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Global Best Practices on
Emerging Chemicals Policy Issues of Concern
under the Strategic Approach to International
Chemicals Management

Lead Paint Reformulation Technical Guidelines

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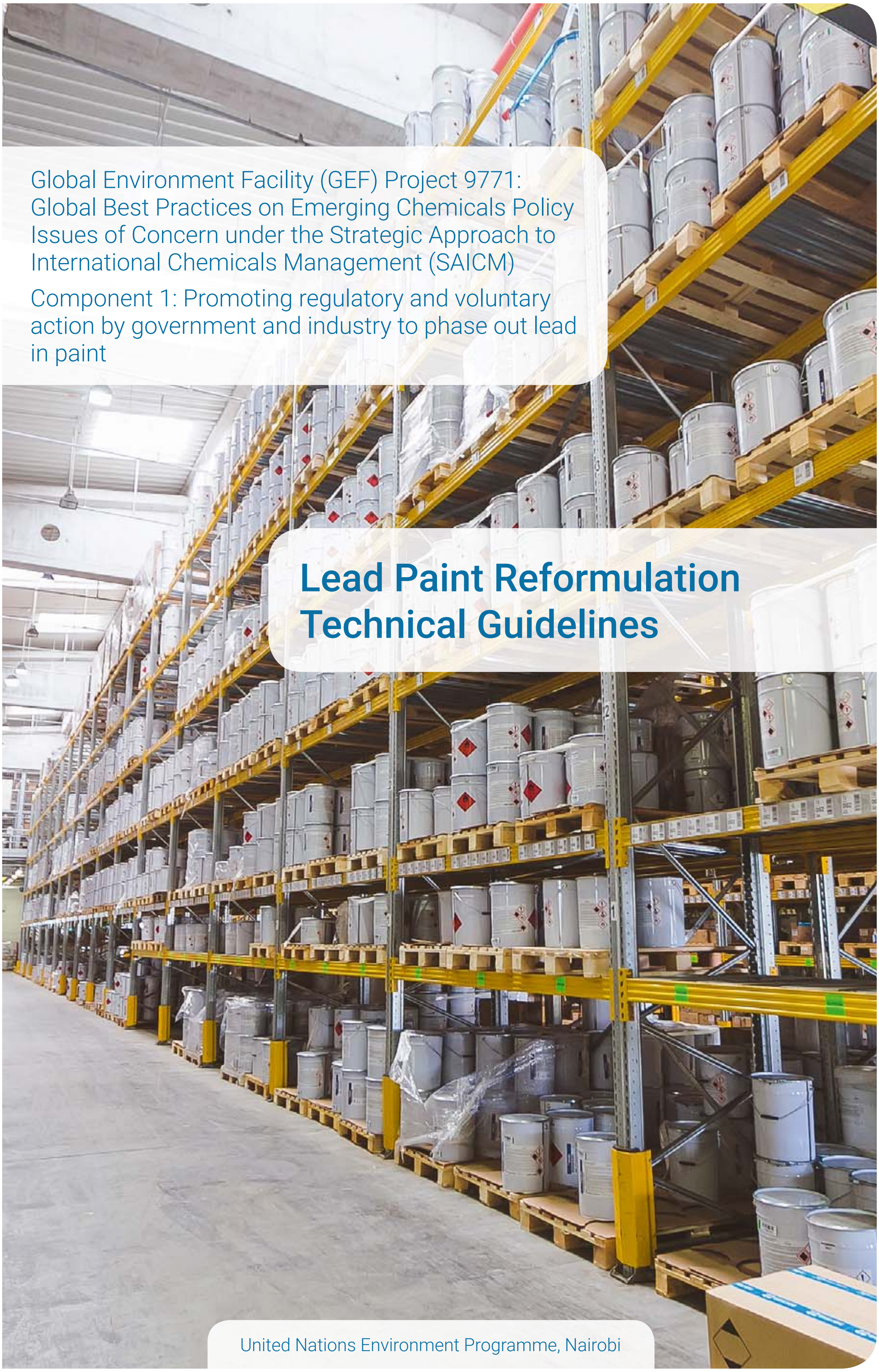
Global Environment Facility (GEF) Project 9771: Global Best Practices on Emerging Chemicals Policy Issues of Concern under the Strategic Approach to International Chemicals Management (SAICM)

Component 1: Promoting regulatory and voluntary action by government and industry to phase out lead in paint

Lead Paint Reformulation Technical Guidelines



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United Nations Environment Programme, Nairobi

