Technical Guidelines for replacing lead oxide in anti-corrosives paints in Tunisia

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Introduction

IPEN has been contracted by the SwitchMed Programme through its Regional Activity Centre for Sustainable Consumption and Production (SCP/RAC) to produce this guideline for replacing lead oxide in anti-corrosive paint in Tunisia.

It is generally agreed that any large, multinational paint manufacturer that still produce lead paint have the means and capacity to quickly and efficiently replace these ingredients with safer alternatives. However, the paint market in many developing countries and countries in economic transition typically include Micro, Small and Medium-Sized Enterprises (MSMEs) that may face challenges to follow suit. Key obstacles that have been identified by MSMEs to reformulating lead paint includes access to information and guidance as well as access to safer alternatives to a competitive price.

The aim of the report was therefore to provide

- general information on paint manufacture such as paint ingredients and their properties, and the manufacturing process
- the use and properties of lead in anti-corrosive paint
- alternatives to lead in anti-corrosive paint and any implications for the paint production process
- specific information relevant to the Tunisian situation

Established in 1998, the International POPs Elimination Network (IPEN), is a global network of not for profit, public interest, civil society organizations in more than 125 countries, primarily developing countries and countries in economic transition, working on issues related to chemical safety. IPEN launched its Global Lead Paint Elimination Campaign in 2008. The Campaign works at international level in cooperation with the United Nations Environment Programme, the World Health Organization and other partners in the Global Alliance to Eliminate Lead Paint, and at the national level with NGO-led lead paint elimination campaigns and programs that promote regulatory controls on lead paint and that raise awareness among business entrepreneurs, government officials, and consumers about the adverse human health impacts of lead paint, particularly on the health of children. Since 2008, IPEN has assisted NGOs in sampling and analyzing paints in approximately 50 low- and middle-income countries and assisted follow up activities such as engaging with the local paint manufacturers to facilitate replacement of lead in their paint formulations.

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This guidance was reviewed by Technical experts at the Cleaner Production Center of Serbia[1] before finalization.

[1] http://www.cpc-serbia.org/

Background, Scope and methodology

Lead paint, i.e. paint that contains added lead compounds, were banned for consumer use in most highly industrial countries in the 1970s and 1980s and is progressively being banned in many countries for all other uses. However, lead paint is still being manufactured and sold in the majority of the countries of the world today.[2] Lead-containing paint ingredients are used for various purposes in paint, the most common ones are:

- Pigments: lead sulphochromate (yellow), lead chromate molybdate sulphate (red), lead carbonate (white), lead oxide (red, also called minium)
- Drying agents: lead naphthenate, lead octoate, lead versatate
- Corrosion inhibition in anti-corrosive coatings: lead (II, IV) oxide, also called minium

The use of lead in anti-corrosive paint was identified as a priority target in Tunisia under the SwitchMed programme, i.e. paint that are used to protect metal surfaces in homes and various industrial applications such as steel structures, machinery and appliances. This report will therefore focus on the replacement of lead oxide in anti-corrosive paint.

It should be noted that zinc chromate has also been used as an anti-corrosive pigment in paint. While the scope of this report does not include the replacement of zinc chromates, these are also toxic and should be replaced. Most of the information provided in this report will be relevant also for their replacement.

The information provided in this report is based on peer reviewed articles, literature on coatings technology, reliable online sources such as technical magazines aimed at the paint industry, interviews with paint manufacturers in Tunisia and the Philippines as well as providers of lead-free raw materials. Also, replacement manuals of lead-based compounds as pigments and drying agents were utilized.[3]

References for specific facts and statements have been provided through footnotes in the report and complemented by a list of materials for further reading that includes more general information at the end of the report.

Terminology

- Lead-free, unleaded and non-lead raw materials, compounds and ingredients all refers to chemicals added to paint that does not contain lead.
- Paint and coating is used synonymously throughout the report.
- An anti-corrosive paint is a paint that prevents surfaces from corroding through various mechanisms
- Anticorrosion pigment is a chemical substance added to paint that prevents corrosion, e.g. lead oxide.
- Lead oxide in this report refers to lead tetroxide (Pb_3O_4), red lead.

