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REVIEW ARTICLE

Usage of heavy metal-free compounds in surface coatings

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Abstract Coatings have been used since time immemorial for decorative and protective purposes. During the initial periods, when not much information was available regarding the health impact of the raw materials, there was no thought given or restrictions put on use of any ingredients in coatings. Some of the raw materials like white lead (lead carbonate), red lead (lead oxide), hexavalent chromium compounds, and other similar compounds were being used in large quantities to get specific paint film properties. This not only affected human health but also with no effective effluent treatment contaminated soil and water resources. With progress in technology and diagnostics, lead and chromium compounds have been identified as carcinogens. The developed countries (Europe and USA) were the first to ban the use of lead in their products in the 1970s and 1980s, but due to mainly economic reasons, these are still being used in the developing countries. As the long-term health impact is too much to bear, regulations/legislations have been enacted by the governments restricting use of lead/chrome in paints. The Global Alliance to Eliminate Lead Paint (GAELP), a joint association formed under the United Nations Environment programme, and World Health Organization have agreed to phase out manufacture and sale of paints containing lead by 2020. Similar restrictions exist for many other compounds used in coatings. The article attempts to present a synopsis of the history of coatings composition, impact of the heavy metals on health and environment, and the options available for shifting to safer coating composition. As major focus of the world is on lead elimination, it has been covered in more detail, but the article also provides information on other metals, namely cadmium, chromium, mercury, arsenic, antimony, tin, nickel, manganese, cobalt, etc., and their current status.

Keywords Lead chromate, Cadmium, Tin, Mercury, Arsenic, Chromium, Antimony, Nickel, Manganese, Cobalt, Heavy metals, Carcinogenic, Lead compounds, Hazardous material, Organic–inorganic pigment mixture, CICP, Lead drier, ICP-OES, XRF

Introduction

Paints can be either water based or solvent based and the intended use can be for decorative (household) segment or industrial segment. Paint is typically made up of pigments, extenders, (also called fillers) binders (also called resins), solvents, and additives. During a paint formulation process, all these components must be adjusted and optimized to get paint with the required quality and properties.[1]

The functions of the coating ingredients are:

- Pigment and Extenders: These are either organic or inorganic material and provide color and hiding power to the paint film. Extenders help in optimizing pigmentation. They help improve specific properties but affect the gloss/image clarity of the paint film.[1]
- Binders/Resins: Functions as a binder to hold the pigment and extender particles together and provides adhesion to the painted surface in addition to a variety of mechanical, chemical/corrosion resistance, and weathering properties.
- Solvent: Acts as a carrier for the pigments and resin.[1]
- Additives: These are ingredients added to enhance specific properties before, during, and after cure.[1]

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Lead compounds used in coatings are either used as pigments/extenders and/or additives. Chromium pigments are used for their anticorrosive properties. Other heavy metal compounds are used for specific properties imparted by the metal compound. For example, tin as special additive in antifouling paints, cadmium as pigment in heat-resistant paints, etc. These elements have an impact on human health as well as the ecological system and hence are restricted for use. The details of each of the heavy metals, its hazards, and its alternatives are covered in the following sections.

Lead

Introduction

Lead is a post-transitional element with the symbol Pb (Latin word: plumbum). Its atomic number is 82 and relative atomic mass is 207.2. Pure lead is soft and malleable. Freshly cut lead shows bluish white color and changes to a dull grayish color while exposed to air. Lead shows a shiny chrome silver appearance when melted into a liquid.[1,2]

Lead was one of the first metals that was smelted by people and used. Archeologists have found lead objects and pigments dating from the early Bronze Age.[3] Metallic lead occurs rarely in nature and is usually found in the form of some ore with zinc, silver, and copper, and it is extracted together with these metals. Galena (PbS) is the main lead mineral which contains 86.6% lead. Other sources include cerussite ($PbCO_3$) and anglesite ($PbSO_4$).[1,2]

Lead uses today

Metallic lead, lead alloys, and lead chemical compounds are being used for many purposes including automobile fuels. (Addition of tetraethyl lead to automotive fuels helps to improve engine performance, but this has now been stopped.) In addition to lead pigments and lead compounds used in paints, other major uses of lead include lead storage batteries, lead pipes, lead solder, lead ammunition, bullets and shot, weights and used as a stabilizer in vinyl (PVC) plastic. Currently, around 80% of lead is used for production of lead batteries.[3,4] Lead is also used as a protective shielding around nuclear reactors, particle accelerators, X-ray equipment, and as containers for transporting and storing radioactive materials because lead effectively absorbs electromagnetic radiation of short wavelengths.[5]

Lead in paints

Lead compounds are used in paints because of the specific properties provided by the compounds. This includes:

PIGMENTS : Certain lead compounds are used as pigments in paints to get the desired color. Apart from being economical, they provide very bright and attractive colors in the yellow, orange, red, and green color range along with excellent opacity. These pigments include lead chromates, lead molybdates, and lead sulfates.[1,3,6,7] White lead (basic lead carbonate) pigment is also a very commonly used (extender) pigment. It also gives good dispersion, gloss control, corrosion inhibition, and rheological control.

DRYING AGENTS AND CATALYSTS : Certain lead compounds are sometimes added to oil-based paints to accelerate the air-drying process and to prevent loss of drying on storage. This compound interacts with the atmospheric oxygen forming peroxide linkages and accelerating the drying process. These include lead naphthenate, lead acetate, lead octoate, and lead oxides.[1,3,8]

CORROSION RESISTANCE AGENTS : Lead oxides and other lead compounds are used to improve the corrosion resistance property of coatings when applied on metal surfaces. These agents include lead tetroxide (red lead), lead carbonates (white lead) and lead chromates.[1,3]

Cathodic electrodepositable coatings or electrocoats also used to contain lead compounds as they provide good corrosion performance. Some examples include lead silicate, lead silico-chromate, and/or lead chromate. There are also reports of the use of lead cyanamide in cathodic electrodeposition coatings, which is used as a supplementary catalyst along with the main catalyst, and gives superior under bake curing without sacrificing chipping properties during overbake cure.[9]

Health impacts of lead

Paint containing lead or lead paint is hazardous. Lead is a cumulative toxicant that has a harmful effect on multiple body systems affecting human health in all age groups; however, children are especially vulnerable. Lead released into the environment is toxic to plants, animals and microorganisms.[3,6,10]

Children are more biologically susceptible to lead than adults because:

- Brain growth, development, and differentiation occur rapidly in children and lead interferes in this process. Brain damage due to chronic, low-level exposure to lead is irreversible and untreatable.
- Exposure to lead early in life can alter genes, which can lead to a change in gene expression and an associated increased risk of disease later in life.
- Gastrointestinal absorption of lead is high during childhood.[3]

Lead enters human body either through inhalation or ingestion. Specifically, in the case of small children through touching of painted wall and chewing of painted toys.[11] The health effects of lead poisoning are catastrophic and affect almost all organs of the body like heart, brain, kidney as well as the nervous system.[12] A single high dose of lead can cause severe symptoms; most people are, however, affected from cumulative exposure over time. Lead exposure is an especially insidious hazard since it has the potential for causing irreversible health effects before the exposure is clinically recognized.[3] Bone accumulates lead during much of the human life span and may become an endogenous source of lead that may be released slowly over many years after the exposure stops.[13]

Need of lead-free coatings

Exposure to lead in paints remains a global public health concern. Lead exposure can occur during any stage of the paint manufacturing, use, as well as removal (Old lead paint films.) The World Health Organization (WHO) has concluded that no level of lead exposure for children is safe. The US Consumer Products Safety Commission has also indicated lead-based paint as the main source of lead poisoning for children as well as adults.[14]

In 2011, Clune, Falk, and Riederer mapped the global environmental lead poisoning in children globally. The blood lead levels were measured and classified in the following categories: <10 μg/dl, 10–19 μg/dl and > 20 μg/dl. Some of the regions in America (Mexico) and Asia Pacific (India) region were shown to have a high level of lead in children. (See Fig. 1).[15]

There are different ways by which countries have specified the limits of lead allowable in paints. Some have fixed numerical limits on the total lead concentration (in parts per million — ppm), while others have limit on the soluble lead concentration in paints. There are also few countries like Turkey and Russia which just restrict use of certain lead compounds such as lead sulfate and lead carbonates in paint without any specific limits on the actual lead content.[16] When paint is tested and is found to contain more than 90 parts per million (ppm) of lead (measured as the total lead content of the dry paint film), it can be taken as an indicator that one or more lead compound was intentionally used in the paint's formulation with some specific purpose either economic and/or functional.[6]

Lead paint is cheaper than the alternatives, which seems to have tempted certain paint manufacturers to use it in preference to the nontoxic and environmentally friendly replacements.[17] Apart from this, poor awareness and inadequate access to information regarding safer alternatives, especially by the unorganized sector (small scale enterprises) of the industry has been highlighted as cause for not changing over to lead-free coating compositions.[18]

Regulations on use of lead in paints

In the 1970s and 1980s, most countries came up with legislations banning the manufacture, sale, and use of lead in decorative paints (household paints). It is being noticed that countries that have established regulatory frameworks have lower lead levels in paint. Various global-level organizations have realized the adverse health and ecological impact with use of the lead paints and have passed resolutions at eliminating or restricting use of such materials. For instance:

- World Health Organization (WHO) & Occupational Safety and Health Administration (OHSA) identify lead as one of the 10 elements of major health concern.[3]
- The European Union has imposed ban and restrictions on lead pigments and other lead compounds used in paints through REACH (Registration, Evaluation and Authorization of Chemicals) certification. The REACH certification is mandatory for any suppliers to do business in the European Union.[3]
- GAELP [Global Alliance to Eliminate Lead paint — a partnership formed by the United Nations Environment Programme (UNEP) and the World Health Organization (WHO)] recommends limit of lead in paint as 90 ppm.[3]
- International Paint and Printing Ink Council (IPPIC) established in 1992, a global council of national trade associations representing the paint and printing ink industries covering Americas, Europe, Asia – Pacific region, passed a resolution restricting the use of lead in paints in 2008.[3]
- The CPSIA (Consumer Products Safety Improvement Act) law passed by United States recommends upper limit of lead in paint as 90 ppm on total lead (dry weight basis) for decorative as well as many other paint categories.[3]
- IPEN, a network of nongovernment organizations (NGOs) in 116 countries, promotes the 90-ppm lead limit standard. The practical difference between a 90-ppm standard and a 600-ppm standard is not very great. If the manufacturer adds lead compounds to paint to serve as a pigment, as a drying agent, or for some other intentional purposes, the lead content of the paint is always substantially greater than 600 ppm; if there is no lead compound added intentionally, the value of lead content is generally below 90 ppm. IPEN´s goal is global lead paint elimination by the year 2020.[3]
- Government of India has notified the "Regulation on Lead Contents in Household and Decorative Paints Rules, 2016" act on November 1, 2016. This has come into force from November 1, 2017**.** The law prohibits the manufacture and sale of paint with lead concentration > 90 ppm.[3]

