

Use of Metal Compound Additives In the U.S. Vinyl Processing Industry

Final Report
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1.1 Introduction

There has been considerable interest recently in the presence of heavy metals in consumer products made of plastics and other materials. Interest in lead in particular has increased with reports of elevated levels of the metal in some imported children's products, including products made of vinyl. For the most part, the U. S. Consumer Product Safety Commission (CPSC) has concluded, based on testing, that imported vinyl products have not posed a health hazard. U.S. regulations limit exposure to lead, and some states have moved beyond federal regulations to establish content limits. Lead is also listed as a persistent, bioaccumulative toxin (PBT) in international treaties, which aim to reduce or eliminate its use.

This paper is intended to summarize the major markets for vinyl products, and to identify the possible uses of lead and other metal compounds in those products. In general, the major use for metal-containing compounds is to heat stabilize vinyl, but these compounds are also used for other purposes, all of which are described further below.

The information below shows that use of lead in the U.S. vinyl market is limited except in wire and cable applications, where it has specific, critical performance properties. Estimates of lead consumption as a heat stabilizer in vinyl applications in the U.S. range from 7,000-11,000 metric tons or about 0.5-0.8 % of the total U.S. consumption of 1,460,000 metric tons of lead in 2005. According to the U.S. Geological Report, consumption of lead in pigments for paint, ceramic, and glass was 14,100 metric tons in 2005. No estimate is made of the percentage of lead for pigments used by the vinyl industry, but the use is expected to be declining consistent with the overall decline in use of these pigments.

We provide information on the regulations and industry programs that limit the use of lead in vinyl. In addition, we discuss some instances where lead has been found in some consumer products, and the actions taken to deal with these issues.

Information in this report is based on industry expert opinion, publicly available literature and in some cases confidential survey information on uses of materials in vinyl products.

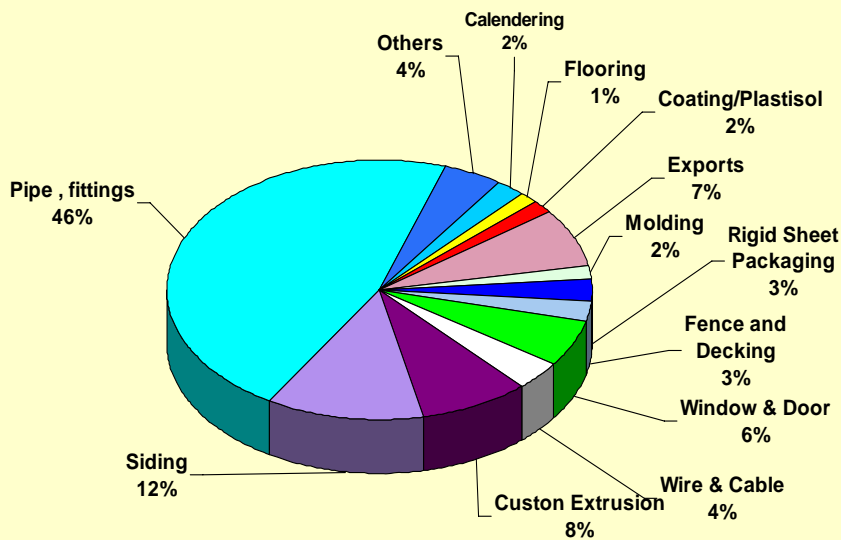
1.2 Manufacture and Uses of Vinyl

Vinyl is the third-largest volume plastic produced in North America (nearly 15 billion pounds in 2006) and among the top two or three plastics in global volume. Pure polyvinyl chloride polymer (PVC or vinyl) is 57 % chlorine and 43 % ethylene and exists as an inert white powder also known as resin. PVC resin has few uses on its own but becomes enormously versatile when turned into vinyl compound through the addition of ingredients such as stabilizers, plasticizers, lubricants, colorants, and others. Depending

on the additives in the formulation, vinyl compound can be molded, extruded, calendered or shaped in other ways into an almost infinite range of products. It can be rigid (e.g., pipe, siding, window frames, fencing), flexible (e.g., shower curtains, beach balls, upholstery, wire insulation, flooring), liquid (e.g., coatings for tools, racks), clear (e.g., blood bags, medical tubing, blister packaging), colorful (e.g., toys, inflatables, signage), and thin yet tough (as in shrink-wrap or tamper-resistant packaging)

Metals such as tin, calcium, barium, zinc, and, to a lesser extent, lead and cadmium are added to vinyl compound either for stabilization or coloring. Stabilizers lubricate and control the integrity of the material in the manufacturing process. Without them, vinyl during product manufacturing could become discolored, release hydrogen chloride or become difficult to process. In finished products, stabilizers keep vinyl from breaking down in sunlight or other weather conditions, and they help products last for many decades.