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List of Acronyms

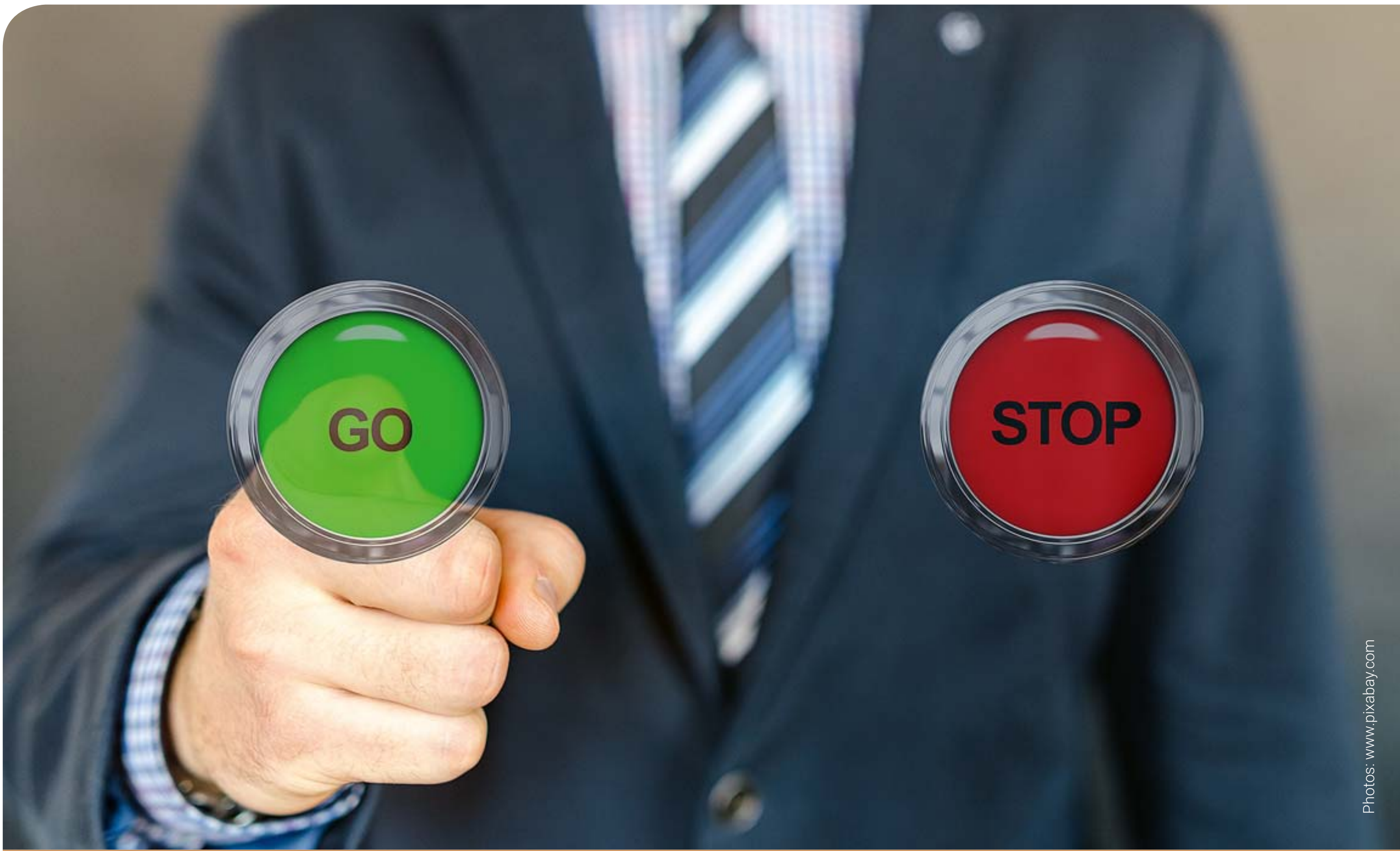
ABA-ROLI	American Bar Association Rule of Law Initiative
CAS	Chemical Abstracts Service (Division of the American Chemical Society)
CI	Color Index
CPVC	Critical Pigment Volume Concentration
EPI	Emerging Policy Issues
GEF	Global Environment Facility
GHS	Globally Harmonized System of Classif cation and Labelling of Chemicals
HEAL	Health and Environmental Alliance
IARC	International Agency for Research on Cancer
ICCM	The International Conference on Chemicals Management
IPEN	International Pollutants Elimination Network
ISO	International Organization for Standardization
NCPC	National Cleaner Production Centre
NGO	Non-governmental Organization
PBr	Pigment Brown
PO	Pigment Orange
PR	Pigment Red
PY	Pigment Yellow
PVC	Pigment Volume Concentration
PW	Pigment White
P2OASys	Pollution Prevention Options Analysis System
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SAICM	Strategic Approach to International Chemicals Management
SDS	Safety Data Sheet
SME	Small and Medium-sized Enterprise
TURI	Toxics Use Reduction Institute
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organization
US EPA	United States Environmental Protection Agency
WCC	World Coatings Council
WHO	World Health Organization
XRF	X-Ray Fluorescence Spectrometry

Contents

"...Colour expresses something in itself. One can't do without it; one must make use of it. What looks beautiful, really beautiful — is also right..."