Figure 2 shows data on the status of countries with respect to paint laws as provided by governments to UN Environment and WHO. As of September 30, 2019, 73 countries had confirmed that they have legally adhered controls on lead in paint, 85 stated that they do not, and information was not available for the remaining 35 countries.[19]

The lead regulation is used for controlling lead in decorative paints. There are generally less restrictions on industrial paints. To avoid any misuse of industrial paints being used on toys or articles which might be used by children or households, it is essential that paint manufacturers put some warning label on the paint containers such as "DANGER: Contains Lead. Do not apply to surfaces accessible to children or pregnant women."[10]

Challenges in lead-free paint development

The challenges faced by paint chemists in developing lead-free coatings compositions include the following:

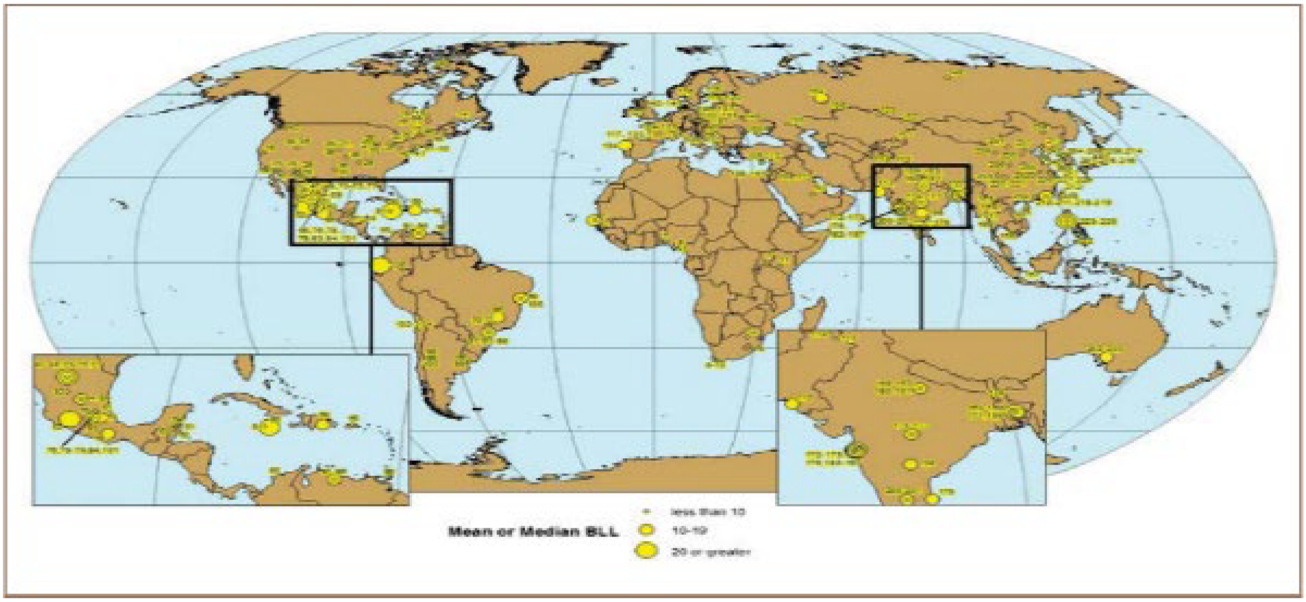

Fig. 1: Global environmental lead poisoning in children[15]

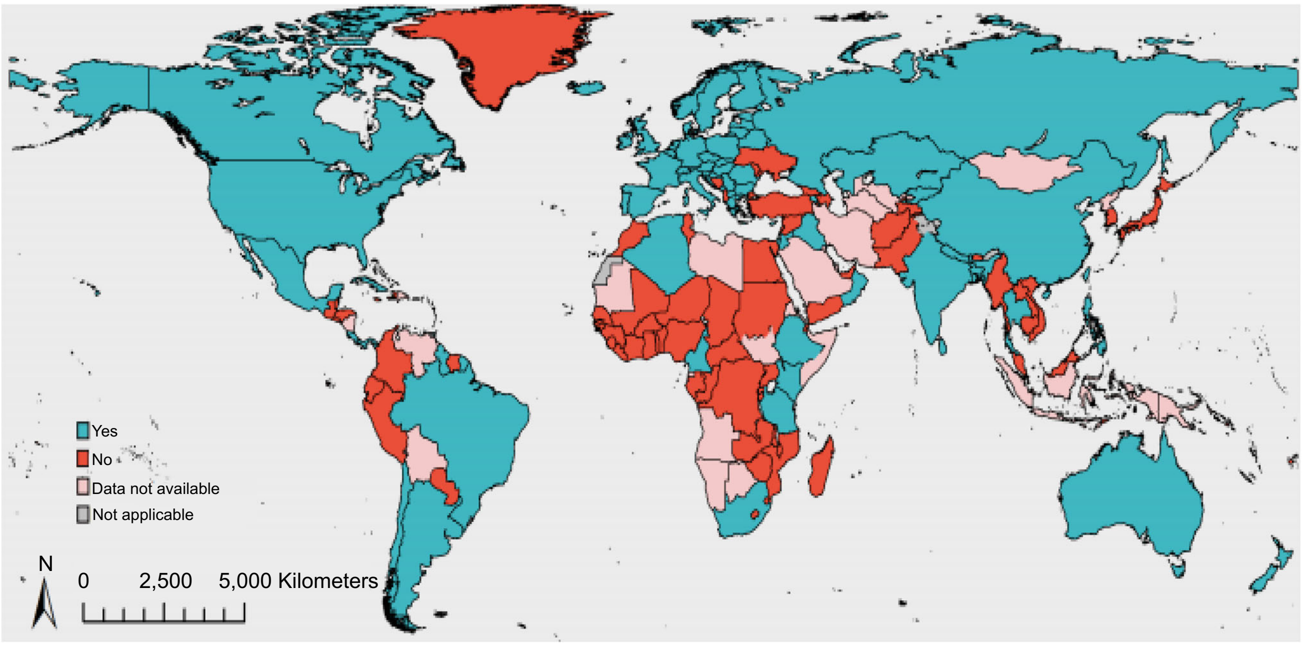

Fig. 2: Countries with lead paint laws, as of September 2019[19]

Coloristic properties

Lead chromes are majorly acclaimed for their excellent opacity, low oil absorption value, very bright shades, and high chroma, thus making them ideal for full shade yellow paints. The coloristic property provided by the pigment(s) is accurately defined by the following three parameters:

a. **Hue:** Represents the color—for example, red, yellow, and blue.

b. **Intensity/Chroma:** Used to describe the brightness and purity of a color. For example, bright red or dull red.

c. **Value:** Represents the lightness or darkness of a color. Value changes are obtained by adding black or white to a hue.

Hue, chroma and value combined give chromaticity of a color.[20] Figure 3 provides a 3D correlation between the three parameters.

There have been attempts to replace the lead compounds with inorganic pigments, but this does not provide the required coloristic properties. Hence, organic pigments are being recommended by pigment manufacturers to achieve the required bright tones.[20]

Opacity/hiding property

Lead pigments have a very good hiding property. This is attributed to the high refractive index (RI) (2.31–2.49) values of such pigments and greater difference between the refractive index value of binders used in the composition.

When the lead pigments are replaced with regular inorganic pigments, they exhibit comparable hiding property. Also, because of low binder demand, higher pigment loading is possible, e.g., yellow iron oxide (PY42). But the inorganic pigment does not give the required bright hue; hence, they are usually used along with organic pigments, e.g., yellow pigment (PY 74/PY 83). Organic pigments typically show higher color strength than inorganic pigments but have low opacity and comparatively high binder demand.[21,22]

Pigment dispersibility

The dispersion process used for processing paint affects hue, gloss, film appearance (i.e., haze, flooding, floating) durability, and stability properties. Majorly used chrome (inorganic) pigments are easier to disperse. Any paint reformulation involves not only substitution of lead pigment by less hazardous alternative, but also requires changes in mill base composition, wetting, dispersing additives, and also the dispersion process.[23,24] Organic pigments are known to be more difficult to disperse compared to inorganic pigments.

Flocculation is a common problem observed in paints having multiple-colored pigments, affecting the shade and also reducing the gloss of the paint film. Improper selection and quantity of additives—either low or even high, are detrimental to the stability of the pigment dispersion.[25]

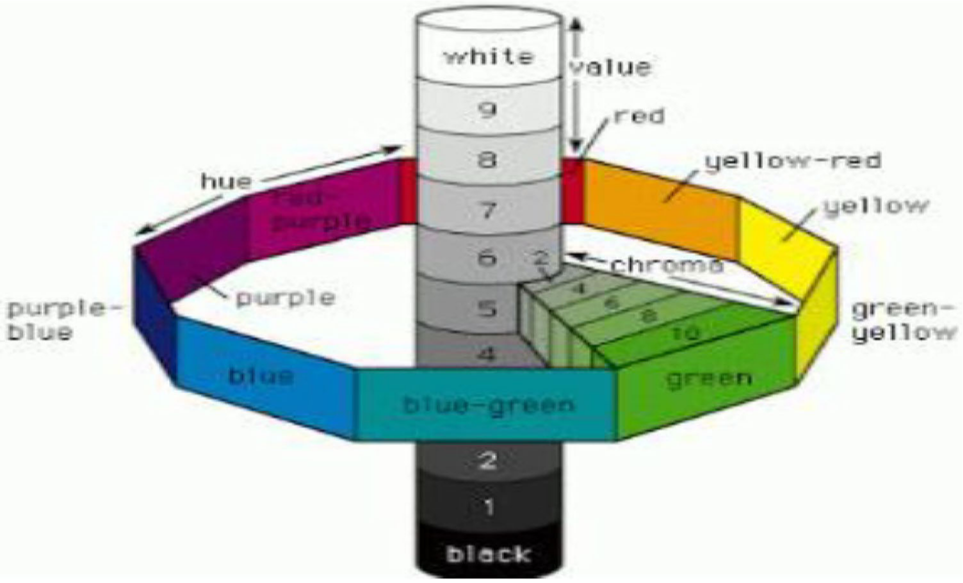

Fig. 3: Color theory[20]

Poor gloss/gloss shrinkage and image clarity

Inorganic (lead) pigments usually have a low oil absorption value and are easy to disperse, resulting in good gloss and image clarity. Organic pigments have a high oil absorption value and have a higher binder demand. This results in lower paint film opacity. Increasing the pigmentation further affects the paint film gloss and image clarity. Hence, it is essential to optimize the organic pigment loading and preferably use a mix of organic and inorganic pigments to achieve the required color, opacity, and visual properties.