PVC Is Used in Many Applications



Total = >15 Billion Lbs. annually

U.S. and Canada, resin content. Flooring includes calendered and coated. Source: ACC Plastics Industry Producers' Statistics Group

1.3 Metal Compounds used as Pigments

Vinyl applications often require the use of colorants for aesthetic reasons, brand recognition, and improvement of ultraviolet (UV) stability, weathering, or electrical conductivity. Colorants are either pigments or dyes. While pigments can be organic or inorganic, dyes are only organic (i.e., they contain little, if any, metal). Pigments are

insoluble substances that can be incorporated into a material like plastic to selectively absorb or scatter light. Depending on the specific pigment used, different visual effects are produced. Inorganic pigments may be obtained from a variety of naturally occurring or synthetically produced mineral sources. The organic pigments are carbon compounds derived from petroleum sources. Thousands of different pigments are used in paints and stains, printing inks, plastics, synthetic textiles, paper, cosmetics, contact lenses, soaps and detergents, wax, modeling clay, chalks, crayons, artists' colors, concrete and masonry products, and ceramics. For example, there are over 240 different pigments for red alone. The main metal-based pigment categories used by vinyl processors are: titanium dioxide; metallic oxides and salts; metallic flake pigments; and phosphorescent pigments. Calcium carbonate, used in large amounts as a filler in many applications, including siding and pipe, also contributes a white color and opacity to products.

During the early part of the twentieth century, the pigments industry relied heavily on lead-based ingredients for their durability and brightness, and to provide a pearlescent effect. One ingredient, lead carbonate (white lead), was known to be toxic as early as the late nineteenth century, and by the mid-1960s paint manufacturers were required to begin phasing out its use. Interest has grown in replacing use of heavy metals such as these in colorants and in other vinyl additives. At the same time, several colorants containing heavy metals are classified as high-performance products (i.e., they provide excellent heat stability and other properties), making it a challenge to find substitutes with equal performance. The substitutes that have been used to date are organic colorants that cost more and in some cases have inferior performance. Nevertheless, according to several industry sources, lead and cadmium colorants have been declining in use.

1.4 Metal Compounds used as Heat Stabilizers

Few applications allow vinyl resin to be fabricated into products without the addition of a heat stabilizer. The purpose of heat (as well as other) stabilizers is to control degradation during processing as well as during use of the product. Stabilizers are incorporated in products that are exposed to sunlight and other weathering conditions. Stabilizers retard the breakdown of polymers under these conditions. Heat stabilizers account for most of the metals used in vinyl products. They are used in both rigid and flexible products, although the types of stabilizers used vary between the two categories. As the chart below shows, lead stabilizers are used primarily in wire cable insulation and jacketing.

Vinyl Processing Category	Estimated Resin Used 2006	Primary Metal Heat Stabilizer	Typical metal wt% of PVC resin used
	Million Pounds		
RIGID VINYL			
Pipe, fittings, Injection molding	6900	Tin	0.1
Siding, Soffits, Eaves	1784	Tin	0.2
Windows,	850	Tin	0.3
Other extrusions	1635	Tin	0.3
Rigid sheet	395	Tin	0.2
FLEXIBLE VINYL			
Wire and cable	539	Lead	2.8
Flooring	190	Barium Zinc	0.2
Flexible Sheet	344	Barium Zinc	0.2
Miscellaneous Plastics /coatings	246	Zinc	0.3
Blown film	200	Calcium/Zinc	0.1

RIGID VINYL

In the United States, tin-based heat stabilizers are the most widely used for rigid vinyl products. They provide excellent short and long-term stability, UV protection, and a high degree of clarity in transparent products. Their solubility parameters are similar to the parameters of the vinyl polymer, which makes them efficient to use. Tin stabilizers are available from a family of n-butyl, n-octyl, methyl, and acrylic ester group compounds. Butyltin and methyltin are the most commonly used. Depending on the product, the amount of tin used to stabilize vinyl can vary from 0.06 % for pipe and fittings and to 0.3 % of resin for windows and other extrusion profiles

Some rigid food-contact applications of vinyl use calcium/zinc stabilizers. See more on mixed-metal stabilizers below.

