor current use	discovered 1880, patented 1907		
Metal -free Phthalo Blue	tetrabenzo-tetraazo-porphin	Pigment Blue 16	74100	used	discovered 1931		
Methylene Blue	zinc double chloride of 3,7-di-dimethylaminophenothiazine	Basic Blue 9	52015	some minor use	discovered 1876		
Peacock Blue	phosphomolybdic-tungstic acid lake of o-chlorobenzaldehyde coupled with N-ethyl-o-toluidine	Pigment Blue 3	42140	used	dyestuff discovered 1896, PMTA forms after 1914		
Phthalocyanine Blue	Cu-tetrabenzo-tetraazo-porphin	Pigment Blue 15	74160	commonly used	discovered in 1928, available England 1928-33, US in 1936		commonly used
Setoglaucine	phosphomolybdic-tungstic acid lake of dimethylaniline condensed with o-chloro-benzaldehyde	Pigment Blue 9	42025	currently used	dyestuff discovered 1896, PMTA forms after 1914	currently used	
Sulphonated Phthalocyanine Blue	Ba lake of trisulphonated Cu phthalocyanine	Pigment Blue 17	74180, 74200	commonly used	discovered in 1928		
Victoria Blue	phosphomolybdic-tungstic toner of phenyl-	Pigment Blue 1	42595	commonly used	dyestuff patented in	commonly	

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	alpha-naphthylamine condensed with tetramethyl-diamino benzophrenone chloride				1883, PTA form patented 1918	used	
Victoria Blue B	phosphomolybdic-tungstic acid toner of N-phenyl-naphthylamine coupled with p,p'-(dichloro-methylene)bis(N, N-dimethylaniline)	Pigment Blue 2	44045	commonly used	dyestuff patented in 1883, PTA form patented 1918	commonly used	
Dibenzanthrone Violet	violanthrone	Vat Blue 20	59800		discovered in 1904		currently used
Dioxazine Violet	carbazole-9,10-dichloro-biphene-dioxazine				discovered in 1953 introduced comercially ca. 1965		currently used
Helio Fast Rubine 3BL	Al lake of sulphonated dihydroxy anthraquinone	Pigment Violet 6	58060	some minor current use	discovered 1906		
Helio Fast Rubine 4BL	Al lake of monosulphonated condensed quinizarin	Pigment Violet 5	58055	some current usage	discovered in 1906		
Helio Fast Rubine 6BL	Al lake of disulphonated condensed quinizarin	Pigment Violet 7	58065	some current usage	developed after 1906		
Indanthrene Violet	1,5-dichloro-anthraquinone coupled with anthranilic acid	Vat Violet 1	60010	used	patented 1908		used
Magenta	phosphomolybdic-tungstic acid lake of nitrobenzene condensed with o-nitrotoluene	Pigment Violet 4	42510	now obsolete	dyestuff discovered 1856, PMTA forms after 1914		
Mauve	amino-phenyl-amino-p-tolyl-ditol azonium sulphate			now obsolete	discovered 1856		
Methyl Violet	phosphomolybdic-tungstic acid toners of a mixture of the hydrochlorides of the more highly methylated pararosanilines	Pigment Violet 3	42535	in common use	dyestuff discovered 1861, PMTA forms patented in 1915		
Quinacridone Violet	quinacridone			currently used	patented ca. 1958		currently used
Quinizarin	Al lake of dihydroxyanthraquinone	Pigment Violet 12	58050	some minor current use	discovered in 1873		
Thioindigo Violet	(4-chloro-2,5-xylylmercapto) acetic acid cyclised and oxidised with chlorosulphonic	Vat Violet 3	73395	used	discovered 1907		used

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	acid						
Bismark Brown	diazotized toluene-2,4-diamine hydrochloride	Pigment Brown 3	21010		discovered 1878		
BON Brown	Cu lake of aniline coupled with 3-hydroxy-2-naphthoic acid	Pigment Brown 5	15800	some current use	discoved 1893		
Toner Brown	Cu complex of p-nitroaniline coupled with 2-naphthol	Pigment Brown 2	12071	some current use			
Aniline Black	oxidised aniline	Pigment Black 1	50440	current use	discovered 1863		
Induline	mixture of aminodianilino, trianilino, and tetraanilinophenyl-phenazinum chloride	Solvent Blue 7	50400	used for toning carbon blacks	discovered 1863		
Nigrosine	mixtures of nitrobenzene, aniline and aniline hydrochloride	Solvent Black 7	50415B	used for toning carbon blacks	discovered 1867		