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[2] http://ipen.org/documents/lead-solvent-based-paints-home-use-global-report

[3] http://ipen.org/documents/replacement-lead-pigments-solvent-based-decorative-paints; http://ipen.org/documents/lead-drier-replacement-solvent-based-alkyd-decorative-paints

General considerations on paint formulation and the key steps of the reformulation process

Paint is typically made up of pigments, binders (also called resins), solvents, fillers and additives. During a paint formulation process, all these components will have to be adjusted and optimized to produce a paint with the intended quality and properties. The first step towards a new paint formulation is therefore to clearly define where the paint will be used and the essential properties of the paint.

Considerations for anti-corrosive paint include effectiveness, hiding power, stain resistance, ease of application, etc. It is also critical to consider requirements for the intended environment where the paint will be used such as salt resistance in marine environments, and any other special requirements such as high temperatures and/or use on abrasion surfaces.

Pigments are small particles of solid materials that are suspended in the paint to provide e.g. color, opacity (i.e. covering capacity) and color intensity. To obtain a specific shade or other required property of the paint, two or more pigments can be used where one provides color and specific properties such as weather resistance and a cheaper pigment might be added to provide opacity (i.e. covering capacity), hardness and adhesiveness of the paint film. The ratio between the two types of pigments as well as the ratio between pigments and binder are crucial in paint formulation to provide the intended properties of the paint to a competitive price. Lead oxide is an anti-corrosive pigment, sometimes also called anti-corrosive additive. While providing a red color its primary function is to prevent corrosion.

Binder (resin) forms a matrix that holds the pigments and additives in the paint film and comes in a wide variety of types and combinations to provide the optimum quality of the paint. Binders also makes the paint stick to the surface. Considerations when selecting binders will therefore include the type of surface the paint is intended for.

Solvent is the vehicle that carries the pigments, binders and additives in liquid paint. The most common solvents used are water and different kinds of organic solvents. Whereas there are additional technologies such as powder coatings, one common distinction is between water-based paint or solvent-based paint and each type is sold under a wide variety of descriptions. However, a water-based paint does not necessarily contain only water since a small amount of organic solvent is sometimes added to the paint as co-solvent to facilitate complete drying of the paint film. The paint solvent also impacts the other components of the paint, since water and organic solvents have very different chemical properties. Anti-corrosive paint can be either solvent-based or water-based, but require different considerations depending on the chosen solvent. Lead oxide is typically only used in solvent-based paint.

During the paint manufacturing process, the lead oxide powder is broken down into individual particles which are coated by and dispersed in the binder. The process is facilitated by adding wetting and dispersing agents in addition to solvents to adjust viscosity. This is known as 'wetting out'. Solvent and potential additives are then added to give the required consistency and specific properties. Each batch of paint is thoroughly mixed in large, stirred containers and mounts ranging up to 40 000 dm^3 of paint may be made in a single batch.

In a reformulation process, both obtaining the required essential paint properties as well as considerations in relation to the manufacturing process must be taken into account. Not only may the replacements demand durability during harsh temperature, weathering or abrasion conditions, additional stirring of the paint at higher speeds may be necessary to completely disperse the pigment. It is also important to evaluate potential toxicity of the replacement to avoid so-called regrettable substitutions, since some alternatives contain other toxic metals such as chromates[4] or have other hazardous properties.

While each paint needs specific considerations based on its brand-specific properties, a general outline of the reformulation process is provided below. Several options for alternative formulations are often available and the process will include a trial-and-error approach to find the most cost-effective formula. Access to technical advice is key throughout this process to ensure that the lead-free paint ingredients provide the same essential properties to the paint. This support is typically provided by the suppliers of raw materials for smaller paint manufacturers without in-house paint chemists or labs.