FLEXIBLE VINYL

Mixed Metals Stabilizers

Flexible vinyl applications tend to rely more on mixed-metal heat stabilizers. When two or more metals are combined in a heat stabilizer, the properties of the metals can complement each other, with high-performance results. Mixed-metal stabilizers usually

contain barium, cadmium and/or zinc. They generally are not used in rigid applications as they act as plasticizers, imparting physical properties that are not desired in rigid products.

In the United States, barium/zinc based stabilizers have the largest usage of all mixed-metal stabilizers. Barium/zinc/cadmium systems provide high thermal stability and good light stability, and are compatible with transparent compounds. The metals are essentially metallic soaps (e.g., octoates, laurates and stearates). Calcium/zinc systems are mainly used in food and medical applications because of their non-toxic properties.

The calendering process is used to produce flexible sheets used in automotive applications, upholstery, shower curtains, etc. In the United States, calendered flexible-filled and pigmented applications normally use barium-zinc stabilizers, with the total amount of metal varying significantly, from about 0.3-1.5 % of resin. Flexible vinyl products that require significant color retention in white and light colors can use high-efficiency powders of barium, zinc and cadmium-based stabilizers at 0.3-1.2 % of resin.

As noted above, use of cadmium is declining. It is being replaced by barium-zinc liquids with phosphite content, at relatively high loadings. Blown and stretch-extruded film used for meat (especially poultry) wrapping, consumer wraps, groceries, and other packaging applications typically contains calcium or zinc stabilizers.

Vinyl plastisols are liquid formulations for dip-molding and spraying. Products include gloves, wallpaper and other wall coverings, automobile parts coatings, artificial leather, anti-corrosive sealants, wire racks, and other protective coatings. Tank and industrial parts can be coated with vinyl plastisols to provide resistance for the chemicals and plating industries. Flexible sheet can also be made using vinyl solutions that are formed through curing. In solution casting, resin and additives are dissolved in solvents. The solvent is evaporated off the process as the film or sheet forms on a moving belt. Casting can also be used as a means of making high quality, tightly controlled, uniformly gauged film and sheet.

Plastisol stabilization usually requires a reduced level (0.1-2 %) of barium and zinc stabilizers. As dispersion resins used in plastisol typically respond well to stabilization with zinc salts, many stabilizer grades are available with zinc levels increased at the expense of barium or cadmium.

Lead Stabilizers

Lead-based heat stabilizers are primarily used in applications where superior electrical properties and/or outstanding long-term heat stability are required. Lead stabilizers offer a number of advantages:

- excellent electrical properties,
- long-lasting stability,
- slow breakdown, preventing catastrophic polymer failure,

- resistance to weathering and
- cost/performance ratio equal to or better than the alternatives.

Vinyl's superior dielectric and fire performance properties make it the material of choice for wire insulation in home construction and telecommunications. Use of lead stabilizers historically has been essential for producing quality vinyl wire and cable compounds, although non-lead alternatives have been introduced to the marketplace.

Without adequate stabilization, vinyl wire covering could be permeated by water and water vapor, particularly at elevated temperatures. If water-soluble ionizable materials are present, the useful electrical properties of the compound rapidly deteriorate, which can lead to power loss and failure. The chlorides of zinc, barium, cadmium, calcium, and tin are water-soluble. Lead chloride is insoluble and inert. If chlorides are present, they can be bound by the lead to form insoluble and inert lead chloride. As a result, the vast majority of vinyl wire and cable compounds use lead stabilizers.

Lead-based stabilizers include tribasic lead sulphate, dibasic lead phthalate, dibasic lead stearate and dibasic lead phosphate. Tribasic lead sulphate (TBLS) is a typical lead stabilizer for wire insulation, but others can also be used.