Letter from Vincent van Gogh to his brother Theo

Photos: www.pixabay.com



INTRODUCTION

The International Conference on Chemicals Management (ICCM) at its second session in 2009 identif ed lead paint as an emerging policy issue under the Strategic Approach to International Chemicals Management (SAICM). At its third to fourth sessions (2012 and 2015) ICCM continued to affirm the goal of eliminating lead paint, and in 2011, the Global Alliance to Eliminate Lead Paint* (Lead Paint Alliance) was created. In 2017, the United Nations Environment Assembly adopted resolution 3/9 to eliminate exposure to lead paint and promote environmentally sound management of waste lead-acid batteries. The resolution reiterated the commitment to eliminate lead paint, invited interested stakeholders to join the Lead Paint Alliance and requested UNEP to assist countries in eliminating the use of lead in paint by providing tools and capacity-building for developing national legislation.

The Alliance is a voluntary partnership jointly led by United Nations Environment Programme (UNEP) and the World Health Organization (WHO) to prevent exposure to lead from paint and guided by an Advisory Council chaired by the United States Environmental Protection Agency (US EPA) (UNEP 2021). The overall goal of the Alliance is to prevent children's exposure to lead from paints and to minimize occupational exposures to lead paint. The Alliance seeks to achieve this goal through promoting the introduction of laws to phase out the manufacture, import and sale of lead paint in all countries. The Alliance works with governments, the paint industry, NGOs and others to raise awareness and promote action on lead paint elimination, which is technically achievable and protective of human health, especially of children.

This publication is a product of the GEF 9771 project entitled Global Best Practices on Emerging Policy Issues of Concern under the Strategic Approach to International Chemicals Management (SAICM), that aims to accelerate the adoption of national and value chain

* For more information about the Lead Paint Alliance, please visit the UNEP website: https://www.unep.org/explore-topics/chemicals-waste/what-we-do/emerging-issues/global-alliance-eliminate-lead-paint.

initiatives to control Emerging Policy Issues (EPIs) and contribute to the 2020 SAICM goal and the 2030 Agenda for Sustainable Development. It is funded by the Global Environment Facility (GEF).*

There are three main components to the project:

- Promoting regulatory and voluntary action by government and industry to phase out lead in paint (lead paint component).
- Lifecycle management of chemicals present in products, and
- Knowledge management and stakeholder engagement.

To support the goal of the Alliance to promote lead paint laws, the planned outcome of the lead in paint component is for 40 countries to legislate and implement legislation to restrict the use of lead paint, and for at least 30 small and medium enterprises (SME) paint manufacturers in seven countries to phase out lead from their production processes**. The lead paint component involves working with governments to support the development of lead paint laws, and working with SMEs to promote the phase-out of the use of lead-containing raw materials. The Technical Guidelines were developed to support the SME paint reformulation, by providing guidance for lead paint reformulation and showcasing some examples of lead paint reformulation in selected SMEs. The project started in January 2019 at an inception workshop and is scheduled to f nish in 2022.

In the framework of the output on "Demonstration pilots with paint manufacturers in Small and Medium-Sized enterprises (SMEs)," work has been focused on assisting SMEs transitioning to lead-compounds free paints. The National Cleaner Production Center (NCPC) of Serbia worked with SMEs on pilot demonstrations for paint reformulation in f ve countries, including Jordan, Ecuador, Peru, Colombia, and China. The International Pollutants Elimination Network (IPEN) worked with its partners in Indonesia and Nigeria towards the same goal. The Technical Guidelines on Lead Paint Reformulation were developed by the project for the use of SMEs' and include case studies of best practices from the SME pilot demonstration projects.

Project partners (NCPC China, NCPC Colombia, NCPC Ecuador, NCPC Jordan, NCPC Peru, Nexus 3- Indonesia and SRADev – Nigeria) worked with selected SMEs on pilots to demonstrate the replacement of lead-containing compounds with non-lead alternatives. SMEs voluntarily chose to participate in the project. Additionally, a number of global raw material suppliers provided lead-free pigments and technical assistance for SMEs to achieve reformulation to paints free of intentionally added lead compounds. The lockdowns resulting from the Covid-19 pandemic heavily impacted the work with companies as lead paint reformulation has to be done in person in a laboratory. This also prevented partners from being able to work with more SMEs. Nonetheless, the experiences from reformulation of several SMEs are included as case studies in this document.

