

Heavy metal contamination in the paint industry

Chapter 3

- Topics discussed include:
- Background.
 - Exposure to lead.
 - Preventative measures.
 - Review articles.
 - Analytical considerations.

PEOPLE WHO FREQUENT Japanese restaurants can now eat without apprehension from the black and red lacquered bowls in which Japanese food is frequently served.

Murasugie and Terada (*Journal of the Japanese Society of Colour Material*, 51, 12 (1978) p. 695) extracted the lacquer with acetic acid and found no cadmium or mercury, and how lead content in only some cases. This is comforting indeed, but obviously of little consequence statistically relative to the problem of lead poisoning.

Heavy metal contamination has been the subject of a great deal of discussion and of many articles in the past decade. For years paint was made with lead. There was no understanding of the fact that this lead could be harmful. Today we know that it is, and getting the lead and other heavy metals out of paints has become a major objective in the coatings industry.

The problem

Prior to 1930, most decorative paint contained white lead, a basic carbonate of lead whose structure is $2Pb \cdot CO_2 \cdot Pb(OH)_2$, and also basic sulfate of white lead, $PbO \cdot xPbSO_4$ was used, but to a much lesser degree. Both

were white pigments. In addition there were colored pigments containing lead, including chrome yellow ($PbCrO_4 \cdot xPbSO_4$), red 1 ($PbO \cdot xPbO$), chrome green (chromic acid plus another pigment known as iron bl) and Brunswick green (chromic yellow 1 iron blue plus barium sulfate). Also, prior to 1930 arsenic pigments also were a source of toxicity, but their use was restricted much earlier. These pigments appeared.

In the period between the world wars lead-based pigments became expensive accordingly were used only in higher quality paints. These so-called higher quality paints, however, still had disadvantages beyond the fact that they were expensive and toxic. Gloss finishes could not be produced with them and unless great skill was used in their application they showed by marks. Drying time was long, and pigments had a tendency to react with sulfide in the air to give black lead salt that discolored the paint.

After 1945, good quality titanium dioxide pigments became available and lead pigments became even more expensive. Thus, their use was limited to primers, wood and metal. Also galvanized steel window frames were painted with primer based on calcium plumbate, $2CaO \cdot PbO$. Window frames, too, were sometimes coated with red lead. Indeed, red lead is still used in primers for metal where corrosion problem and surface preparation is limited.

make high performance coatings more attractive.

Q—How much of the paint on a structure is put on in the shop?

A—A first coat usually is put on in the shop, but the rest is done on the site after the structure has been completed. Most shops want to do as little painting as possible in the shop.

Q—How does the SSPC interact with ASTM? Are these organizations competitors?

A—SSPC and ASTM try not to duplicate efforts. Many people are active in both organizations and attempts are made to coordinate activities. SSPC specifications reference ASTM methods and ASTM raw material specifications. SSPC has cooperated with ASTM on developing visual standards of surface preparation and a joint standard has been issued.

Reichhold completes acquisition of certain Du Pont business

White Plains, N. Y., June 22—Reichhold Chemicals, Inc. announced it completed its previously announced acquisition of Du Pont's Elvac® vinyl acetate/ethylene emulsion business.

The acquisition includes Du Pont's Elvac® manufacturing facility at Seneca, Ill., together with all relevant patent, trademark, manufacturing and marketing data. C. Robert Powell, Reichhold chairman and chief executive officer, said the purchase price of approximately \$20 million was funded out of proceeds received from Reichhold's divestiture program, initiated last year.

DeSoto dividend

Des Plaines, Ill., June 22—The board of directors of DeSoto, Inc. declared a regular cash quarterly dividend of 31 cents per share. The dividend is unchanged from the previous quarterly payout and is payable July 22 to stockholders of record at the close of business on July 1.

He then described the Keane-Tabor surface profile comparator, which provides a series of standards to compare to a surface in order to determine the quality of its profile.

Keane discussed another project on painting of "weathering" steel. This special alloy was designed so that it would not need to be painted, but in highly corrosive environments even it cannot survive without additional protection. Therefore, there is considerable interest in establishing the best coatings for such steel. The SSPC project has shown that certain surface preparations and zinc-rich coatings can provide longer life for "weathering" steels, he said.

Keane invited the audience to attend the next SSPC Annual Meeting to be Dec. 5-9, in Cocoa Beach, Fla. The meeting will be co-sponsored by the Federation, the Painting and Decorating Contractors Association, and the National Association of Corrosion Engineers. There also will be a tie-in with NASA and the Florida Department of Transportation. There will be a seminar on the painting of public structures and a large number of product committee sessions.