Improper dispersion could also cause inferior gloss and under development of color strength. Hence, selection of appropriate wetting and dispersing agents with proper concentration is essential. The concentration of the wetting dispersing agent is often arrived at through a ladder study of the additive doses.

Durability

The light fastness and weather resistance of lead chromates depend on the types used and their surface stabilization. Similar to lead chromates, organic pigments vary greatly in weatherability.[20] Cost-optimized pigment preparations can replace standard lead chromates. To achieve weathering performance, pigment preparations and hybrid pigments are formulated in such a way that they outperform standard lead/chrome-based products.[22]

Figure 4 shows the weathering performance of lead-free yellow composition prepared by three different methods.[26]

A) Organic yellow plus titanium dioxide
B) Colored inorganic product, such as bismuth vanadate plus organic yellow
C) Hybrid pigment

In example (A), organic yellow plus titanium dioxide, over the life of the coating, the organic yellow degrades, i.e., loss of color (chromophoric loss) happens over time with a ‘‘concentration‘‘ gradient of colored yellow pigment. Color change is observed from higher concentration to lower concentration near the surface. Hence, faded yellow becomes white.[26]

In example (B), colored organic and inorganic, the similar type of weathering phenomenon occurs as the organic yellow is destroyed. However, the end point is no longer white, but shows some yellow hence perceived to be less fading.[26]

In example (C), the hybrid is a co-finished pigment and its organic part is partially protected by inorganic portion hence giving positive synergistic impact on fading and appearing yellow.[26]

Lead chromates-based coatings show good accelerated weathering performance. To get equivalent coloristic and hiding property, a combination of organic and inorganic pigments is recommended. The choice of inorganic part decides the performance of the system. Titanium dioxide with organic pigment shows comparable cost but limited durability with binder degradation. Ni/Cr titanate-based system shows mid-performance and no photoactive behavior. Bismuth vanadate, inorganic and organic pigment combination shows the best durability results but at higher cost.[27]

Metamerism

Certain lead/chrome colors when developed using lead-free pigments may show color difference when observed under different light sources. This phenomenon is referred to as metamerism. It refers to situations where two colors appear to be identical under one light source and different under a different light source, i.e., the two colors have different spectral graphs. In such cases, other pigment options need to be looked in to having a complete spectral match. In certain cases, where alternate options are not available, the most acceptable option will need to be implemented.[21]

Cost escalation

Lead pigments are cheaper compared to the organic or inorganic pigments which are used for getting equivalent color and opacity property. The cost of organic pigments is further increased when shifted from azo grade pigments to high-performance pigments based on polycyclic chemistry. Hence, proper selection of organic–inorganic pigments is essential as is the optimization of pigmentation level in the composition to minimize the impact on cost.

Approaches for lead-free paint development

Based on the role performed by the lead compound in the paint composition, appropriate alternatives need to be identified and required formula modifications to be done while formulating the paint. The following are the major functional domains where lead alternates are required.

1. Pigments — color property
2. Corrosion resistance
3. Driers
4. Special additives

Pigments

The major use of the lead pigments is due to the bright and attractive colors provided by the pigments. The lead compounds provide very bright yellow, orange, and red shades at very good opacity. Some of the commonly used lead pigments are chrome yellows and orange. e.g. (refer Table 1).

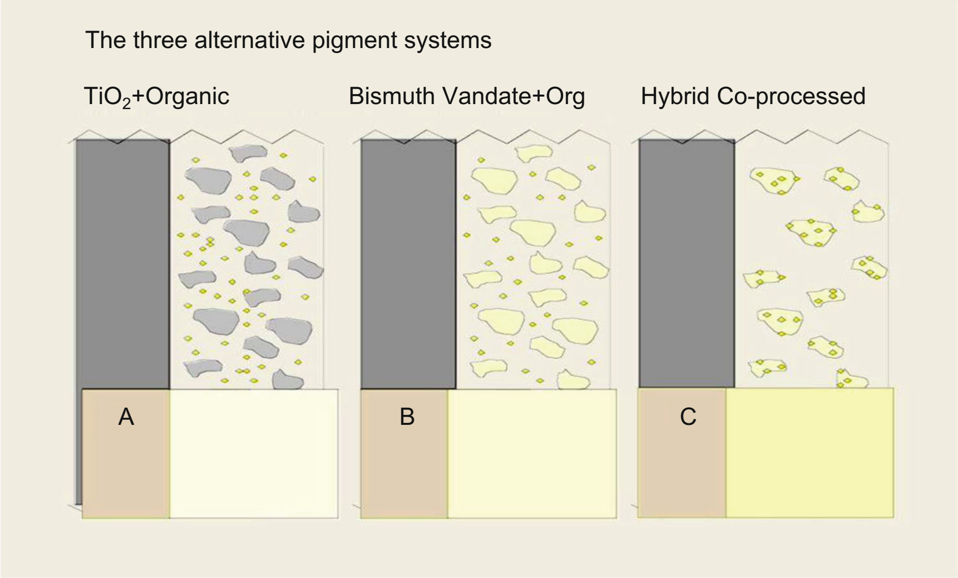

Fig. 4: The three alternatives "A," "B" and "C" (left to right)[26]

Table 1: Commonly use lead pigments[28]

Sr. No.	Shade	Composition	Color index number
1	Pale Primrose	Lead chromate with 30–50% lead sulfate and stabilized	PY 34
2	Primrose or Pale Lemon	Lead chromate with 45–55% lead sulfate	PY 34
3	Lemon	Lead chromate with 20–45% lead sulfate	PY 34
4	Middle	Lead chromate	PY 34
5	Scarlet	Scarlet lead chromate, lead sulfate and lead molybdate	PY 34/PY 104

Pigment producers are actively involved in developing environmentally friendly alternatives to the above pigments including inorganic, organic, and organic/inorganic hybrid solutions, but to date, there are no one-to-one replacements identified for the lead chrome pigments. In noncritical applications, quite often a compromise is arrived at regarding color and/or performance.[29]

Generally, formulations developed fully on inorganic pigment alternates are comparatively dull in color. There are only a few inorganic pigments, e.g., bismuth vanadate (PY 184) that give clean shade and bright colors.[20] For formulating lead-free alternatives, typically bismuth vanadate (PY 184), Complex Inorganic Color Pigments (CICPs) (PY 53, PBr 24, PY 164), and iron oxides (PY42, 43, PR 101, 102) are used. The choice of inorganic pigment will depend upon the strength, shade, and brightness (chromaticity) of the color required.[20]

The color range of the three inorganic pigments is as follows:

- Bismuth Vanadate — (Color range greenish yellow)
- Iron Oxide — (Color range red and yellow)
- CICP — (Color range yellow, orange, green, blue, and black)[20]

By use of bismuth vanadate or CICPs, the brightest colors can be developed. Iron oxides can be used in general applications, but they give dull colors in comparison to lead chromates. A few coloristic properties of the pigments are listed in Table 2.

Generally, the end colors developed and being marketed are multi-pigmented, i.e., each paint composition consists of a mix of pigments. This gives flexibility during the use of lead-free alternate pigment. The desired color and balance of properties in lead-free composition are achieved by using a combination of organic and inorganic pigments. The inorganic pigment provides the opacity (through higher refractive index) and also the weathering performance, while the organic pigment is used to obtain the required clean color. Organic pigments could be azo type or high-performance pigments based on polycyclic chemistry.[11,20,30]

Table 2: Inorganic pigments[20]

Pigment type	Color index	Comment
Bismuth vanadate	PY 184	Modified bismuth vanadate – cover color space between green shade yellow and yellow shade orange
CICP	PY 53	Nickel antimony titanium yellow rutile (bright yellow in color)
CICP	PBr 24	Chrome titanate (brown)
CICP	PY 164	Titanium antimony manganese rutile
Iron Oxide	PY 42, 43	Yellow iron oxides
Iron Oxide	PR 101, 102	Iron oxides (Red)

Table 3: Comparative properties of organic and inorganic pigments[20]

Properties	Inorganic pigment	Organic pigment	
		Azo Type	HPP (High Performing Pigment)
Opacity	Excellent	Transparent	
Coloring strength	Low to average	Several times better than inorganic pigments	
Purity, Chroma	Dull	Bright	
Light fastness	Good to excellent	Low to average	Good to excellent
Weather resistance	From mediocre to excellent	Mediocre	Good to excellent
Heat resistance	normally > 500°C, not often <200°C	150–220°C	200–300°C
Bleed resistance	Excellent	Average to good	Good to excellent
Chemical resistance	Mediocre to excellent depending upon the chemistry	Excellent except for the salt	Excellent
Pigment cost	low to average	Average	High

The comparative properties of organic and inorganic pigments are as follows (refer to Table 3):

Suggestions for lead pigment replacement

Going from lead-based design to lead-free design requires more judgment and iterations rather than set of scientific principles.[17,20] Depending upon the required properties of the paint, the following generalized approaches are suggested.

1. For clean shades: use organic yellow, red or orange pigments.
2. For opacity: use inorganic pigments (bismuth vanadate, CICP, or Iron oxide).
3. For opacity + clean shades: combine organic and inorganic pigments or use hybrid pigments.[20]

Paints for interior use do not need to have excellent weather resistance or light fastness. In this case, modified azo pigments can be used. These give good acid and base resistance but have limited weather fastness. Weather fastness in full tone is very good, however, when tinted these pigments lose their durability.[21] Modification of azo linkage (N=N) increases the cost but improves the weathering performance. In general, the pigment price and weathering performance increase in the given order:

- Monoazo — (color range from greenish yellow to orange)
- Disazo — (color range green yellow to reddish yellow, orange and red)
- B Naphthol — (color range orange to red)
- Naphthol AS — (color range yellowish and medium red to brown and violet)
- Bona — (color range yellowish red to bluish red)
- Arylide and diarylide — (color range greenish yellow to orange)
- Azo Condensation — (color range green shade to red shade yellow)
- Benzymidazolone — (color range green shade yellow to red)[20]

For exterior purpose, HPP (high performance organic pigments from the polycyclic range) provides a high level of weathering performance (comparable to inorganic pigments) but is expensive in comparison to inorganic pigments and azo type organic pigments.

