Bull. Environ. Contam. Toxicol. (2002) 69:617–623

DOI: 10.1007/s00128-002-0105-7

Bulletin of Environmental Contamination and Toxicology

Isotopic Characterization of Six Major Brands of White Basic Lead Carbonate Paint Pigments

M. B. Rabinowitz,[1] G. S. Hall[2]

[1] Marine Biological Laboratory, 7 MBL Street, Woods Hole, MA 02543, USA
[2] Chemistry Department, Rutgers University, Piscataway, NJ 08854, USA

Received: 2 May 2002/Accepted: 10 August 2002

Much of contemporary American environmental lead contamination and human exposure is the result of the manufacture and use of lead-based paint pigments many decades ago. The ability to identify the manufacturer of a particular pigment would encourage efforts to make the responsible polluter pay for damages and remediation (Kaiser 1998). To this purpose, we sought to isotopically analyze samples of the different brands of basic white lead carbonate, the principle pigment in lead-based paint. From these samples, together with historical records of the sources of lead used by the various manufacturers of basic white lead, a comprehensive picture of the isotopic patterns among the brands would emerge, which might be useful for brand identification.

The commercial term "white lead" generally referred only to forms of basic lead carbonate ($2Pb(OH)_2 \cdot PbCO_3$). It was typically manufactured by the corrosion of highly refined lead metal by the so-called "Old Dutch" process. Its major uses were as a paint pigment and in ceramic glazes. In the twentieth century white lead was also used in rubber tires and electrical batteries. Overall, more than 95 percent of it was used in paint. The earliest mention of its manufacture date from 2400 years ago by the Greek Theophratus. The practice was revived and improved in Holland in the 1600's, hence the name "Old Dutch". In 1777 Samuel Wetherill of Philadelphia was the first to manufacture white lead in America, and by 1810, over three hundred tons were manufactured annually. In 1887 more than twenty plants nationwide were using the Old Dutch process, when the largest three formed the "White Lead Trust" and began to acquire their competitors. In 1890, it reorganized into National Lead (NL), which became the largest producer. By 1910 NL had 30 factories with a 90 kilotons (kt) annual combined capacity, marketed under the Dutch Boy brand. Carter Lead, controlled by NL since 1906 but not merged until1930, had two factories producing 20 kt/yr, and the ten other independent companies produced 35 kt/yr combined. Eagle Picher (EP) was the largest of these with 12 kt/yr (Bendelari 1929).

Between 1900 and 1940 about three million tons of white lead were produced, with peak years from 1925 to 1929, at about 150 kt/yr, accounting for nearly a quarter of lead production (Weaver 1989). The 1930's and 40's saw continued declines in the industry, and between 1940 and 1960, only one million tons were

Correspondence to: M. Rabinowitz

made (Larson and Calbeck 1949). In 1934 NL bought Wetherill, but by 1940, NL had only 7 plants, and only four other independents survived: EP, Sherwin Williams (SW), Anaconda and Glidden. In 1946 EP took over the Anaconda East Chicago factory, which first opened in 1919, closing it in 1951. In 1947 EP closed its venerable Cincinnati plant, dating from1843 and for many years the world's largest, as it was becoming a more diversified industrial company (Anon. 1947). In 1951 EP ceased production of lead carbonate but continued sales of it until 1973. Between 1953 and 1972 Glidden and NL supplied white lead to EP. In 1953 SW closed its Pullman IL corroding works, opened in 1919, and NL closed its largest plant, Atlantic Lead in Brooklyn, built in 1908. The Glidden works in Scranton PA, bought in 1926, closed in 1958. As late as 1968 NL was still making white lead in Perth Amboy, Oakland, Chicago and Philadelphia.

Although basic lead carbonate was the primary compound used to make lead-based paint, other lead based white pigments were developed, but they were of minor importance (Madson 1948). Over the years the term "white lead" was also used to refer to these other white lead pigments. One was lead sulfate ($2PbSO_4 \cdot PbO$), first made in 1876 in Joplin MO by collecting the fumes of roasting ores. This required very pure ores and never exceeded 18kt/yr. Leaded zinc oxide was another alternative ($2Pb_2SO_4.PbO+ZnO$). It was first made in 1877 from roasting complex Pb-Zn ores, but from 1930 it was also made by mixing lead sulfate with zinc oxide. SW made it in Coffeyville KS, and EP made it in Galena KS and Hillsboro IL (Anon. 1947). Production peaked in the 1940's but never exceeded 50kt/yr. Basic lead silicate ($PbO \cdot PbSiO_2$) was first marketed in 1940 by EP as a paint pigment, and later by NL. NL introduced lead titanate compounds in 1941. Additionally colored lead pigments including yellow and orange lead chromates and red lead oxides were widely used, but basic lead carbonate was the predominant lead pigment. Between 1926 and 1945 2,029 kt of basic lead carbonate were made but only 162 of lead sulfate and 720 of leaded zinc oxides were made (for example, Meyer and Mitchell 1938).