The draft version of the guidelines was pilot tested during the work on reformulation with the assistance of the NCPCs and IPEN in selected SMEs, consultation meetings with paint industry associations, standards and metrology organizations and government bodies in participating countries. Several comments were suggested and accepted to finetune the Guidelines. Finally, the Guidelines were validated at a validation workshop***, which took place in April 2021.

We hope that these Guidelines will be a useful tool to help SMEs worldwide successfully reformulate lead-containing paint products and that the case stud-ies are compelling examples of how to achieve paints free of lead ingredients with similar or better properties (e.g., resistance to light or heat, mechanical, anticorro-sive and decorative properties).

* Additional information about the SAICM GEF project can be found here: https://www.saicm.org/Implementation/GEFProject/tabid/7893/language/en-US/Default.aspxx

** More information please visit the site https://www.saicm.org/Implementation/GEFProject/tabid/7893/language/en-US/Default.aspx

*** Materials and presentations from the participating organisations are available here: https://saicmknowledge.org/event/validation-workshop-paint-reformulation-guidelines

1 SUMMARY

The Technical Guidelines on Lead Paint Reformulation were developed to help address both capacity constraints and technical barriers to the substitution of lead compounds in paints with focus on the needs of SMEs for the effective and efficient reformulation of paint.

Paint is defined as a pigmented coating material which, when applied to a substrate, forms an opaque dried film having protective, decorative, or specific techni-cal properties. Paints are formulated to meet different technical properties like specific chemical or weather resistance, signal or camoufl-aging effect, decorative ef-fects, insulation or conductive properties, antibacterial properties, etc. Paint is also formulated to adapt to a variety of substrates and methods of application. Since there are many different initial lead-containing formula-tions for colour and other paint properties, the Technical Guidelines provide only general information on paint reformulation processes. In-depth analyses and more specif c data were provided through pilot demonstra-tions through the GEF Lead Paint Project to participat-ing companies, according to their specific needs, and is described in the Case Studies (see Appendix 3).

Terms related to paints in the Technical Guidelines are in accordance with International Standard ISO 4618:2014: Paints and varnishes — Terms and definitions.

Paint formulation consists of a large number of components such as binders, solvents, additives, plasticisers, fillers and pigments. Paint performance is mainly determined by film-forming raw materials. However, pigments, extenders, additives, proper production pro-cesses and methods of application are also important factors to consider. A signifcant requirement for these components is that they should not be very hazardous to human health and the environment.

Lead compounds in paints (mostly pigments and driers) meet strict technical requirements but are never-theless extremely hazardous to the environment and to human health. SMEs should not use any raw materials containing lead and should seek to ensure low levels of lead in raw material ingredients. However, the lead compound alternatives used should have the least hazardous properties possible.

The Technical Guidelines indicate the hazards of lead compounds and their alternatives by referring to the conventions of the Globally Harmonized System of Classif cation and Labelling of Chemicals* (GHS). The GHS facilitates the def nition and classif cation of the hazards of chemical products and communicates health and safety information on labels and safety data sheets. It was developed under the auspices of the United Nations and the goal is to establish a harmonized system to classify hazards, and to develop labels and safety data sheets (SDS) at the global level.

The GHS labelling conventions are used to illustrate hazards and enable SMEs to choose among available alternatives.

The Guidelines start with a **short description of the hazardous properties of lead and the lead compounds used in paint formulations** (Chapter 4).

Lead compounds used in paints are extremely hazardous to human health and the environment and should have priority in substitution. Switching to alternatives should result in reduced overall risks to human health and the environment. **Chapter 5 provides guidance on the general approach and steps in the substitution process** to help SMEs choose alternatives that are not as hazardous or more hazardous than the lead compounds they wish to substitute.

In addition, to providing colour, forming effects, and providing hiding power, there are other technical demands that specif cally should be met by pigments, including complete insolubility in the surrounding media, good fastness to light and weather exposure, heat resistance, and lack of sensitivity to the effects of chemicals as well as environmental and health safety properties. **In Chapter 6, the properties of alternative pigments are presented**. The anticorrosion properties of alternative anticorrosive pigments are compared to lead tetra oxide (Pigment Red 105).

The topcoat reformulation process usually demands colour matching - brief information on colour theory is presented. To provide orientation on function (durability, dispersibility, heat stability, bleeding, gloss retention), environmental, health and safety properties, economic feasibility, and availability of alternatives to PY 34 and PR 104 are presented.

Since paint colour and properties depend to a large degree on the dispersion process and additives for dispersion, information about this is also brief y presented in this chapter.