Depending on the color to be developed, the following pigment range can be used to make desired shades:

- Isolindolone — (color range red shade yellow)
- DPP (diketo pyrrolo pyrrole) — (color range orange- bluish red)
- Perylene — (color range red)
- Perylone — (color range orange)
- Quinacridone — (color range reddish violet to blueish red)[20]

Organic pigments generally have higher color strength compared to inorganic pigments with some exceptions, e.g., bismuth vanadate P.Y. 184. Therefore, organic pigments are ideally suited for compensating the deficient color strength of hiding inorganic pigments in pigment combinations.[7]

As there is no 1:1 replacement available for the lead pigments, the best approach is to combine the required color parameters of different pigments, namely value L*, chroma C*, hue angle h°, and hiding power (contrast ratio, CR), in such a way that the color coordinates of the combination match the lead pigment to be replaced.[31]

Pigment manufacturers have noted the advantages and shortcomings of organic and the inorganic pigments. Organic pigments have strengths in chroma and tint strength but are weaker in weather resistance and opacity, while inorganic pigments have good opacity and weather resistance property but inferior coloristic properties.[26] A logical way out was to use a combination of organic and inorganic pigmentation to give the desired combination of properties in the final film.[17,20] Pigment manufacturers realized this and came up with blend of organic and inorganic pigments and supplied as "Hybrid Pigments."

Hybrid pigments are adjusted in color, color strength, and opacity to match lead pigments. Durability of hybrid pigments can be further adjusted through smart combinations of organic and inorganic pigments. It helped reduce the complexity in replacing lead pigments, but they are expensive.[27]

Corrosion resistance

Many factors contribute to the corrosion process, for example, air pollutants such as sulfur dioxide, the salts present in marine environments, and also lower pH. Lead oxide (red lead) and lead carbonate (white lead) and hexavalent chromium compounds were used to get good corrosion resistance performance.

Corrosion resistance of paint is influenced by several factors, like resin type, relation of pigment volume concentration (PVC) to critical volume pigment concentration (CPVC), type of anti-corrosive pigment and fillers, dispersing conditions, and entire formulation. All these factors must be taken into consideration during the paint reformulation process.[32] The alternates for the pigments are as follows:

RED LEAD - LEAD OXIDE (Pb_3O_4) (PIGMENT RED 105) : Red lead is the oldest and most common anticorrosive pigment used in coatings giving excellent anticorrosion performance. This pigment is mainly used for rust-proof metal primers. This pigment reacts with the acidic groups present in the resin to form soap, which has corrosion inhibitory properties. Hence, it is an indirect inhibitor.[33]

There are several alternatives now available for replacing red lead. The alternate does not give the same reddish-brown color, but as primers, usually coated further with colored topcoats, the primer color should not be so significant. Table 4 provides information on alternate pigments for corrosion performance and also the mechanism of action of the various pigments.[34]

WHITE LEAD - LEAD CARBONATE ($2PbCO_3.Pb(OH)_2$) : White lead (PW1) was used as an extender along with other pigments in paint formulation for a number of reasons, both technical and economic. It improves water resistance making the coating washable. Also, it neutralizes the acidic decomposition products of some of the oils that make up the paint, making the coating tough as well as flexible and crack-resistant for longer periods.[30]

This has been successfully replaced with titanium dioxide TiO_2 (PW 6) which gives better hiding property—approximately ten times better, providing scope for reduction in concentration.[20,31,35] Corrosion and better drying properties are achieved through balancing of the paint composition with other pigment and drier additive package.[20]

LEAD CHROMATES : The chromate film acts as a barrier to corrosion, given its relative insolubility in aqueous environments that spans the environmental pH spectrum, and its adherence to the underlying metal. A similar comprehensive anticorrosion compound is yet to be identified for implementation in primers and coatings. As an alternative, anticorrosive pigments based on zinc and strontium like zinc phosphate, along with appropriate extender combinations, are made use of to get the required anticorrosive performance.[36]

LEAD COMPOUNDS IN ELECTROCOATS : There have been several modifications done in cathodic electrocoat primers over the last 35 years. Progressively, the anticorrosive pigments and the pigmentation were reduced/replaced and performance improved using enhanced polymer technology. This, apart from corrosion performance, helped in reducing settling and enabled easy mixing of the batch constituents. Apart from stringent environmental legislations,

Table 4: Alternates to red lead pigments[34]

Pigment type	Pigment	Mechanism of action
Chemically active anticorrosive pigments	Zinc oxide (ZnO), zinc phosphate ($ZnPO_4$), modified zinc phosphate, calcium phosphate, modified calcium phosphate	Bind corrosion stimulators such as chloride or sulfate by forming insoluble compounds and/or stabilizing the pH value of the medium. Hence, slight solubility in the corrosion medium is necessary.
Electrochemically active anticorrosive pigments	Zinc phosphate ($ZnPO_4$), modified zinc phosphate, calcium phosphate, modified calcium phosphate	Passivates metal surfaces by forming thin layers, such as chromate or phosphate layers. Solubility and reactivity are critical parameters of active pigments.
Active, cathodic protective anticorrosive pigments	Zinc dust	A special type of active pigment that acts by cathodic protection when applied to ferrous substrates. Acts as sacrificial anode and protects the metal substrate. The paint has to be formulated to yield good electrical contact between substrate metal and sacrificial pigment particles. The most important requirement that enables zinc-rich primers to afford corrosion protection is PVC close to or above the CPVC.
Passive anticorrosive pigments	Micaceous iron oxide and aluminum silicates	Barrier pigments - act by reinforcing the paint film and reducing its permeability to corrosive agents. These are chemically inert pigments with a platelet like or lamellar particle shape. These shapes form a wall of flat particles which protect substrate from contact with water and electrolytes.

increased performance expectations of end customers were the major drivers for the changes. Currently, all the formulations of E-Coats are lead free and perform well over low nickel and chrome-free pretreatments.[37]

EXTENDERS : Extenders have a positive influence on mechanical properties and corrosion resistance property of coatings. Extenders which are platy shaped prevent water, oxygen, and other chemicals from reaching the substrate as particles overlap in a film. For example, talc (hydrated magnesium silicate) is a proven anticorrosive, hydrophobic extender, limiting the penetration of water and corrosive agents into the paint film. It reduces corrosion, peeling, and blistering of the paint film. Due to its particle shape and chemical inertness, talc also promotes adhesion increasing the paint's durability. Other extenders which improve corrosion resistance include mica and China clay.[38]

Driers

Driers (metal soaps) are added to air-drying coating systems to accelerate the transformation from a liquid film to solid state within an appropriate time after application.[32] There are several steps involved in the drying process of a coated film. First is physical drying; in this step, the solvent evaporates from the system, leaving a coalescence film behind. Then, chemical drying occurs which involves oxygen interaction, peroxide linkage formation, and then complete solidification. This chemical drying part can be accelerated by a metal catalyst generally called a drier.[35]

The metals that have been used in drier compounds may be grouped in three categories: primary driers (also called active or oxidation driers), secondary driers (also called through-driers), and auxiliary driers.[34] The metals used for the driers in each category are listed in Table 5.

Lead drier is used as secondary drier. Secondary driers are active in the crosslinking steps of drying and are responsible for overall drying throughout the entire paint layer. Lead drier activity as the sole drier is very low and has a synergistic effect in the presence of auxiliary driers. Lead also improves the flexibility and durability of the film.

The following alternatives have been recommended for replacing lead drier:

STRONTIUM DRIER : Strontium is nontoxic and has good drying performance. It provides auxiliary drying characteristics, resulting in improved storage stability and reduced "loss of dry" — especially beneficial in systems that are heavily pigmented or contain a high level of additives.

Table 5: Metal driers[34]

Primary driers	Secondary driers	Auxiliary driers
Cobalt	Lead	Calcium
Manganese	Zirconium	Zinc
Iron	Bismuth	Lithium
Cerium	Barium	Potassium
Vanadium	Cerium	–
–	Strontium	–

Strontium is the most prominent choice for lead substitution vis-à-vis zirconium. Additionally, it is used as good wetting and dispersing agents, as it prevents haze and wrinkling. However, outdoor performance may be affected negatively when strontium is used. There are studies mentioning that three parts of lead could be replaced with one part of strontium.[11,34]

ZIRCONIUM DRIER : Zirconium-like lead serves as a through drier. It is only effective when it is used in combination with primary driers. It promotes surface and through drying. Similar to lead, zirconium works well in the presence of auxiliary driers like calcium, etc. The drying phenomena of cobalt/calcium/zirconium combination, at ambient temperature and humidity conditions, are quite similar to that of the lead-based combination drier.[34] Usually, a higher concentration is added as replacement.

SPECIAL ADDITIVES : Some of the compounds like lead pastes and litharge (PbO) have been used for getting specific properties in paints, namely, to prevent drier absorption and corrosion improvement. Better nontoxic alternatives are now available for use.

- Litharge, lead monooxide (PbO), is a yellowish or reddish, odorless, heavy, earthy, water-insoluble, solid.[39] Litharge has been replaced with zinc phosphate and other zinc compounds.
- Lead pastes can be replaced with zirconium complexes or cobalt compounds.

Cadmium

Introduction

Cadmium is a transition metal and represented by the symbol Cd. It has the atomic number 48 and a relative atomic mass of 112.41. It is a soft, malleable, ductile, silvery-white metal. Cadmium was discovered by Stromeyer and Hermann in 1817 as an impurity in zinc carbonate.[40]

Cadmium is produced mainly as a by-product from mining, smelting, and refining sulfide ores of zinc, and to a lesser degree, lead and copper. Atmospheric deposition of contaminated particles is supposed to be the major source of cadmium followed by commercial phosphate fertilizers and landfills of discarded products and production waste for cadmium.[41]

Cadmium uses today

Cadmium in its hydroxide form is used as one of the two principal electrode materials in Ni-Cd batteries which have extensive consumer applications.[40,42] The general trend in the global cadmium consumption over the last two decades has been a steep increase in the use of cadmium for batteries and a decrease in the use for nearly all other applications.[41]

Cadmium sulfide and cadmium sulfoselenide are used as bright yellow-deep red pigments in plastics, ceramics, glasses, enamels, and artists colors. They are also used in many electrical or electronic applications where a good combination of corrosion resistance and low electrical resistivity is required. It is also used as an anticancer drug and for making sensors.[40,42]

Cadmium in paints

Cadmium pigments provide very bright hues and tones of red, yellow, and orange, very good color permanence, good tinting strength, and heat resistance up to 300°C. For example, commonly used cadmium pigments include the following[43]:

- Cadmium yellow (Cadmium sulfide- CdS): C.I Pigment Yellow 37
- Cadmium sulfoselenide red: C.I Pigment Red 108
- Cadmium sulfoselenide orange: C.I Pigment Orange 20
- Zinc cadmium sulfide: C.I Pigment Yellow 35.