White lead left the pigment factory as a paste of 95% pigment powder and 5% linseed oil (Heckel 1934). This paste was the main ingredient used to make paint, either blended and canned in a paint factory or thinned and mixed at the work site by the professional painter. In 1914 nationwide, 585 businesses were engaged in the manufacture of lead–based paints and lead pigments, which increased to over one thousand by 1929. Only a few of the largest paint companies made their own white pigments. Most paint companies simply bought the pigments to make their paints (Schulenberg 1987).

All of the pigment makers also marketed their own line of paint, even if only for a short time. In order to get samples representing known pigment makers, we only examined samples of their own brands of pastes and paints, ignoring the many smaller paint companies who did not make their own pigments.

Our goal was to determine if these pigment brands could be identified isotopically. White lead was made from refined lead metal ingots, and we have shown some isotopic variation among brands of refined lead, reflecting their diverse geological origins (Rabinowitz 2002). The lead ores fall roughly into three groups of lead 206/204 ratios: the low, narrow Idaho values below 17; the other Western mountain states and Mexico with a wider range of 17.3 to 18.9; and the much higher and wider range of values from the Mississippi Valley districts, above 19. Generally, the brands of refined lead reflect their proximate source ores. Thus brands of white lead may also show systematic variability, depending on which brands of lead metal were actually used to make the white lead.

The largest lead refiner, American Smelting and Refining (ASARCO) produced 455 kt in 1925 of corroding grade refined lead. ASARCO had refineries in Missouri, Nebraska, New Jersey, and California, but they did not make white lead. Neither did three other major refined lead producers: Bunker Hill and Sullivan of Idaho (35 kt in 1930), St Joseph of Missouri (67 kt in 1930), and US Metal Refining of Utah (72 kt in 1928). International Smelting and Refining (ISR), which owned Anaconda, made 53 kt in 1930 of refined lead metal, while its white lead plant made only 25 kt. So they too had refined lead to sell.

In contrast, SW, primarily a paint company, had some mining interests, but they were insufficient for the needs of its Chicago corroding works. In 1930's they made about 15% of the paint sold in the United States (Anon.1953). Glidden, also a paint maker, with a 5% market share in 1949, did not make refined lead (Anon. 1945). NL and EP mined, smelted, and sold refined lead, but their needs also required them to purchase refined lead on the open market. NL accounted for over 60% of the white lead sold between 1936 and 1942, and EP was the second largest at 15 to 20%, although they refined only 10 kt of lead in 1930. MacGregor, opened in 1945 in Chicago, was owned by Armstrong Paint, and sold the Scotch Laddie brand. It was relatively small and also required refined lead.

All these pigment makers bought refined lead. So, since there was some variability among the brands of ingots, there also might be variability among the white lead brands, depending on who actually bought which brands of refined lead metal. For example, if one white lead company tended to have used more Idaho metal, it would differ from one that used only Missouri lead. We examined available samples of pastes and paints to explore any systematic patterns among the brands of white lead.

MATERIALS AND METHODS

We (MR) collected as many cans of lead paint as possible by attending 15 community sponsored household hazardous waste collection events in Massachusetts between 1997 and 2001. Cans were retrieved if their label was

clearly legible and stated any form of lead, if the can did not leak, and if the can did not appear to have been reused. Twenty-four cans were purchased on an internet auction site and a few more were purchased in response to newspaper advertisements from outside of New England. Eight were received from public health workers and lawyers aware of our work. A few were obtained in searches of corporate records. The brand name of the paint and the ingredients, especially the type and amount of lead, if listed, were recorded. Often the can was full of paste or paint. A total of 284 cans were collected, representing 75 different brands of paint. Among the most popular were 60 Dutch Boy (NL), 22 Carmote, 13 Touraine, and 13 SW. One hundred and four of the cans listed lead carbonate as the only pigment, 20 had lead sulfate, 35 had lead silicate, and 10 more had mixtures of these. Ten had leaded zinc oxide, 24 had various lead oxides and chromates, and 49 had some unspecified lead, likely a lead drier. In order to get samples of known white lead pigment makers we only consider the 42 cans of paste and paint made by those pigment makers, which contained only lead carbonate as the pigment. We had sought to obtain as many samples as possible, but since the peak of the American white lead industry in the late 1920's and its decline, the passage of time has made getting examples of every desirable sample impossible. The samples that were collected over-represent the more recently made paints. About half, 126, had warning labels to protect children, which were not generally required until after 1959.