To ensure the effectiveness of the new paint there are several standardized functional corrosion protection tests that can be utilized depending on the purpose of the paint and the intended environment for use. For example, ISO Technical Committee (ISO/TC 156 Corrosion of metals and alloys) has developed 88 standards in the field of corrosion of metals and alloys including corrosion test methods, corrosion prevention methods and corrosion control engineering life cycle, with further 24 under development.[5] Some of the technical details of such tests are described further in the publicly available coatings resource *BASF Handbook Basics of Coating Technology* (see link in general references).

There is a multitude of technical consultant companies in Europe, the U.S., Asia and elsewhere that provides the service of so called accelerated testing of coatings according to these standards. This includes subjecting the sample coatings to controlled environmental variables such as humidity, light, heat and air pollutants but in a way that the corrosion process is accelerated, and the durability of the paint can be evaluated rapidly instead of the often slow natural process.

For manufacturers without in-house labs, this could be a cost-effective option when evaluating the new paint formulations.

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[4] https://en.wikipedia.org/wiki/List_of_inorganic_pigments

[5] https://www.iso.org/committee/53264/x/catalogue/

Process step	Considerations
1. Inventory of leaded paint ingredients currently used	In which paints are leaded raw materials used? What properties are they providing?
2. Define required paint product properties	E.g. hiding power, weather resistance, stain resistance, ease of application, etc.
3. Investigate lead-free replacements	What alternatives are available? Are there single substance replacements or must a combination of alternatives be used? Will my current supplier be able to provide these replacements to a competitive price?
4. Reformulation Process: Trial and error using different alternatives	Do we have in-house experts that can provide advice in the process, or do we need to seek outside expertise?
5. Evaluation of new paint properties	Does the replacement(s) provide the intended properties? Is the intended quality obtained?
6. Final new paint product	Is this the most cost-effective way to produce this paint? Do I need to increase the retail price?

The use of lead oxide as anti-corrosive pigments in paint

Metal surfaces are prone to corrosion, especially in humid climates and marine environments. However, there is typically little need for corrosion protection in very dry areas. Many factors can increase the corrosion process, for example the salts present in marine environments, air pollutants such as sulphur dioxide and a low pH. Even a small amount of corrosion can be detrimental to the function of the surface and hence very costly. It is also of environmental importance for materials to have a high durability in terms of energy and raw material efficiency. Corrosion prevention is therefore of high priority, especially to metals of high industrial importance such as iron and steel.

Corrosion is defined by ISO as a "physicochemical interaction between a metal and its environment that results in changes in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system, of which these form a part".[6]

The corrosion process is galvanic, i.e. it is an electro-chemical reaction where electrons are transferred from the metal (the anode) to the oxygen (the cathode). For iron and steel surfaces a metal oxide commonly known as rust is formed. This occurs spontaneously for many metals when exposed to air in a humid environment. Many text books describe this process in detail in relation to protective coatings, see e.g. (Tracton, 2007) in the list of further reading at the end of the technical guidance.

This process can be inhibited through various, non-exclusive, mechanisms provided by a coating. The coating can serve as a physical barrier to the outside environment preventing access to corrosion inducing substances. The coating can also serve as an insulator preventing the galvanic process to occur. Finally, chemicals such as lead oxide in the coating can serve as anti-corrosive pigments (Kendig & Mills, 2017). According to ISO, a corrosion inhibitor is defined as a "chemical substance that when present in the corrosion system at a suitable concentration decreases the corrosion rate, without significantly changing the concentration of any corrosive agent".[7]

The choice of anticorrosive agent depends on the metal. One of the most commonly used anti-corrosive pigments on steel and iron structures is lead oxide (Pb_3O_4, red lead). This function comes both from the ability of lead oxide to provide good mechanical strength, water resistance, and adhesion to the steel surface, as well as its ability to bind corrosion-promoting chloride and sulfate ions (Van Alphen, 1998). In a red lead anti-corrosive paint the lead content is typically very high, more than 50% of the dry weight of the paint. Lead oxide is unsuitable for preventing corrosion on aluminum surfaces.