Cadmium yellows and reds act as heat-resistant pigments (work up to temperatures well above 300°C) and are used in coatings for process chemicals and steam pipes. It is also incorporated in latex and acrylic coatings.[42]

Health impacts of cadmium

Cadmium compounds get accumulated in the kidney leading to renal tubular dysfunction, which results in increased excretion of low molecular weight proteins in the urine and it is generally irreversible. In humans, the biological half-life is 10–35 years. It has been classified as extremely toxic by Occupational Safety and Health Administration.[44,45]

Disturbances in calcium metabolism and the formation of kidney stones are noticed with high intake of cadmium. Softening of the bones and osteoporosis may occur in those working in cadmium-contaminated areas. In an area of Japan where soil was contaminated with cadmium from zinc/lead mines, Itai-itai disease used to be widespread and its symptoms are still seen in women over 50 years of age.[44]

Long-term occupational exposure to cadmium through cadmium fume leads to the development of lung cancer. There is limited evidence that cadmium may also cause kidney and prostate cancer. International Agency for Research on Cancer (IARC) has defined cadmium and cadmium compounds as carcinogenic to humans (Group 1), indicating that there is enough evidence for their carcinogenicity in humans.[44]

Regulations on use of cadmium in paints

European countries have banned uses of cadmium and cadmium compounds as stabilizers in plastics, colorants in plastics and paint, etc.[41]

The European Chemical Agency Commission had given proposal to amend the REACH restriction provisions covering cadmium entry 23 in Annex XVII of REACH and contained the following provision dealing with the placing on the market of paints: “Paints shall not be placed on the market if the concentration in cadmium (expressed as Cd metal) is greater than 0.01% by weight.”[46]

Approaches for cadmium-free paint development

Many alternatives are available in the market. The choice is a matter of costs versus color and other preferred characteristics like weather resistance, torsion stability, and brilliance. For example, Hansa yellow developed in 1911 is cooler (dull) than cadmium yellow; it is not a perfect match and is usually combined with other pigments to create the required hue. Indian yellow is nearer to cadmium, but has its own fundamental qualities such as larger pigment particles, which also makes it highly opaque. For making cool reds, quinacridone pigment is used. Decent warm red became available as a cadmium alternative only when naphthol red was introduced. Figure 5 shows the comparative hue of cadmium yellow and other alternatives. Currently, many new combinations are available to create wide range of colors.[45]

Chromium

Introduction

Chromium is a transitional metal with the symbol Cr. It has the atomic number 24 and the relative atomic mass of 51.99. Chromium metal is a lustrous, hard, brittle transition metal and steel-gray in color. While chromium metal and Cr (III) ions are not considered toxic, hexavalent chromium (Cr (VI)) is both toxic and carcinogenic.[47,48]

Chromium uses today

Hexavalent chromium remains the benchmark corrosion preventive compound in essentially all industries.[36] The formation of metal alloys accounts for 85% of the available chromium’s usage. The excess of chromium is used in the chemical, refractory, and foundry industries.[49]

Chromium in paints

Chromium compounds are mainly used as pigments and have various uses, namely

- Crocoite (lead chromate, $PbCrO_4$) was used as a yellow pigment. It has very strong yellow color.
- The deep red shade of chrome red pigment, which is lead chromate with lead (II) hydroxide ($PbCrO_4 \cdot Pb(OH)_2$), is widely used to formulate red oxide primer.
- Chrome green is a mixture of Prussian blue and chrome yellow.
- Green chromium (III) oxide is extremely lightfast and as such is used in cladding coatings. It is also the main ingredient in infrared reflecting paints used by the armed forces to paint vehicles and to give them the same infrared reflectance as green leaves, e.g., Chrome green (PG17): Anhydrous Chromium (III) oxide (Cr_2O_3),[47] Viridian (PG18): Hydrated Chromium (III) oxide $Cr_2O_3 \cdot 2H_2O$.[50,51]

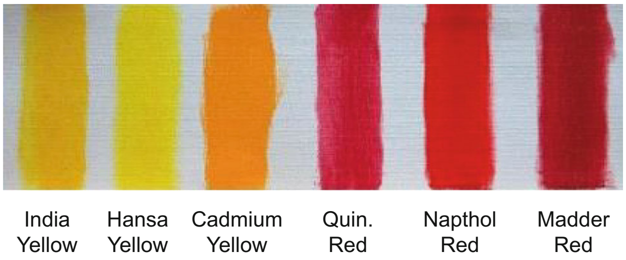

Fig. 5: Comparison of yellows and red pigments[45]

Health impacts of chromium

Hexavalent Chromium: Hexavalent chromium is now known to induce irreversible health damage including nose, throat, eye, and skin irritation and significantly increases an individual's risk of lung cancer. In addition, chromates have also been documented to induce genotoxicity on aquatic and botanic life through soil and water contamination.[36]

Challenges in chromium-free developments in paints

The Cr_2O_3 film can serve as a barrier to corrosion, given its relative insolubility in aqueous environments that span the environmental pH spectrum, and its adherence to the underlying metal. A similar ''worldwide'' anticorrosion compound is yet to be found out for implementation in coatings and primers.[36,52]

Approaches for chromium-free paint development

Trivalent chromium-based formulations remain the most common Cr6+ replacement to date for chemical conversion coatings on aluminum or zinc alloys. Other approaches include rare earth (Ce or La)-based composition; vanadate-based composition, Li containing composition, and phosphate-based coatings.[36]

An alternative for lead chromes has been covered under the ''Lead'' element section. Regarding alternates for green chromium oxides, pigment grades PG17 and PG18 are now replaced with Pigment Green 7.

Mercury

Introduction

Mercury is a chemical element represented by the symbol Hg. It has the atomic number 80, and its atomic mass is 200.59. It is commonly known as quicksilver. It is a heavy and silver colored metal and is the only metallic element that is liquid at standard conditions of temperature and pressure.[53]

Mercury uses today

Mostly mercury metal is used in thermometers, barometers, manometers, sphygmomanometers, float valves, mercury switches, mercury relays, and other devices. Mercury as an amalgam is used for dental restoration. It is also used in fluorescent lighting.[54,55]

Mercury in paints

Phenyl mercuric acetate is regularly added by some paint manufacturers to interior latex (water-based) paint as a fungicide and bactericide to enhance the paint's shelf life.[56] Mercury compounds were used in antifouling paints, where their main role was as a biocide and helped prevent growth of barnacles and molds on ship hulls. Other uses include the brilliant red pigment vermilion, which is obtained by grinding natural cinnabar or synthetic mercuric sulfide.[57]

Health impacts of mercury

Mercury poisoning symptoms include muscle weakness, poor coordination, numbness in the hands and feet, skin rashes, anxiety, memory problems, trouble speaking, hearing, or seeing.[58] High-level exposure to methyl mercury is known as Minamata disease. Methyl mercury exposure in children may result in acrodynia (also called as pink disease) in which the skin becomes pink and peels. Long-term complications may include kidney problems and decreased intelligence.[59] Heavy or prolonged exposure can do irreversible damage, in particular in fetuses, infants, and young children. Young's syndrome is suspected to be a long-term consequence of early childhood mercury poisoning.[60]

Approaches for mercury-free paint development

There are several replacements identified for mercury-based pigments. Vermilion pigment was replaced initially with cadmium red pigments. But this was also found to be hazardous and hence also replaced. Today, a lot of alternatives are available in modified azo pigment range and polycyclic compounds. This has been covered in detail in the ''Lead'' and ''Cadmium'' element sections.

Use in antifouling paints was replaced initially with tin compounds and later with copper compounds along with biocides. This is covered in detail in the ''tin'' element section.

Arsenic

Introduction

Arsenic is a chemical element and represented by the symbol As. It has the atomic number 33, and its atomic mass is 74.92. It is available as pure elemental crystals or as mineral compounds, generally in combination with sulfur and metals. Arsenic is a metalloid and occurs in various allotropic forms. The gray form, which has a metallic appearance, is most used by the industry.[61]

Arsenic uses today

Arsenic and its compounds have been produced and used commercially for many centuries. Arsenic is used currently and historically as a wood preservative, in pharmaceuticals, in agricultural chemicals, and for applications in the mining, metallurgical, glass-making, and semiconductor industries.

Arsenic and arsenic compounds are widely used in the manufacture of pigments, sheep-dips, leather preservatives, and poisonous baits. They are also used as pharmaceutical substances, pyrotechnics, dyes and soaps, ceramics, and in electrophotography.[62]

Arsenic in paints

In earlier days, arsenic was being used in the form of bright orange and yellow pigments called as Realgar and Orpiment (arsenic sulfide), respectively. These pigments used to fade on weathering.[63] Scheele's green which is chemically copper arsenite ($CuHAsO_3$) and Paris green ($CuOAs_2O_3{\cdot}Cu\ (C_2H_3O_2)_2$) were two other pigments which were prominently used as pigments but have been discontinued due to their toxicity.

Arsenic was used as an antifouling agent in paints. Many antifouling compounds like mercury, DDT and organotin compounds including arsenic have been widely banned and others including copper continue to be under scrutiny.[61,64]

Health impacts of arsenic

Arsenic and its compounds have been linked to both cancerous and noncancerous health effects. These include cancer of the bladder, nasal passages, skin, lungs, kidney, liver, and prostate. Arsenic ingestion has also been linked to cardiovascular, pulmonary, immunological, and neurological effects. Prolonged exposure to arsenic may cause several diseases popularly known as arsenicosis.[65]

Approaches for arsenic-free paint development

Arsenic pigments in coatings can be replaced with modified azo pigment range and polycyclic compounds. This has been covered in detail in the "Lead" element section. Use of arsenic in antifouling coating has been superseded by lead compounds and recently by copper compounds.