For isotopic analysis, typically 1-ml of liquid paint was mixed with 2ml of concentrated ultra high purity nitric in an acid washed, polypropylene tube and warmed for 24-hours (by GH). A 10-uL aliquot was diluted with 10-mL of water containing 80 ppb Tl as an internal standard. The resulting solution was analyzed on a VG PQ2+ Turbo inductively coupled plasma mass spectrometer, operated in scan mode, covering the mass/charge peaks from 200-212, measuring peak areas. Each sample was measured with three scans. Every 12th sample the NIST-981 certified lead standard was analyzed. Mass fractionation corrections were applied.

All three isotope ratios were measured and reported, but often only the 206/204 ratio is shown, because the three ratios all covary so strongly. Quality assurance was addressed by analyzing NIST standard 981 with each batch of samples. Seven assays gave a mean value of 16.95 (std dev 0.07), indistinguishable from the certified value of 16.93. The measured 206/207 values were 1.093 (0.001) with a certified value of 1.093. So, the analytical uncertainties are more than 100 times smaller than the range of values encountered here. Statistical analyses were performed (by MR) with NCSS97 (Kaysville UT).

Historical documentation of the flow of lead from mine to paint was established by systematic searches of many sources (by MR). Annual Moody's Manuals of Investments, US Bureau of Mines Minerals Yearbooks, particularly the chapters on lead and lead and zinc pigments, and corporate records of EP and of Bunker

Hill, including smelter logs, bills of lading, and correspondences were thoroughly reviewed. The following journals were also completely searched: "Mining and Metallurgy", "Mining Congress Journal", "Engineering and Mining Journal", "Paint, Oil and Chemical Review", "Oil, Paint, and Drug Reporter", "Painter and Decorator", "American Painter", and "Carter Times". A total of 560 articles, 164 Bureau of Mines publications, and 28 books were abstracted.

RESULTS AND DISCUSSION

The data from the 42 cans of basic white lead carbonate, representing six pigment makers, are shown in Figure 1. The 22 NL samples include a Wetherill (value 18.4) and two Carter samples (19.7 and 19.6), because they became NL brands. The Anaconda brand is considered separately, because when those samples were made, and for most of its life, it was owned by ISR, its sole supplier of lead, all smelted in Utah, even though EP briefly owned the factory.

The isotopic values for most of the brands show considerable variation, and the overall pattern shows considerable overlaps in the ranges of the brands. This is because different brands of refined lead metal were used to make the white lead, depending on market conditions, and these sources could change month to month or year to year, even at one plant, as indicated by bills of lading and summary tables prepared by management. No director of any of the lead refiners served on a board of directors of any of the white lead companies. Thus, that was not a factor in brand preferences. In the case of NL, which made Dutch Boy at various factories across the country, the variability was considerable, as the factories were each located near different lead refineries. Generally, the values are consistent with the historical record, including the multiple sources of lead metal used by most white lead factories.

To search for any systematic differences among the brands that would be useful for identification, one-way analysis of variance was applied. With six brands the 206/204 ratio gives an F ratio of 2.95 (42 df) $p=0.025$, and the power to reject the hypothesis that the means of the brands are the same is 0.79 (alpha =.05). So, the brands are not all the same. The 206/207 or 206/208 ratios confirm this (F ratios 11.0 and 12.2, $p=.05$ and .03). Using Duncan's multiple comparisons tests to identify the pairs of brands that differ; only the most extreme two brands, MacGregor and SW, differed significantly ($p<.05$).

The statistical significance depends on the number of samples as well as any differences between the brands. Only a few samples of MacGregor or Anaconda were available, so most statistical tests were inappropriate. To compare all the other groups Aspin-Welch t-tests were performed for each of the 6 pairs of brands. Comparing SW versus NL gave $t=2.7$ (2-tailed $p= 0.02$), versus Glidden $t=3.3$