Alternatives to lead oxide in anti-corrosive paint and their properties

There is a range of anti-corrosive pigments with varying properties, effectiveness and cost that can replace lead oxide. These can be classified in different ways, for example based on their chemical composition as inorganic or organic or through their mechanism of corrosion protection as anodic, cathodic or anodic-cathodic mix. Inorganic

[6] https://www.iso.org/obp/ui/#iso:std:iso:8044:ed-4:v1:en
[7] https://www.iso.org/obp/ui/#iso:std:iso:8044:ed-4:v1:en

anti-corrosive pigments generally works through inhibiting the reactions at the cathode or anode, whereas the organic anti-corrosive pigments generally works through forming a film adsorbing to the surface and protecting it (Dariva & Galio, 2014).

The most common replacement for lead oxide in solvent-based anti-corrosive paint for general use is zinc phosphate and zinc-aluminium phosphates, the latter being one of its so-called second-generation pigments. Zinc phosphate is a cost-effective replacement with a straight-forward application and the addition of aluminium further increases its protective properties. It should be noted that these alternatives provide a grey color instead of the traditional red. However, corrosion protection paints are in most cases used as so-called primers, i.e. they are applied on metal surfaces solely to provide protection and are then covered with additional layers of paint, and their color is therefore not a key feature.

These zinc phosphates provide their corrosion protection by acting as an anode instead of the iron or steel surface and providing cathodic protection, i.e. releasing electrons to the iron and thus preventing it to release electrons and degrade. Through this process oxides are formed, which provides an additional physical barrier that protects the surface from corroding.

For producing paints with top-of-the-line anticorrosive properties, zinc dust is sometimes used in combination with a suitable binder. However, this is a very expensive technology primarily offered by the largest paint manufacturers.

Other replacements include calcium and barium phospho-silicates and boro-silicates. Two complementary anti-corrosive mechanisms are suggested for these, that they both act by increasing the pH in contact with water as well as a similar mechanism to that of zinc.[8]

Process related issues to replacing lead oxide in anti-corrosive paint

Case Study with Paint Manufacturer Pacific Paint (Boysen) Philippines

Research and Development

When Boysen started reformulating their anticorrosive paints in 2005, it took them less than one year to undertake the research and development processes necessary to reformulate their anticorrosive paints. Marketing, obtaining necessary certificates, and other government requirements took some additional months, meaning that the whole process took slightly more than a year from start until having finished products for sale. No changes in the production process were needed for the new paint formulations.

During the reformulation process, samples of the new, alternative formulations were sent to a third-party laboratory in the US for accelerated testing of their effectiveness and other key properties of the paint. The accelerated testing paves the way for shorter turn-around time (TAT) to get results. TAT varied depending on the expected performance of the product but in general, anticorrosive paints have a TAT of 100 hours whereas anticorrosive marine paints may take around 300 to 500 hours of TAT. During

[8] Jones, F.N., Nichols, M.E., Socrates, P. (2017). Organic Coatings: Science and Technology https://www.wiley.com/en-us/Organic+Coatings%3A+Science+and+Technology%2C+4th+Edition-p-9781119026891

the reformulation process, Boysen decided to invest in an in-house salt spray/cyclic corrosion chamber for accelerated testing.

For preparing the test samples, Boysen used standardized cold rolled steel (CRS) certified through ASTM or ISO to ensure reliability and reproducibility. While there is cheaper CRS sold in hardware shops these rolls may vary depending on the location on the roll the steel the samples are taken as well as in between batches and produce unreliable results.

Choice of Pigment/Color

Since lead oxide has a strong color, certain opacity and good anticorrosive properties, several alternative pigments and raw materials were tried to address these properties. In the end they selected zinc phosphate as the most cost-effective replacement providing the necessary anti-corrosion properties. However, they found that it was difficult to substitute the exact color of lead oxide (bright orange) with alternatives like iron oxides, e.g. red oxide and yellow oxide. They therefore decided to stop trying to produce anti-corrosive paint with bright orange colors and instead focused on promoting the gray colors provided by zinc phosphate. One key approach was to educate their customers by explaining that anticorrosive paints are undercoats that are typically covered by additional layers of topcoats and that the color does not matter. The success of their reformulation and subsequent promotion of the new grey formulations is verified through the sustained sales of their anti-corrosive brand.