Antimony

Introduction

Antimony is a chemical element and represented by the symbol Sb. It has the atomic number 51, and its atomic mass is 121.76. It has a lustrous gray color and is found in nature mainly as the sulfide mineral stibnite (Sb_2S_3). Antimony compounds have been known since ancient times and were powdered for use in medicine and cosmetics.[66]

Antimony uses today

Antimony is used in production of polyethylene terephthalate as catalyst. It is also used as fining agent to remove microscopic bubbles in glass, mostly of digital screens. Antimony also possesses a semiconductor property and is used in semiconductors as a dopant in n-type silicon wafers specially used in infrared sensors.[67,68]

Antimony in paints

Antimony is widely used in fire retardant applications; the flame-retardant property comes by the formation of halogenated antimony compounds with use of antimony trioxide.[69] It is also used with polyester resin along with fiberglass to provide flame-retardant coating for light items like light aircraft engine covers. Antimony used to act as antichalking agents in old paints while new paint compositions used antimony for producing brightly colored paints.

Health impacts of antimony

A few compounds of antimony are toxic in nature, especially antimony trioxide and antimony potassium tartrate.[70] Antimony exposure shows similar effects to arsenic poisoning.[71] Workplace (occupational) exposure may cause respiratory irritation, pneumoconiosis, antimony spots on the skin, gastrointestinal symptoms, and cardiac arrhythmias. In addition, antimony trioxide is potentially carcinogenic to humans.[72]

Approaches for antimony-free paint development

Antimony compounds have been replaced with titanium dioxide in most applications and where fire resistance property is required, by intumescent compositions based on boron, etc.

Tin

Introduction

Tin is a post-transitional metal with the symbol Sn. It has the atomic number 50 and relative atomic mass of 118.71. It is a silvery metal that characteristically has a faint yellow hue.[1] It is basically produced from the mineral cassiterite, which contains stannic oxide, SnO_2.[73]

Metallic tin does not easily oxidize and resists corrosion because it is protected by an oxide film. Tin resists corrosion from demineralized water and soft tap water. It can be attacked by strong acids, alkalis and acid salts.[74]

Tin uses today

Tin is used in the form of alloys along with other metals. Bronze (made of 1/8 tin and 7/8 copper) is used for hatchets, mirrors, and sickles. Pewter (85–90% tin, and copper, antimony, and lead) is used for making kettles, pots, cups, and plates. Bell metal, a copper–tin alloy containing 22% tin, is used for making bells and related instruments. The niobium–tin alloy (Nb_3Sn) is used for superconductors; tin oxide is used for making ceramics and in gas sensors.[73,74]

Tin has been used along with lead for soldering mainly for pipes and electric circuits. Nowadays, tin is widely used in food preservation in the form of tin cans, as it has high resistance to corrosion. Organotin compounds are used as PVC stabilizers for plastics. Organotin compounds also have its applications in the electrodes of batteries such as in the Li-ion batteries. They are also used for their biocidal properties as fungicides, pesticides, algaecides, antifouling agents, and wood preservatives.[73]

Tin in paints

As such, tin metal is not used in coating industry. Normally, organotin compounds are used in paints. Organotin are compounds composed of one to four organic components attached to a tin atom via carbon-tin covalent bonds, e.g., tributyl tin (TBT) compounds.[75] TBT compounds are a highly toxic biocide material that has been used widely in antifouling paints to prevent the growth of marine organisms on the hulls of large ships.[75,76] Figure 6 shows a typical picture of marine growth on hull of a boat.

Fig. 6: Without antifouling paint coating[78]

Another major use of organotin compounds is in 2K polyurethane coatings as a catalyst. Dibutyltin dilaurate (DBTDL) is one of the most preferred compounds for 2K polyurethane systems and is considered as the workhorse of urethane catalytic reaction. DBTDL shows excellent catalytic activity because of its Lewis acid properties. It forms a complex structure with the central tin element of DBTDL with the -NCO group, which is a key step in the catalysis of urethane reaction.[77]

In electrocoats, also, tin compounds are known to be used as catalyst for good curing, especially at low temperature. But newer versions of electrocoats are now available which are tin free.

Health impacts of tin

Tributyltin can enter the body by inhalation of contaminated air, ingestion of contaminated food or through contact with the skin. Shipyard workers exposed to TBT (exposed to dusts and vapors) developed skin irritation, difficulty in breathing, dizziness, and flu-like symptoms. Eyes and nasal openings may also become irritated upon exposure. Excretion of TBT happens through the bile rather than the urine. TBT can be transferred across the blood–brain barrier and from the placenta to the fetus.[75]

Tributyltin is extremely toxic to marine molluscs. The harmful effect of organotin on the reproduction and growth of various marine life forms has resulted in regulations to restrict, or if possible eliminate its use by many countries.[75,79]

Regulations on use of tin in paints

Many countries have restricted the use of TBT antifouling paints because of effects on shellfish. The regulations vary from country to country, but most ban the use of TBT paints on boats 25 meters in length or less and abolish the use of antifouling paints with an average leaching rate of more than 4 micrograms of TBT per square cm per day. Some countries have excluded boats with aluminum hulls from this ban.[75,80]

Approaches for tin-free paint development

There are numerous patents and ideas relating to biofouling control, but as of now, few have been found to be practical, economical, or effective.[81]

Copper

The most common alternative biocide to organotin compounds is copper. This is mainly added to a paint matrix in the form of cuprous oxide. Copper-based antifouling paints also contain co-biocides, or booster biocides, to increase their efficacy against microfouling and algal slime. A few of the co-biocides used have an adverse environmental effect, which has led some countries to ban their use.

Nonstick and fouling-release

Considering the impact on the environment, nonstick and fouling-release technologies offer the most attractive options for biofouling control. Actual use of nonstick surfaces was stimulated after synthesis of polytetrafluoroethylene (PTFE) and other hydrophobic plastics in the late 1950s. However, these coatings were unable to impart sufficient nonstick characteristics to prevent attachment by macrofouling organisms.[81]

Silicones are the only identified alternatives to fluorinated compounds having nonstick and fouling-release properties.[81] The disadvantages of silicones include that they —

- Exhibit poor adhesion to the substrate
- Are easily damaged
- Require some form of hull cleaning
- Are expensive.

These drawbacks can be partially addressed by improved coating application and shipyard practice, improved fendering and hull care, and new technology for in-water cleaning.[81]

Copper–nickel alloy

As per research, it is known that the 90:10 copper–nickel alloys provide excellent mechanical, corrosion, and antifouling properties. They are used as the hull plate material on several boats and recently as cladding materials.[81]

Alternative catalyst

In 2K polyurethane systems, several metals compounds have been studied like salts or carboxylates of lead, mercury, zinc, manganese, iron, zirconium, bismuth, aluminum, nickel, and others as a catalyst.[77]

Bismuth being less toxic compared to tin metal was studied and reported to show good curing performance.[77] There are also reports of compounds like bismuth vanadate and zinc carboxylates being used as a catalyst in 2K polyurethane systems.

In the case of electrocoats, also, bismuth compounds have been used as a catalyst. Bismuth (in the form of bismuth trioxide) is adequately dispersed in electrocoating compositions and used as a catalyst to speed the reaction between epoxy amine adduct and polyisocyanate crosslinking agent. It resulted in very good film properties like adhesion, corrosion resistance, chip resistance, better than lead and tin catalyst.[82]

Nickel

Introduction

Nickel is a transitional metal with the symbol Ni. Its atomic number is 28 and relative atomic mass is 58.69. It is silvery white metal with slight golden tinge. It is known for its hardness and ductile properties and behaves as magnetic element at room temperature.[83,84]

Nickel uses today

The major use of nickel, nearly 70%, is in the production of stainless steel followed by nonferrous alloy, electroplating, and other industry. Nickel is widely used in many specific and recognizable industrial and consumer products, such as electric guitar strings, alnico magnets, coinage, and microphone capsules.[84,85]

Nickel in paints

Due to the corrosion resistance nature of nickel and its compounds, it has been used in paint formulation as pigments, e.g., nickel ferrite black, nickel rutile (PY 53). The use of these pigments has now been discontinued.[86]

Health impacts of nickel

Nickel is a naturally occurring element also known as Niccolum sulfuricums. Metallic nickel can have lethal and sublethal effects.[70] Exposure to nickel can be through food and water. Inhalation of paint odor is another major route of exposure, and it is the most hazardous. If soluble nickel is inhaled from a painted surface, it dissolves and enters into the kidneys and liver. Insoluble and metallic nickel remains in the lungs.[87] Long-term exposure may lead to asthma, bronchitis or other respiratory diseases.[88]

Approaches for nickel-free paint development

Nickel-based pigments are not in use nowadays and have been substituted with aluminum pigments, etc.

Manganese

Introduction

Manganese is a transition metal with the symbol Mn. Its atomic number is 25, and its atomic weight is 54.94. It is a silvery-gray metal that resembles iron. It is hard, very brittle, difficult to fuse and easy to oxidize. It is often found in minerals in combination with iron.[83,89]

Manganese uses today

Manganese is mostly used in stainless steel and aluminum alloy.[90,91] It is used in gasoline to increase the octane rating and reducing the knocking. Manganese oxide is used in Portland cement mixtures.[92,93] Manganese dioxide (MnO_2) is used to build amethyst glass and to counteract the yellowish green color of iron oxide in glass. It is used as a black glaze and for painting on porcelain.[94]

Manganese in paints

Manganese dioxide (MnO_2) ore is the primary source for manganese metal.[95] Both natural and synthetic manganese dioxide has been used as paint pigments and as a colorant in mortar. Manganese reacts with naphthenic and octoic acid-forming manganese naphthenate and manganese octoate which are used as auxiliary driers in paints.[94]

The following manganese-based pigments are used in paints[96]

- Manganese violet (manganese ammonium pyrophosphate, PV16)
- Manganese blue (barium manganate, PB33)
- Magnesium black (manganese dioxide, PBk14)
- Manganese ferrite (PBk26)

Health impacts of manganese

Manganese is an essential element of the human diet. In the human body, it is available as a coenzyme in several biological phenomena, which include metabolism of macronutrients, formation of bones, and free radical defense systems. It is a very critical chemical element in many proteins and enzymes.[97] The human body usually has 12 mg of manganese, mostly in the bones. Overexposure or intake may lead to a neurodegenerative disorder known as manganism that causes dopaminergic neuronal death and symptoms similar to Parkinson's disease.[98]

Approaches for manganese-free paint development

While alternates for pigments are now available, the use of manganese as paint driers (additives) is still being continued for want of an equivalent alternative.