Finally, **Chapter 7 provides information on the role and type of driers, and alternatives to lead driers**.

In addition, appendix 1 provides tips for f nding information on less hazardous alternatives, and examples of reformulations and case studies from the pilot reformulation projects with selected SMEs are available in appendices 2 and 3 respectively. In appendix 4, a list of selected ISO standards for general test methods for paints and varnishes is given. The list includes methods for testing the performance properties of paint. Finally, in appendix 5, a non-exhaustive list of suppliers as of May 2021 is provided.

Figure 1 – Headspace Sampling Machine


Photo: © Kansai Helios

According to the paint industry, the reformulation of paints to eliminate lead compounds is feasible, and the technical and cost impacts are manageable.

Lead compounds elimination may also provide potential economic advantages as well. By producing or using paints without lead compounds, paint manufacturers and users (such as toy manufacturers) can ensure access to markets where lead content in paint has already been restricted.

* For more information, please visit the website https://www.osha.gov/dsg/hazcom/ghsguideoct05.pdf

Text box 1 – Key Findings

The following findings have been observed during the paint reformulation pilot test with the SMEs under the SAICM GEF project.

- In most of the SMEs working in the project, lead driers are not in use and all case studies are related to lead pigment substitution.
- We learned during the project that lead pigments are used in solvent-based and water-borne paints
- Some small enterprises do not have all the necessary equipment to carry out paint performance testing and scale-up. Lack of grinding equipment can be addressed by using pigment pastes.
- Suppliers have less commercial interest in small markets (users) and the availability of lead-free pigments is limited (Jordan, Ecuador). This was a factor that slowed down the project in these countries, in addition to the COVID pandemic.
- All participants agreed that suppliers' technical support is important. Some of the project partners organized meeting with the project technical, which resulted in a better understanding of the reformulation process and accelerated the right pigment selection.
- SMEs successfully and significantly reduced the concentration of lead in reformulated paints – as shown in Case study 3 (Appendix 3). Lead content is reduced from 34,689 ppm in starting formulation to less than 56 ppm in reformulated alkyd paint
- Economic costs of reformulation varied. In some cases, the lead alternative raw material was less expensive lowering the cost as shown in Case study 1 (Appendix 3). In other cases, the price of the paint increased significantly.
- Companies reformulated their lead paints successfully, but further work is needed on fine-tuning of shades and cost optimization.

See appendix 3 for more information on SME case studies.

For readers seeking more information, references are provided.

2 BACKGROUND

The Global Alliance to Eliminate Lead Paint (Lead Paint Alliance or Alliance) is a voluntary partnership jointly led by UNEP and the WHO to prevent exposure to lead by promoting the phase-out of paints containing lead. The Lead Paint Alliance is guided by the Advisory Council chaired by the US EPA), and which consists of Government representatives from Colombia, the Republic of Moldova, Kenya, Thailand, and representatives from IPEN, the Health and Environmental Alliance (HEAL), the World Coatings Council (WCC), the American Bar Association Rule of Law Initiative (ABA-ROLI), AkzoNobel (a multi-national paint manufacturer), Boysen (an Asian paint manufacturer), and the United Nations Industrial Development Organization (UNIDO).

The overall aim of the Alliance is to prevent the exposure of children to lead-containing paints and to minimize occupational exposure to lead paint. The overall goal is to phase out the manufacture and sale of lead paint and to eliminate lead poisoning risks. In order to reach this goal, the Alliance is focusing its efforts on promoting the establishment of appropriate national regulatory frameworks that will stop the manufacture, import, export, and sale of lead paint and products coated with lead paint. The Alliance's aim is for at least 100 countries to have in place legislation that will serve to ban lead paint by 2023.*

According to the Alliance, as of September 2021, 83 countries have legally binding controls in place to limit the production, import and sale of lead paints, which is around 43% of all countries globally. This number is expected to continue increasing. However, as many as 100 low and middle-income countries have yet to set legal limits on lead paint, and some countries that have lead paint laws have very high lead paint limits that are not as protective of public health and the environment or have gaps in the enforcement.

* Addendum to the Lead Paint Alliance Action Plan (June 2021) to be published soon on https://www.unep.org/explore-topics/chemicals-waste/what-we-do/emerging-issues/global-alliance-eliminate-lead-paint

To help promote lead paint laws*, the Global Environment Facility (GEF) is supporting a SAICM project on global best practices for emerging chemical policy issues of concern. Component 1 of the project is concerned with the phasing out of lead paint (hereinafter referred to as the GEF Lead Paint Project). The project works with governments to promote lead paint laws and with Small- and Medium-Size Enterprises (SMEs), working to promote the reformulation of lead paint.