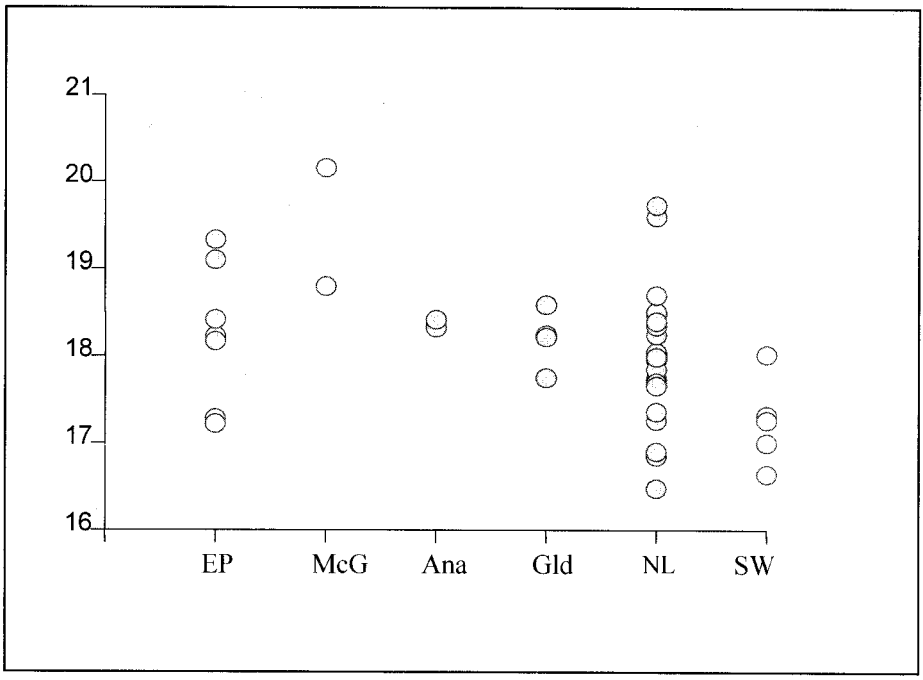

Figure 1. Pb 206/204 ratios of six brands of white lead carbonate: Eagle Picher, MacGregor, Anaconda, Glidden, National Lead, and Sherwin Williams.

(p=.01), and versus EP t=2.6 (p=.03). No other pairs of brands were statistically different.

Lead based paints were made simply by thinning the white lead paste with linseed oil and adding turpentine and a drier, usually a metallic salt of lead, manganese, or cobalt. Tints might be added, perhaps yellow or orange lead chromate made from other grades of lead at another plant, such as Glidden's Hammond IN factory. So, the isotopic signature of a single layer of lead paint would be dominated by the white lead, but it would also reflect lead from these other components. Realistically, multiple layers of dried paint are often encountered on walls and in dust.

Only a limited number of samples were available upon which to reconstruct the isotopic patterns of each brand. Those samples were collected primarily in Massachusetts, and they over-represented paints made in the later years of the industry. These restrictions on available samples may be have biased these results to some unknown extent compared to a nationwide sampling. From these limited results, the isotopic composition alone could not distinguish each brand uniquely. Thus, for a given unknown sample, brands likely could not be ruled in or out as a match, except those with the most extreme values. Despite the passage of many

decades, sufficient samples still exist to demonstrate variations among and within these brands, consistent with the historical record, reflecting their multiple sources lead.

Acknowledgments. The Eagle Picher Personal Injury Settlement Trust provided funding and access to corporate records. Lary Ball of the Woods Hole Oceanographic Institute performed additional mass spectrometry. The Special Collections Library of the University of Idaho and the East Chicago IN Public Library were exceptionally helpful in searching corporate records.

REFERENCES

Anonymous (1945) House that Joyce built. Fortune 32 : 97-171

Anonymous (1947) Eagle-Picher: This lead and zinc house presents a case study in industrial transition. Fortune 36:79-192

Anonymous (1953) 18,500,000 gallons of paint. Fortune 12: 70-83

Bendelari AE (1929) Eagle-Picher-a large factor in the lead industry. Mining Congress J 15: 857-859

Heckel GB (1934) A Century of progress in the paint industry. J Chem Educ 11: 487-493

Kaiser J (1998) Hunt proposed to find lead sources. Science 279: 1293

Larson LP, Calbeck JH (1949) Comparison of pre-and post- war white outside house paints. Paint Oil Chem Rev 112: 25-50

Madson WH (1948) White hiding pigments. In: Von Fischer W (ed) Paint and Varnish Technology. Reinhold, New York, p 63-82

Meyer HM, Mitchell AW (1938) Lead and zinc pigments and salts. In Hughes HH (ed) Minerals Yearbook. US Bur Mines, Wash DC, p 155-166

Rabinowitz MB (2002) Isotopic characterization of various brands of corroding grade refined lead metal. Bull Environ Contamin Toxicol (in press)

Schulenberg F (1987) Cleveland: Part II: Sherwin, Williams and Fenn. American Paint Coatings J 71: 41-49

Weaver JC (1989) A white paper on white lead. J Coatings Technol 61:147-151