Cobalt

Introduction

Cobalt is a ferromagnetic metal represented by symbol Co. Its atomic number is 27 and it has an atomic weight of 58.93.[83] It is a hard, lustrous, silver-gray metal. Cobalt is a weakly reducing metal; hence, it is protected from oxidation by a passivating oxide film.[99,100]

Cobalt uses today

To impart a rich blue color to glass, glazes, and ceramics, cobalt compounds have been majorly used for centuries.[101] Cobalt is mainly used in the form of alloys. Cobalt alloys with chromium and tungsten carbides are very hard and wear resistant.[102] Special cobalt–chromium–molybdenum alloys like vitallium are used for prosthetic parts (hip and knee replacements).[103] Lithium cobalt oxide ($LiCoO_2$) is widely used in lithium-ion battery cathodes. Several cobalt compounds are oxidation catalysts. Cobalt acetate is used to convert xylene into terephthalic acid. It is the precursor for the bulk polymer polyethylene terephthalate (PET bottles).[104]

Cobalt in paints

Before the 19th century, cobalt was primarily used as a pigment and it has been used since the middle ages to make smalt, a blue-colored glass.[105] It is also used as a base primer coat for porcelain enamels. The following cobalt-based pigments are used in paints[96]

- Cobalt violet (PV14 and PV49)
- Cobalt blue (PB72, PB73, PB74, PB28, PB35)
- Cobalt turquoise (PB36 and PG50)
- Cobalt green (PG19, PG26 and PG50)
- Cobalt yellow (PY40)
- Cobalt black (PBk13)

Cobalt reacts with naphthenic and octoic acid to form cobalt naphthenate and cobalt octoate which are used as drier in paints.[94,106] These are still being used in coatings. Cobalt soaps were introduced around 1900 and are the most significant active drier used in air-drying coatings for accelerating the autooxidation process. Cobalt can be present in more than one valence state and can readily undergo oxidation–reduction reactions. The various stages in the drying process, namely quiescent period, oxygen absorption, peroxide formation and decomposition, and free radical reaction, are highly impacted by the presence of cobalt drier.[107]

Health impacts of cobalt

Cobalt is an essential element for life in small amounts. The median lethal dose value for soluble cobalt salts has been estimated to be between 150 and 500 mg/kg.[108] The National Institute for Occupational Safety and Health (NIOSH) has set a recommended exposure limit (REL) of 0.05 mg/m^3 time-weighted average. The IDLH (Immediately Dangerous to Life and Health) value is 20 mg/m^3.[109] It causes respiratory problems when inhaled. It also causes skin problems when touched; after nickel and chromium, cobalt is a major cause of contact dermatitis.[110,111]

Approaches for cobalt-free paint development

Major use of cobalt in pigment form has reduced. But the use of cobalt as paint drier (additive) is still being continued.

There is no equivalent alternate for cobalt driers in nonmetallic compounds, as they do not show any catalytic activity as secondary driers. Among the other active driers, iron and cerium compounds have been proposed as replacements. But their performance varies with the environment conditions. Cerium works at low temperature and high humidity, whereas iron drier is most efficient at elevated temperature. The other most suggested alternate for cobalt driers is vanadium and manganese driers. Manganese driers are modified with chelating compounds to improve the catalytic activity. Commercially vanadium and manganese-based driers are available in the market as an alternate to cobalt drier.[112]

Other metal elements: zirconium (Zr), titanium (Ti) and zinc (Zn)

Zirconium

Zirconium is a chemical element with the symbol Zr, atomic number 40 and Atomic Mass 91.22. It is a very strong, malleable, ductile, and lustrous silvery-gray metal. Zirconium shows extremely resistant properties against heat and corrosion. The chief ore is zircon ($ZrSiO_4$).[113]

There are four majorly established areas of application for zirconium compounds:

(a) Zirconium paint driers (basically soaps of C8-C10 acids) used in oil-based coatings and paints. Conventionally the most regular ‘‘through driers’’ used to be lead compounds. This has now been replaced with zirconium drier. Zirconium shows better properties in terms of color, yellowing, and stability compared to other secondary driers.

(b) Thixotropic agents for colloid stabilized emulsion paints such as the Magnesium Elektron product Zirgel K.

(c) Zirconia, used in coatings for high ultraviolet light reflectance.

(d) Zirconia-coated titanium dioxide pigments improve their performance in coatings. [114]

One other area of application of zirconium is in pretreatment chemicals. These are inorganic compounds that form a chemical bond with the metal substrate, which enhances the adhesion and anticorrosive performance of the coating system. Almost all automotive and industrial OEM manufacturers have a pretreatment layer applied on their components prior to coating applications. This is also referred to as conversion coatings and is basically phosphate compounds. Traditionally, iron phosphate coatings and zinc phosphate were majorly used as pretreatment layers. Usually, a mix of metals like zinc, nickel, and manganese is used to get good corrosion resistance performance. The phosphate layer needs to be immediately coated with some coating layer as the pretreatment layer itself does not provide any barrier protection to the metal substrate.

Due to several process and performance benefits, iron and zinc phosphates are being replaced with zirconium conversion coatings. Zirconium coatings have the following advantages:

- Ability to work at ambient temperatures. Savings on energy consumption.
- Operating pH range of around 5, hence less corrosive.
- No phosphate generation/effluent discharge risk, which is restricted in certain countries.
- Unlike phosphate coatings, no accelerator is required in composition. Less sludge formation.
- Less hazardous to health and safety of the operators.[115]

Some reported disadvantages of zirconium coatings are flash rusting, iron build in bath, high coating weights, and alkaline drag-in.[115]

National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 5 mg/m^3 over an 8-hour workday (also as per Occupational Safety and Health Administration (OSHA)) and a short-term limit of 10 mg/m^3. At levels of 25 mg/m^3, zirconium is instantly dangerous to life and health. Nonetheless, zirconium is not viewed as an industrial health hazard. Moreover, reports of zirconium-related adverse reactions are rare and, in general, rigorous cause-and-effect relationships have not been established. There is no proof to date that zirconium is carcinogenic or genotoxic.[116,117]

Titanium

Titanium is a chemical element with the symbol Ti and atomic number 22 and atomic weight 47.86. It has low density and high strength, lustrous transition metal with a silver color. The element is present in a number of mineral deposits, principally rutile and ilmenite, which are widely distributed in the Earth's crust and lithosphere. The most common compound, titanium dioxide, is a popular photocatalyst and is used in the manufacture of white pigments[118]

Pigment-grade titanium dioxide is used in a range of applications including:

- *Paints and coatings*: It provides opacity and durability, while helping to ensure the longevity of the paint and protection of the painted surface.
- *Plastics, adhesives, and rubber*: It helps reduce the brittleness, fading, and cracking that can occur in plastics and other materials as a result of light exposure.
- *Cosmetics*: Pigment-grade TiO_2 is used in some cosmetics to aid in hiding blemishes and brightening the skin. It permits use of thinner coatings of make-up material for the same desired effect.
- *Paper*: Titanium dioxide is used to coat paper for making it whiter, brighter, and opaque.
- *Food contact materials and ingredients*: Titanium dioxide gives visible opacity and ultraviolet light protection to food, beverages, supplements, and pharmaceuticals thereby preventing premature degradation and increasing durability of the product. In specific cases, high purity pigment-grade titanium dioxide is also used in drug tablets, capsule coatings, and for decoration purpose in some food preparations.[119]

Titanium dioxide is the most widely used pigment in the coating industry. It was discovered in 1821 but went for bulk production only in 1916 by Titanium Pigment Corporation of Niagara Falls, New York, and the Titan Co. AS of Norway. Prior to this white lead (basic lead carbonate), zinc white (ZnO) and lithopone (mixture of barium sulfate and zinc sulfide) were being used as white pigment.[120] This has been identified as cancerous in CLP notifications sent to European Chemical Agency (ECHA).[121] Chemours, one of the biggest manufacturers of titanium dioxide, classified it under category 2 (irritant) as per GHS classification.[122]

International Agency for Research on Cancer (IARC) has also classified titanium dioxide as "possibly carcinogenic to humans," as per study on rat's which has showed increased lung tumors on inhalation. Nonetheless, immense studies on titanium dioxide industry workers did not indicate an association between occupational exposure to titanium dioxide and increased cancers in humans.[119] There has been no alternative identified to date having similar whiteness and refractive index (opacity) values. This is currently the primary choice of the world for whites. Green Seal, a global nonprofit organization founded in 1989 and involved in ecolabeling and certification of products and services also gave an exception for use of titanium dioxide under health and environment section.[123]

Workplace Exposure Limits of Titanium Dioxide:[124]

As per OSHA: The legal airborne PEL (permissible exposure limit) is 15 mg/m^3 average over an 8-hour work shift.

As per NIOSH: The REL (recommended exposure limit) is 2.4 mg/m^3 for fine titanium dioxide, and 0.3 mg/m^3 for ultrafine titanium dioxide, average over a 10-hour work shift.

As per ACGIH: The TLV (threshold limit value) is 10 mg/m^3 average over an 8-hour work shift.

Zinc

Zinc is a chemical element with the symbol Zn, atomic number 30, and atomic weight 65.38. Zinc is a slightly brittle metal at room temperature and turns blue-silvery color when oxidation is removed. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral. [125]

Zinc is a trace element; it is essential for human health and nontoxic. When a trace quantity is absorbed by the human body, loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores have been experienced. Shortage of zinc can cause birth defects. Humans can handle proportionally large amount of zinc; however, too much zinc can still lead to absolute health problems, like stomach cramps, nausea, skin irritations, vomiting, and anemia. Large-scale exposure to zinc chloride can cause respiratory disorders.[126,127]

In electromotive series (EMF), zinc is placed higher than metals like copper, mercury, iron, etc. Hence, it is used to remove the cations of these metals from solutions for anticorrosive purposes. Zinc is used in paint industry as zinc oxide, zinc dust, zinc phosphate, zinc chromate, and zinc octoate/naphthanate (drier).[128]

There is no established occupational exposure limit (OEL) for zinc as such, but it is available for zinc oxide which may be formed during processes of burning, welding, or other fuming processes.[128]

Workplace exposure limits of zinc oxide: [128]

As per **OSHA PEL** final rule limits for zinc oxide dust are 10 mg/m^3 (total) and 5 mg/m^3 (respirable).

As per **NIOSH REL** for zinc oxide (dust/fume) is 5 mg/m^3 10-hour TWA with a 15 mg/m^3 ceiling limit (15-minute sample) for zinc oxide dust and a 10 mg/m^3 STEL for zinc oxide fume (15-minute sample).