The Technical Guidelines for Lead Paint Reformulation were developed as part of SAICM GEF Lead Paint Project SME work to provide information on paint reformulation. It contains information (see Resources Section) on other materials developed by the Lead Paint Alliance to promote lead paint laws, such as The Model Law and Guidance to Regulating Lead Paint (or Model Law). The Model Law was developed to provide countries with guidance on how to develop new laws or modify existing laws. Countries may use the Model Law to help develop their own laws, in accordance with existing legal frameworks and other national circumstances.

Countries that have enacted laws to limit lead content in paint have generally used one of two approaches: (1) established a set of chemical-specif c regulatory limits based on the risks of individual lead compounds that are used as pigments or additives in paint (currently used in the European Union REACH regulation; or (2) established a single regulatory limit on the total concentration of lead in paint from all sources. Both approaches have been successful in limiting lead content in paint.

The Model Law recommends the establishment of a single regulatory limit on the total concentration of lead in paint. It outlines the following key objectives of a successful lead paint law:

- the prevention of the manufacture, sale and import of paint that contains lead above the established legal limit.
- the development of methods for compliance and enforcement.
- the establishment of institutional responsibilities and arrangements for the management and enforcement of the lead paint law.

The Model Law proposes legal provisions for the prohibition of the sale, offer for sale, manufacture for sale, distribution into commerce and import of paint that exceeds the established legal limit. The proposed legal limit is 90 mg/kg, based on the weight of the total non-volatile content of the paint. This limit was proposed as it provides the best available health protection and is technically feasible. The Model Law recommends that the industry (manufacturers, distributors, and importers) certify that the paint is below the established limit. SMEs should not use any additives containing lead and should seek to ensure low levels of lead in raw material ingredients.

As more countries develop and implement lead paint laws, these Technical Guidelines are intended to help SMEs achieve compliance with a low legal limit on the total lead content in paint by developing formulations that do not intentionally use any lead compounds and that take into account potential residual lead content in raw material ingredients.

* Lead paint law is meant in the broadest sense to include any mandatory legal requirement with consequence for non-compliance. It can be a statute, a regulation or a standard, as long as it includes an enforcement mechanism.

3 TERMS AND DEFINITIONS

Additive (ISO 4618:2014) any substance, added in small quantities to a coating material, to improve or otherwise modify one or more properties

Bleeding (ISO 4618:2014) - migration of a coloured substance from a material into another material in contact with it, which could produce an undesirable staining or discoloration

Coating material (ISO 4618:2014) - product, in liquid, paste or powder form, that, when applied to a substrate, forms a layer possessing protective, decorative and/or other specif c properties

Chroma - the purity or intensity of colour which can be described or seen as colours being: 'Dirty' or 'Washed out' in appearance

Colour (ISO 4618:2014) - sensation resulting from the perception of the light of a given spectral composition by the human eye (NOTE to entry: a colour is characterised by hue, chroma, and lightness)

Corrosion (ISO 8044:2015) physicochemical interaction between a metal and its environment that results in changes in the properties of the metal, and which may lead to the signif cant impairment of the function of the metal, the environment, or the technical system, of which these form a part

Corrosion inhibitor (ISO 8044:2015) - chemical substance that when present in the corrosion system at a suitable concentration decreases the corrosion rate, without signif cantly changing the concentration of any corrosive agent

Critical pigment volume concentration (CPVC) (ISO 4618:2014) - value of the pigment volume concentration at which the voids between the solid particles, which are nominally touching, are just f lled with binder and above which certain properties of the f lm are markedly changed

Dirty or dull colour – Colour with reduced chroma

Durability (ISO 4618:2014) - ability of a coating to resist the damaging effects of its environment

Dyestuff (ISO 4618:2014) - coloring material, soluble in the application medium

Floating (ISO 4618:2014) - separation of one or more pigments from a coloured coating material, causing streaks or areas of uneven colour on the surface of the coat

Flocculation (ISO 4618:2014) - formation of loosely coherent pigment or extender agglomerates in a coating material

Flooding (ISO 4618:2014) - movement of pigment particles in a liquid coating producing a colour which, although uniform over the whole surface, is markedly different from that of the freshly applied wet f lm.

Extender - substance in granular or powder form, insoluble in the medium and used to modify or inf uence certain physical properties.
NOTE 1 to entry: in German, the terms 'Extender', 'Extender pigment', 'Pigment extender' or 'Verschnittmittel' should be avoided.

Filler - coating material with a high proportion of extender, intended primarily to even out irregularities in substrates to be painted and to improve surface appearance.
NOTE 1 to entry: the term 'f ller' is also widely used in the sense of extender.

Hiding power (ISO 4618:2014) – the ability of a coating to obliterate the colour or colour differences of the substrate.