Although use of lead is limited to a small segment of the vinyl market, it accounts for a relatively high percentage of the total metals used to stabilize vinyl products.

The recycling of lead-stabilized cable scrap material can result in lead stabilizers being found in some non-cable products. One particular application is the use of recycled materials in the manufacture of garden hoses. Hoses made of vinyl can be manufactured to meet drinking water standards. These hoses normally are made with non-lead vinyl compounds. Or, they are manufactured using lead-stabilized vinyl with a non-lead inner liner to eliminate possible exposure to lead compounds. However, many hoses, including garden hoses, are not made to meet drinking water standards and are typically provided with a warning that they are not to be used for drinking water service.

1.5 Regulations Controlling use of Lead in Vinyl Products

Although lead stabilizers have specific benefits, mandates have limited their use in vinyl products made in the U.S. These mandates can also affect imports. Below is a list of applicable regulatory and voluntary requirements regarding lead in vinyl products.

Coalition of Northeast Governors (CONEG)

Nineteen U.S. states have "toxics in packaging" laws that prohibit the sale or distribution of packaging containing intentionally added cadmium, lead, mercury, and hexavalent chromium, and set limits on the incidental concentration of these materials. This model legislation was originally drafted by the Source Reduction Council of CONEG in 1989.

The purpose of these laws is to prevent the use of toxic heavy metals in packaging materials that enter landfills, waste incinerators, recycling streams, and ultimately, the environment.

Consumer Product Safety Commission (CPSC)

The CPSC bans “lead containing” surface paints and coatings above 600 part per million (ppm) in children’s toys and furniture. With respect to vinyl consumer products, the CSPC’s guidance to manufacturers is that they should eliminate the use of lead that is accessible in children’s products and evaluate products on a case-by-case risk assessment to determine if a product is a hazard. CSPC uses a trigger level for risk assessment of 600 ppm lead content. The risk assessment is based on a policy goal that young children should not chronically ingest more than 15 micrograms per day ($\mu\text{g}/\text{day}$) of lead from consumer products. The CPSC holds importers, manufacturers and retailers responsible for ensuring products are non-hazardous and enforces its policies through product recalls.

U.S. Food and Drug Administration (FDA)

When packaging or other materials are in contact with food, any migration from the material into the food potentially causes the migrating substance to become a food additive, subject to the premarket approval requirements of the federal Food, Drug, and Cosmetic Act (FD&C Act). All food additives are required to undergo FDA premarket approval in accordance with Section 409 of the FD&C Act. Neither lead nor any lead compound is authorized for use in food-contact material.

State of Illinois

Illinois’ Lead Poisoning Prevention Act, H.B. 4853, 94th Leg. Session. (Ill. 2006) (codified at 410 Ill. Comp. Stat. § 45/2-45/12.1) bans use of “lead bearing substances in dwellings, buildings, child care facilities and in or upon any items, including, but not limited to, clothing, accessories, jewelry, decorative objects, edible items, candy, food, dietary supplements, toys, furniture, or other articles used by or intended to be and chewable by children.” “Lead bearing substance means any item containing or coated with lead such that the lead content is more than six-hundredths of one percent (0.06 %) lead by total weight; or any dust on surfaces or in furniture or other nonpermanent elements of the dwelling; or any paint or other surface coating material containing more than five-tenths of one percent (0.5 %) lead by total weight (calculated as lead metal) in the total non-volatile content of liquid paint.”

California Environmental Protection Agency

Proposition 65 sets a No Significant Risk Level (NSRL) for lead as a carcinogen at 15 $\mu\text{g}/\text{day}$ (oral) and a Maximum Allowable Dose Level (MADL) for Chemicals Causing Reproductive Toxicity for lead at 0.5 $\mu\text{g}/\text{day}$. Vinyl products that have been the subject of Proposition 65 proceedings and settlements include cables (Proposition 65 settlement

with the Mateel Environmental Justice Foundation (“Mateel”) 2002), and garden hoses (2004).

1.6 Certification Programs and Industry Voluntary Initiatives to Eliminate Use of Lead in Vinyl Products

A number of product certification programs and voluntary initiatives have been launched to reduce and/or eliminate lead in products.