As per **ACGIH TLV** for zinc oxide is 2 mg/m^3 (respirable fraction) with a short-term exposure limit (STEL) of 10 mg/m^3 (respirable fraction).

Testing methods for detection of heavy metal elements in paints

Methods for measuring and monitoring the metal content in paint range from simple qualitative tests to highly accurate laboratory-based methods. The following analysis techniques are used to determine the metal content in liquid paints and painted film:

a. Use of chemical test kit-for laboratory or onsite testing.
b. Portable X-ray fluorescence (XRF) — device for onsite testing.
c. Laboratory tests using various analytical techniques.[6]

Chemical tests kits

There are several chemical test kits available to detect the presence of metal qualitatively as well as quantitatively with some approximation. The change in color of the chemical reagent is checked indicating the presence of the metal.[129]

The chemical kit tests the paint by two ways — (i) test the paint using a swab soaked in a chemical reagent that is rubbed onto the painted surface; (ii) require the removal of a chip of paint of a specified area that is then mixed with reagents in a tube.[129]

Examples: The sodium sulfide test and the sodium rhodizonate test for detection of lead. The chemical test solutions are colorless liquids. For testing purpose, it requires painted surface or scraped paint film from the substrate. For sodium sulfide test, if lead is present in the paint then sodium sulfide turns gray, brown, or even black and for sodium rhodizonate turns pink when lead is present.[4,52] Most advanced spot test kits use fluorometric or photometric methods on paint chips.[129] Typical chemical test kit is shown in Fig. 7.

Fig. 7: Wet chemical field tests (like Lead Check®)[52]

Advantages

Chemical test kits are simple, cheap, and immediate and do not require any specific training. The test can also be carried out onsite.[52,129]

Disadvantages

1. Unlike white paint, colored paints are hard to access.
2. The presence of other metals in sample can cause the same type of color change; hence, it is difficult to identify the metals present.
3. This is used as a qualitative test rather than a quantitative test.
4. Only exposed layers of paint can be tested; underlying layers of paint cannot be tested.
5. Dirt on plaster/paint surface can hide a color change.[52]

Engineering of the pigment composition by the pigment manufactures, to resist dissolution in standard acid used for chemical tests, thereby reporting nil/or lower values is also identified as a drawback of the chemical test method.[4]

Where exact quantification of metal content is required, other advanced methods are preferred. Other method used includes the following:

X-ray fluorescence (XRF) analysis

X-ray fluorescence spectrometry is built on the principle that when exposed to high-energy radiation, metal elements (like many other elements such as Pb, Mg, Al, Si, and P) emit X-rays at a characteristic frequency. The intensity of emitted X-rays can be measured and correlated with the amount of metal per unit area (milligrams per square centimeter).[52] Figure 8 shows a typical XRF spectrophotometer.

Portable XRF analyzer instruments can measure the total amount of metal in a painted surface in situ without damaging the paint film or the substrate. Portable XRF devices are very easy to operate but due to radiation hazard, require training prior to use.[129,130] Figure 9 shows a typical portable XRF spectrophotometer.

Advantages

1. The XRF machine is small and portable so it can be used on site.
2. The accuracy of portable XRF devices is rapid and good, but borderline measurements are confirmed by laboratory analysis method.

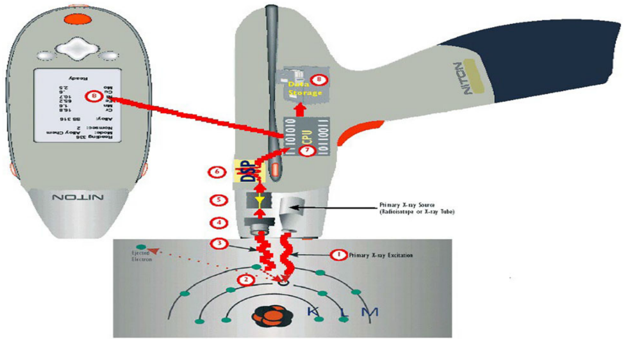

Fig. 8: XRF spectrophotometer[52]

Fig. 9: Portable XRF[131]

3. It does not damage the painted surface like paint chip laboratory analysis does hence most of the analyzers prefer this method.
4. Its memory can retain and display readings or download them to computer software and recall data whenever you want.
5. The instrument requires little maintenance and no consumables.[52,129]

Disadvantages

1. High humidity, high temperature, radio waves, and vibration can give erroneous readings.
2. Depending on their size and characteristics, XRF device requires a comparatively large and flat surface to do a measurement. Some surfaces like corners and narrow edges can be difficult to be measured by XRF. Newer generation instruments might be able to take care of this shortcoming.
3. They are relatively costlier.[52,129]

Laboratory-based analytical techniques

Laboratory analytical techniques require that a sample of paint, either liquid paint or dried film be removed from the surface and analyzed in a laboratory using various techniques.[129] Procedure involves extraction of metal compounds by acid digestion method followed by use of modern analysis instruments. The real testing can be done using different techniques.

Three regularly used methods are (in order of higher to lower limit of detection):

i. Flame atomic absorption spectrometry (FAAS)
ii. Graphite furnace atomic absorption spectrometry (GFAAS)
iii. Inductively coupled plasma optical emission spectrometry (ICP-OES)

Flame atomic absorption spectroscopy (FAAS)

Flame atomic absorption spectroscopy is a very common technique used for detection of metals present in samples. It is based on the principle that ground state metals absorb light at a specific wavelength and convert into vapors within the light path of the instrument by flame. When a known wavelength is supplied, the amount of light absorbed is measured and from readings concentrations of samples can be calculated. This technique is used for qualitative as well as quantitative determination of metal content.[129,132]

ADVANTAGES: FAAS is a sensitive technique for the quantitative determination of more than sixty metals.[129]

Graphite furnace absorption spectroscopy (GFAAS)

Basically, it is AAS technique in which an electrically heated graphite tube is heated at 3000°C to vaporize and atomize the analyte prior to its detection. It gives very low detection limits and requires only small amount of digested sample volumes. Measurement of GFAAS operates on significant interference from light scattering and molecular absorption by matrix components, but this can be adequately corrected using various approaches, including the use of matrix modifiers. GFAAS devices must be handled by trained laboratory technicians.

GFAAS devices are widely available, and options of autosamplers are also available to increase precision and productivity. Initial instrument cost is intermediate, and maintenance and consumable costs are notable.[129]

Inductively coupled plasma optical emission spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is also referred to as inductively coupled plasma atomic emission spectroscopy (ICP-

AES). It uses an inductively coupled plasma (a very high temperature ionized gas composed of electrons and positively charged ions) source to dissociate the sample into its constituent atoms or ions. Under these high-energy conditions, many elements emit light at characteristic wavelengths. The amount of light emitted can be measured and results correlated with the concentration of particular metal in the sample. This instrument is the most advanced and can determine several elements simultaneously.[129]

Paint companies and other environmental agencies now use ICP-OES instrument because of consistent and reliable results for the detection of lead and many other elements.[129]

Out of above three methods, chemical test kit and XRF methods are fastest test methods (speed test) to detect metal elements in paints while for accurate determination, laboratory analytical methods are used which can detect metal elements in less than parts per billion quantities.

Some of the international standards test methods for determination of heavy metals are as follows-

- ASTM D564 - 87 (2017) Standard Test Methods for Liquid Paint Driers[133]
- ASTME1613–04 This method is useful for determination of lead by inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), or graphite furnace atomic absorption spectrometry (GFAAS) techniques. West Conshohocken, PA, ASTM International, 2004.[129]
- ASTM E1645-01 (2007) Standard practice for preparation of dried paint samples by hotplate or microwave digestion for subsequent lead analysis. West Conshohocken, PA, ASTM International, 2007.[129]
- ASTM E1729 - 05 Standard practices for field collection of dried paint samples for subsequent lead determination, West Conshohocken, PA, ASTM International, 2005.[129]
- ASTM D2350 – 90 (2015) Standard Test Method for Antimony Oxide in White Pigment Separated from Solvent-Reducible Paints.[134]
- ASTM D2373-05 (2011) Standard Test Method for Determination of Cobalt in Paint Driers by EDTA Method.[135]
- ASTM D2375 – 05 Standard Test Method for Manganese in Paint Driers by EDTA Method.[136]
- ASTM D3335 - 85a (2020): Standard Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy.[10,137]
- ASTM D3624 - 85a (2015) Standard Test Method for Low Concentrations of Mercury in Paint by Atomic Absorption Spectroscopy.[138]
- ASTM D3717 - 85a (2015) Standard Test Method for Low Concentrations of Antimony in Paint by Atomic Absorption Spectroscopy.[139]
- CPSC-CH-E1003-09: Standard operating procedure for determining lead (Pb) in paint and other similar surface coatings. Gaithersburg, MD, United States Consumer Product B Safety Commission, 2009.[129]
- ISO 6503: Paints and varnishes — Determination of total lead — Flame atomic absorption spectrometric method.[10]
- OSHA Method ID-103 Hexavalent Chromium 1982, Revised February 1990.[140]

Conclusions

Heavy metals and other mentioned compounds are now proven to be hazardous for human beings as well as the environment. This has been made well known to all statutory officials and government bodies of the world, including the pigment and paint manufacturers through various initiatives by local government bodies as well as global NGOs platforms. However, the goal of achieving hazardous material-free products is yet to be achieved.

It is noticed that countries having legislations or regulations on hazardous material usage for decorative or household applications have better controls in their products. The government or statutory bodies should have a periodic monitoring plan in place to check adherence to regulations. Also, it is essential to have proper enforcement actions in place in case of noncompliance, namely penalties, confiscation of goods, stoppage of production, and in extreme cases even imprisonment. Wherever exceptions are allowed, proper labeling indicating "Hazardous Material" needs to be put in place alerting the users of the product. Most of the multinationals have moved away from heavy metals and other banned compounds for architectural segment. It is required that the local paint manufactures also start complying with the rules.

The technical challenges in replacing the heavy metals have been greatly sorted out by development of new alternates by the manufacturers. Now there are multiple options available to the paint chemist for replacing the hazardous materials. This includes organic pigments, inorganic pigments, hybrid pigments, complex inorganic color pigments and even can be tailor made as per requirement. For corrosion protection, several zinc compounds are now available providing equivalent performance.

With the available information on heavy metal-free alternatives, it is now possible to have paint products which can meet the global aspiration of making our products more user friendly and thereby safeguarding the health of its citizens as well as the environment.

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