In closing, Keane described the SSPC's plans for the future, which include a broadening of services, more performance-oriented voluntary consensus specifications, more work on public structure painting and on maintenance of coatings, a membership drive, and a big push on publications.

A question and answer period followed:

Q—Which of all the coatings available would give the least cost per square foot over time?

A—That depends on the environment. But in a severe environment, the most cost-effective coating would be a high-performance one. The Sewickly Bridge over the Ohio river near Pittsburgh is like a demonstration for this idea. It has a semi-inorganic zinc-rich primer, an epoxy intermediate coating, and a polyurethane topcoat. It is an expensive coating combination, yet should be the cheapest in terms of cost per year. A milder environment might demand less surface preparation and three or four coats of an alkyl paint. High labor costs

In the mid-sixties it was determined that paint containing lead can be of great danger to children either because they ingest the flakes or else because they actually chew on the paint which has a sweet taste. Thus, the permissible lead content in decorative paints has gradually been lowered.

There are three solutions to the problem of surfaces coated with lead-containing paint.

One is to cover the surface with barrier materials such as wallboard, plywood, or vinyl fabric. Also, a thick layer of a cementitious paint or a textured paint can be used. This solution is satisfactory for walls but not for painted interior woodwork.

A second solution is paint removal, but this too can present problems if dry sanding or abrasion releases lead paint dust into the atmosphere. Thus, the paint must be stripped chemically, but hazards are associated with the use of solvents that give off volatile or toxic fumes.

A third solution, of course, is to ban lead so that coatings applied do not contain it. This has effectively been done in the United States except for lead primers.

Numerous studies point to the fact that a problem exists. The increase in the lead content of Greenland snow is a case in point. The lead content of Greenland snow in 1750 has been determined by dust deposited within the ice layer of northern Greenland, which has remained undisturbed for thousands of years. Thus, the snow deposited at the beginning of the Industrial Revolution, i.e., about 1750, contains 0.011 parts per billion of lead, some 25 times greater than the natural level. The lead content, however, of Greenland snow tripled during the 65-year period from 1750 to 1815 and then doubled from 1815 to 1933. Since then, the lead concentration rose at an even faster rate to well over 500 times the natural level. The increase prior to 1940 is attributed to coal burning and lead smelting, while combustion of alkyl lead derivatives in automobile fuels are said to account for the rapid rise since 1940.

The problem of lead contamination is not new. The Romans used lead to make pipes

for carrying water. Indeed, the word plumbum comes from the Latin word plumbum, which means lead. The Romans also made their wine kegs of lead. And there are some who contribute the decline and fall of the Roman Empire to rulers made mad and irrational by poisoning from the lead they ingested from their wine and water.

Lead was widely used for pipes until the 20th century when it was replaced by other cheaper and more readily available metals primarily, of course, iron. But the problem of contamination by lead pipes was minor compared to the problem of lead from antiknock additives.

The Greenland snow data have been criticized for a number of reasons, one of which was that the surface snow layer has been subjected to local contamination. More conclusive evidence (*Chemistry International*, No. 4 (1981) p. 4) was found in the lead content of bodies of Tasmanian aborigines as compared to the lead content in present-day humans. These aborigines had already disappeared by the time worldwide industrialization had set in. Also, the bones were found to be in an excellent state of preservation and were mixed with sea shells, which created an alkaline environment that prevented the leaching of heavy metals. The bones of modern man contain at least 100 times more lead than the bones of the aborigines. The actual levels reported in the United States and England today are of the order of 17 to 30 parts per million.

Thus, there is little question but that environmental lead can come to rest, at least in part, within the human body. This appears not to be a problem unless, of course, levels become sufficiently high to cause lead poisoning. Even so, it is disconcerting to know that we walk around with contaminants in our bodies such as lead and DDT. Since modern men and women live as much as five times as long as their prehistoric progenitors, we might conclude that lead and DDT in the body serve a useful purpose. Conventional wisdom, however, dictates against this, and this accounts for the heroic effort that has been made to remove lead from the environment.

An excellent discussion of environmental lead, only a small portion of which probably comes from paint, is contained in an article in *Chemical & Engineering News* by Ember (June 23 (1980) p. 28). The article describes how regulation has grown up and some of the controversy associated with these regulations. A serious controversy has arisen as to how disease-producing is lead in paint. One study shows that if lead were removed from gasoline, most children would benefit, whereas only a few would benefit if the lead paint problem were solved. There appears to be little question but that lead paint is a serious problem for children living in the so-called poor, inner-city lead belts. One estimate indicates that 600,000 children in the United States have dangerous levels of lead in their blood.