Metamerism (ISO 4618:2014) - phenomenon perceived when two specimens have the same colour under the lighting of an illuminant, but different spectral ref ection and transmission curves.

Paint (ISO 4618:2014) pigmented coating material which, when applied to a substrate, forms an opaque, dried f lm having protective, decorative or specif c technical properties

Pigment (ISO 4618:2014) colorant consisting of particles, insoluble in the application medium (e.g. coating material or plastic).

Pigment volume concentration (PVC) (ISO 4618:2014) – ratio, expressed as a percentage, of the total volume of the pigments and/or extenders and/or other non-f lm-forming solid particles in a product to the total volume of the non-volatile matter.

Raw material - Unprocessed material of any kind used in manufacture.

NOTE: Please see explanation below on the use of some of the above terms in the Guidelines:

- **Additive** – in line with ISO 4618:2014, term used for any paint ingredient that is added in small quantities (driers, dispersing agent etc.)

- **Lead compound** – term used for synthetic pigments (PY 34, PR 104) and driers which are "pure" compounds of one specif c chemical, in contrast to natural pigments and f llers that are unknown mixtures of compounds

- **Raw materials** – in line with ISO 4618:2014, term used for any kind of unprocessed material used in manufacture (natural or synthetic pigments, all kind of additives, resins, solvents, synthetic or natural f llers)

Photo: www.istockphoto.com

4

LEAD IN PAINT

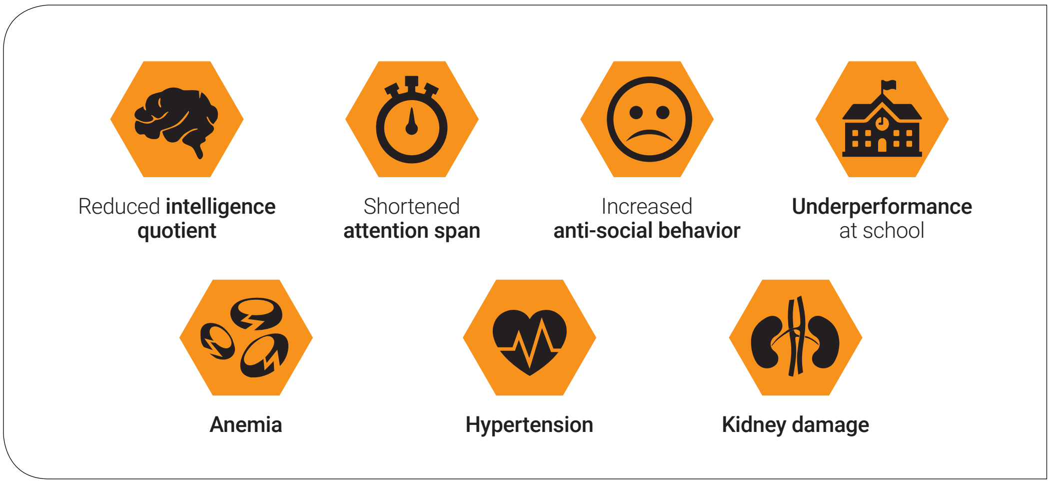
Lead is a naturally occurring toxic metal found in the Earth's crust. Its widespread use has resulted in extensive environmental contamination, human exposure and signif cant public health issues in many parts of the world. The World Health Organization has identif ed lead as one of ten chemicals of major public health concern.

There is no known level of lead exposure that is considered safe. Lead can cause permanent damage to the brain and nervous system, resulting in decreased IQ and increased behavioural issues. Lead exposure may also cause anaemia, increase the risk of kidney damage and hypertension, and impair reproductive function. Young children and pregnant women (whose developing foetus may be exposed) are especially vulnerable to the adverse effects of lead. Even relatively low levels of exposure can cause serious and irreversible neurological damage. Besides, lead in the body is distributed to the brain, liver, and kidney. It is stored in the teeth and bones, where it accumulates over time. Human exposure is usually assessed through the measurement of lead in blood. Lead in the bones is released into the blood during pregnancy and becomes a source of exposure to the developing foetus.

The Institute for Health Metrics and Evaluation has estimated that, based on 2019 data, lead exposure accounted for 901,700 deaths and 21.6 million years lost to disability and death due to long-term health issues (Institute for Health Metrics and Evaluation GBD).

Lead released into the environment from any source, including lead paint, is also toxic to plants, animals and micro-organisms. In all animals studied, lead has been shown to cause adverse effects in several organs and organ systems, including the blood, central nervous system, kidneys, reproductive and immune systems. It bio-accumulates in most organisms, with environmental exposures occurring through multiple sources and pathways.