Certified PVC Pipe

The NSF International General Policy GP-60 for pipe carrying drinking water states: “There shall be no lead as an intentional ingredient in any material contacting food or drinking water, except brass meeting the definition of ‘lead free’ under the specific provisions of the Safe Drinking Water Act of the United States, as amended in 1986. In the absence of further regulatory guidance, the EPA Action Level of 15 ppb shall be used for purposes of establishing the maximum extraction levels for Products contacting food or drinking water.”

Vinyl Siding and House Cladding Products

The 2006 International Residential Code and the 2006 International Building Code require that all vinyl siding be certified and labeled by an approved quality control agency to show it conforms to ASTM D3679, which prohibits the use of lead. The Vinyl Siding Institute (VSI) Vinyl Siding Product Certification Program ensures that certified vinyl siding meets that requirement. Certified vinyl siding accounts for approximately 95 % of the vinyl siding sold in the United States.

Vinyl Window and Door Profiles

The American Architectural Manufacturers Association (AAMA) Window and Door Profile Certification Program prohibits participating companies from adding lead to profiles for windows and doors sold for installation in the United States, Mexico, and Canada. This would restrict lead from being added to any compound, organic coating or laminate used in certified profiles intended for use or sale in the U.S, Mexico or Canada. The lead content .and/or trace amounts of lead from external sources shall be less than 0.02 % by weight for the substrate or any surface treatment. An officer of the company licensed under the AAMA Certification Program must furnish a signed affidavit indicating that the licensee complies with section 2.2 and verifying that no lead has been added to profiles intended to be sold in the United States, Mexico or Canada.

Window Mini-Blinds

In 1996, CPSC investigated the potential release of lead from various brands of imported vinyl mini-blinds by measuring the amount of lead available in the dust on the surface of the blinds. Results indicated that deterioration of the non-glossy vinyl mini-blinds from exposure to sun and heat could cause lead in the plastic to become available as dust on the surface of the slats. CPSC found that in some blinds, the levels of lead in the dust were high enough to warrant concern for health effects on young children who might ingest the dust. As a result of the investigation, the industry ended the use of lead stabilizers in these products.

Global Automotive Industry

The automotive industry uses what is known as the GADSL (Global Automotive Declarable Substance List). Materials listed in the GADSL are either prohibited or declarable. Lead compounds are prohibited within the automotive industry (with some specific lead exemptions).

Electrical/Electronic Equipment Industry

Because of the global marketplace and the introduction of European Commission's Restriction on the use of Hazardous Substances (RoHS) in Electrical and Electronic Equipment, many U.S. manufacturing companies are replacing lead in products in this industry.

1.7 Conclusions

Overall, the uses of lead stabilizers and lead pigments are limited in the U.S. vinyl market, mostly for the wire and cable industry. Lead is not allowed in critical water delivery piping and food contact uses, is voluntarily restricted in some major vinyl market sectors, and is restricted in use in vinyl children's products to ensure safety. Awareness and continued enforcement of these regulations and voluntary requirements are critical in the management of lead use in these products.

1.8 References

1. "Technical Guidelines for the Identification and Environmentally Sound Management of Plastic Wastes and for their Disposal Including: Technical Guidelines on the Environmentally Sound Management of Plastic Coated Cables" *prepared by the Technical Working Group of the Basel Convention*. UNEP, 2002
2. U.S. Geological Survey Minerals Yearbook — 2005
3. ASTM International, *ASTM D3679-06a*, 2006

4. NSF International, <http://www.nsf.com>
5. “1996 Annual Report to Congress, United States Consumer Product Commission”, Ann Brown. <http://www.cpsc.gov>
6. U. S. Food and Drug Administration, <http://www.fda.gov/default.htm>
7. Coalition of Northeast Governors, <http://www.coneg.org/>
8. American Architectural Manufacturers Association <http://www.aamanet.org/>
9. Global Automotive Declarable Substance List <http://www.gadsl.org/>
10. European Commission Directive on Waste Electrical and Electronic Equipment http://ec.europa.eu/environment/waste/weee/index_en.htm
11. *Handbook of PVC Formulating*, Edited by Edward J. Wickson, 1997
12. Titow, W.V, *PVC Plastics Properties, Processing and Applications*, 1990.