Beyond that, however, the deleterious effect of lead-based paint on the population is questionable. The article should be read by anyone who is trying to arrive at an opinion about the seriousness of lead contamination and, perhaps more important, the source of this contamination.

A study covering 35 years of experience on the physiology of lead in humans is titled "Oral and Inhalation Lead Exposures in Human Subjects" and has been published by the Lead Industries Association (292 Madison Ave., New York, N.Y. 10017).

Exposure to lead

Lead pollution in the Birmingham area is the subject of a similar investigation (Dept. of the Environment, Pollution Paper No. 14, HMSO (1978)). The study shows that the opening of a new interchange that caused traffic to increase in a given area did not increase the lead concentration in the air nor were blood lead concentrations of school children or adults in the area abnormally high. There was, however, a relatively high proportion of preschool children with high blood lead levels.

Campbell and Baird (*British Journal of Industrial Medicine*, 34, 4 (1977) p. 298) reported on the development of lead poisoning in workmen who used acetylene torches to cut metal beams coated with many layers

of paint. The paint was subsequently shown to contain as much as 20 percent lead and exposure to it created serious problems.

The lung cancer hazard associated with the manufacture of zinc and lead chromates has been studied by Davies (*British Ink Maker*, May (1978) p. 117). It was found there was no excess of lung cancer among workers in the factory that manufactured lead chromate pigments only. In the factories that manufactured both lead and zinc chromates, however, there was indication of a small, but significant, lung cancer hazard. An article by Christoph (*Review Abstracts*, 13, 1 (1977) Abstract 74) describes the sources of lead in humans, mentioning of course the ingestion of lead pigmented paints. The effect of the lead and how to monitor it are described.

Preventative measures

Several years ago (*Plastics World*, August (1977) p. 9) Detroit car manufacturers indicated they would stop using lead chromate-containing primers. Chromatic pigments are the most widely used inorganic pigments in the United States after titanium dioxide. Obviously, one way to eliminate heavy metal toxicity is to stop using the pigments that contain them.

A booklet by Chapman and Kowalski (U.S. Government Printing Office, Washington, D.C. 20402) describes some of the costs associated with lead paint abatement.

Niemann (*Industrie-Lackier-Betrieb*, 46, 11 (1978) p. 399) points out red lead does not pose a health hazard if the paint is applied manually. The danger comes from the inhalation of vapors during spraying. The article describes the German health regulations related to the use of lead-based paints.

One proposal for detoxifying lead paint on walls is to coat the surfaces with zinc sulfide (*CHENATECH*, February (1979) p. 84). The lead salts are converted to insoluble non-toxic lead sulfide.

The detoxification of lead paint is also the subject of U.S. patent 4,112,191 (1978).

Review articles

A review article on occupational exposure

Basketball surface coating

An acrylic outdoor basketball surface that applies over asphalt and creates a smooth, non-slip surface was introduced by Tru-Flex Recreational Coatings. The Tru-Flex Outdoor Basketball Surface is unaffected by heat, cold, or UV exposure and is non-flammable. Tru-Flex Recreational Coatings, Everett, Mass.

Acrylic sealer

UPC Industries introduced Acrylic Sealer No. 100, a clear, non-yellowing sealer for terrazzo, slate, tile, magnesite, flagstone, marble, exposed aggregate, concrete, masonry, and other stone surfaces. The product penetrates and seals pores, increasing density, providing protection from water, oil, air pollutants, grease, dirt, and acids. The sealer complies with air pollution control regulations and possesses a flash point over 100°F. It dries to touch in 30 minutes. UPC Industries, Santa Monica, Calif.

Pool paint

A chemical resistant swimming pool paint was introduced by Cambridge Coatings, Inc. The paint is an alkali and chemical resistant coating based on chlorinated rubber and inert plasticizers. The paint is resistant to swimming pool chemicals and contains no swappable material. It requires 30 minutes to set and 3 hours to dry hard. Twenty-four hours are required between coats. The paint is available in aquamarine, light blue, black and white. It also can be tinted to pastel shades using universal colorants. The paint is applied using a sprayer, brush or roller and is thinnable with xylene or rubber base thinner. Cambridge Coatings, Inc., Cleveland.