Choice of Solvent

One other consideration had to do with the impact of solvent when changing the paint formulation for more specialized paint such as paint used in marine environments and reflectorized road marking paint. The specialized paints require specific binders that will impact what solvent or combination of solvents are used to uniformly dissolve all film-forming ingredients in paints, and may therefore require a longer reformulation time.

Cost implications of replacing lead oxide in anti-corrosive paint

The cost of the reformulation process can be divided into two types, the direct costs of the raw materials, testing of new formulations and potential new equipment and the indirect costs incurred by devoting staff time to the process. However, using safer alternatives may also lead to cost savings throughout the production chain, e.g. in handling less hazardous waste.

The direct costs of the lead-free raw materials compared to lead oxide must be calculated as the production cost of the whole paint. Since paint is a combination of various components, it is unlikely that the new paint formulation is a simple 1:1 replacement of lead oxide with an alternative, but rather an optimized combination of the replacement and other paint ingredients in the most cost-effective way.

In the case of Boysen, they increased the price of their new anticorrosive paints by ten percent or more depending on product and production volumes. However, their sales did not suffer from this increase. In fact, since they very successful introduced a new grey anti-corrosive product line, other manufacturers saw the potential for sales and introduced similar products. In time, the competition on the market will stimulate innovation and lead to competitive prices for these paints.

As demand for alternatives is increasing, price of the alternatives is gradually going down. At the same time the price of lead has increased approximately three times since 2005.[9] This means that the financial implications of replacing lead oxide is becoming less and less dependent on the paint ingredients.

It is likely that many Micro, Small and Medium-Sized paint manufacturers lack in-house capacity for accelerated corrosion protection testing or financial means for setting-up such facilities. In addition, some may lack the technical know-how, making it more difficult for them to undertake research and develop alternative formulations to lead-containing anticorrosive paints.

A cost-saving approach that have been suggested are for manufacturers to work closely with experienced raw material suppliers that can provide detailed knowledge about the durability, corrosion protection and other properties of replacement formulas. Also, groups of manufacturers and/or manufacturer´s Associations can negotiate as a group with technical consultants to provide the necessary tests to a reduced price.

Aspects of replacing lead oxide in anti-corrosive paint related to the Tunisian

[9] http://markets.businessinsider.com/commodities/lead-price

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Appendix 1 -Suppliers of alternatives to lead oxide

Company name	**Country HQ**	**Website**
Alba Aluminiu	Romania	http://www.albaaluminiu.ro/
AVL	Belgium	https://www.avlmetalpowders.com/en
BASF	Germany	http://www.basf-coatings.com/global/ecweb/en/
BassTech International	USA	http://basstechintl.com/
Clariant	Switzerland	https://www.clariant.com/en/Corporate
ECKART	Germany	https://www.eckart.net/
Evonik	Germany	http://corporate.evonik.com/en
Ferro	USA	https://www.ferro.com/
Grace	USA	https://grace.com/en-us
Heubach	Germany	https://www.heubachcolor.com/
Hoffmann Mineral	Germany	https://www.hoffmann-mineral.com/Highlights
ICL\ Advanced Additives: HALOX®	USA	https://www.halox.com/
New Brook International, Inc.	USA	http://www.newbrookintl.com/
Novasol	Belgium	Novasol North America Inc
Revelli Chemicals	USA	Revelli Chemicals
Sasol Performance Chemicals	South Africa	http://www.sasol.com
Sun Chemical	USA	http://www.sunchemical.com/
UNIQCHEM	Germany	http://www.uniqchem.com/
Venator	UK	http://www.venatorcorp.com/