Greenhouse coatings

Sierdex, a plastic membrane coating marketed by Penaggon Plastics, Inc., is designed to reduce heat loss and maintenance in greenhouses. A thick, waterproof skin that adheres to glass, wood, putty and old paint, the coating is for the maintenance of glazing bars, both inside and out. Because it seals cracks and crevices, it can reduce heat loss. The coating's elastic skin keeps water out while it "breathes" out any excess moisture trapped in the surface beneath. It contains non-toxic fungicides. Another product, Isoclad is a seamless membrane applied by brush or spray. It eliminates corrosion on metal surfaces and is for coating table bases, irrigation pipes, etc., the company says. Penaggon Plastics, Inc., West Palm Beach, Fla.

High-solids polyurethane

A VOC-complying two-component polyurethane high-solids finish is available through Chemical Coatings Division of The Sherwin-Williams Company. Designated Polane® H, it was originally developed for the business machine industry. The urethane can be applied directly (without the use of a primer) to structural foam such as polyphenylene oxide, polycarbonate, polystyrene and ABS. It also can be applied directly to SMC, fiberglass and most injection molded over pretreated aluminum and steel or primed metal products such as machine tool equipment. Its characteristics include 3 lbs./gal. (360 g/l) or less VOC. The coating will air dry or it can be force dried for 30 minutes at 140°F. to 180°F., depending on the heat sensitivity of the substrate. Polane H has a shelf life of 12 months. It has a pot life of 30-45 minutes and requires two components equipment for production-type conventional spray application. The Sherwin-Williams Co., Chicago.

to lead including such operations as the wetting or burning of lead-painted substrates is contained in an article by Nelson [Kettering Abstracts, 13, 4 (1977) Abstract 1018]. An article by Duligal [Proc. of 6th National Symposium on Non-Conventional Coatings, Oil & Colour Chemists' Association of South Africa, Port Elizabeth (1976)] describes how lead enters the body from paint and discusses the types of toxicity that result. Lead-containing paints fall into three main groups including: interior linings for food containers, water pipelines, wine vats, coatings for children's toys, etc.; use in food factories; and general use in engineering operations where the paint may be removed by burning or welding. Limits of heavy metals including lead for each category are proposed.

Some of the problems of lead in paints have been reviewed by Malavolti [Rivista del Colore, 14, 153 (1981) p. 8]. An article by Ashford et al. [World Surface Coatings Abstracts, (1979) Abstract 4861] describes the cost to industries that must comply particularly since the regulation establishes a maximum blood level of 60 micrograms per 100 grams. This means a number of employees would have to be removed from their jobs at considerable cost to both them and the companies.

Analytical considerations

Regulations regarding lead content are of little value unless analytical procedures exist for monitoring. Thus, there are numerous articles in the literature describing analytical methods for lead determination. The use of x-ray fluorescence for determining the quantity of lead in tin coatings used on brass and copper has been described by Nagai et al. [Research and Industry, 24, September (1979) p. 171]. The tin coating is removed from a brass or copper vessel, dissolved in dilute nitric acid, and the tin and lead content in the solution are determined by x-ray fluorescence.

The determination of low concentrations of lead, cadmium, and cobalt in paint by atomic absorption spectroscopy is the basis for a standard method published by the

American National Standards Institute and the American Society for Testing and Materials (1978 Annual Book of ASTM Standards, Part 27, p. 651). The method allows for the determination of lead in dried paint films at levels of 0.01 to 5 percent, of cadmium at levels of 50 to 150 ppm, and of cobalt at levels of 50 to 2000 ppm. The method is not applicable if the samples contain antimony pigments.

The use of atomic absorption for the determination of lead in paints has been specified by the General Services Administration for paints used in government contract work. All of these paints must have no more than 0.06 percent lead, and originally the test involved x-ray fluorescence spectrometry. The high cost of such equipment in part motivated the change to atomic absorption techniques.

X-ray fluorescence analysis of paints for lead has been described by Cramp and Burr [Proc. of 4th Joint Conference on Fencing of Environmental Pollutants, New Orleans (1977) p. 354] who emphasize in particular portable analyzers. They also describe reference materials containing 0.6, 1.5, and 3.0 milligrams per square centimeter of lead to be used for calibrating and assessing the performance of the instruments.

The use of differential-pulse anodic stripping voltammetry for determining lead in paints has been described by Lai and Fung [Analytic, 103, 1233 (1978) p. 1244].

A thin layer chromatography method for analyzing traces of lead in oil has been published by Turina and Turina [Chromatographia, 10, 2 (1977) p. 97]. The technique devised is said to be reliable for samples containing 0.002 to 1/10th ppm of lead based on a 25 millimeter sample.

Some of the problems involved in monitoring work places for lead, particularly where lead chromate pigmented paints are sprayed, have been discussed by Kaplan [Kettering Abstracts, 13, 4 (1977) Abstract 1019].