Figure 2 – Health Effects on Children's Exposure to Lead*

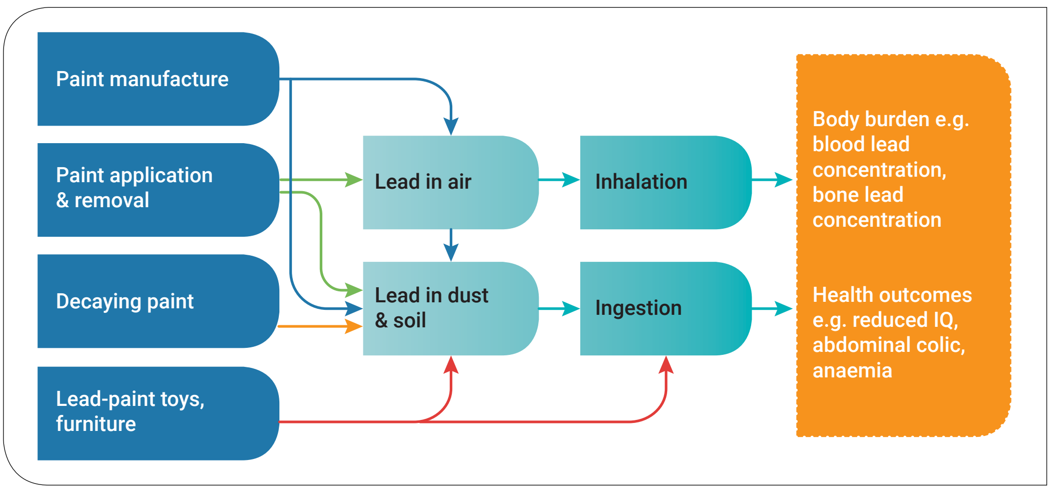


Source: United Nations Environment Programme (2020), Update on the Global Status of Legal Limits on Lead in Paint, https://wedocs.unep.org/bitstream/handle/20.500.11822/35105/GS-2020.pdf?sequence=3. Accessed on September 2021.

Lead is a well-documented ecotoxicant, posing threats to both aquatic and terrestrial ecosystems (UNEP 2010). Studies have shown that forests act as sinks of atmospheric particulates. Atmospheric lead is deposited on foliage and is transported to soil in rainwater or as leaf litter fall. Consequently, organisms in the forest ecosystem can be exposed to particularly high lead concentrations (Zhou et al. 2019). Lead contamination is also known to affect a variety of bird species and to pose a threat to biodiversity (Haig et al. 2014). Aquatic ecosystems including aquatic plants, invertebrates and f sh have also been shown to take in lead when present in contaminated water. In f sh, for example, lead can have haematological and neurotoxic effects and can disrupt enzyme function, thereby decreasing long-term survival and reproductive success (Demayo et al. 1982).

Historically, lead compounds have been added to decorative and industrial paints and other coatings to enhance colour, reduce corrosion on metal surfaces or shorten drying time. Today, non-leaded pigments and driers are widely available for use in paints. Also, some raw materials used in paint can contain naturally-occurring high levels of lead. After the application of lead paint, weathering, peeling or chipping of the paint releases lead particles into dust and soil in and around homes, schools, playgrounds and other locations. Decorative paint for household use has been identif ed as the main source of children's exposure to lead found in paints. Lead exposure is preventable. The elimination of lead exposure at its source, through establishing laws promoting reformulation to lead-free raw materials in paint production, is the most effective action to protect people and the environment from the harmful effects of lead.

Figure 3 – Pathways and Routes of Human Exposure to Lead from Paint. Source: WHO 2020



Lead-contaminated soil and dust are easily ingested and inhaled, particularly by young children while playing on the f oor or outdoors and when they put their hands or other objects into their mouths. Children may also ingest lead through toys painted with lead paint. Both children and adults may be exposed to lead found in paint chips and dust when old lead paint is removed. Lead is particularly harmful to young children because they absorb 4–5 times as much ingested lead as adults from a given source.

The negative impact on the development of children's brains resulting from exposure to lead has staggering economic costs that are borne by the affected children, their families and societies at large. These include health care costs, productivity losses and intellectual disability. The largest economic burden of lead exposure is borne by low- and middle-income countries. Estimated annual costs (in international dollars) of lead exposure by global region, based on the loss of IQ, include the following: Africa - $134.7 billion USD; Latin America and the Caribbean - $142.3 billion USD; and Asia - $699.9 billion USD.*

Occupational exposure to lead can occur during paint manufacture, application aging and removal of paint if the appropriate engineering controls and occupational hygiene measures are not in place, and workers do not have adequate personal protective equipment (Were et al. 2014), (Rodrigues et al. 2010). During the manufacturing phase, workers can be exposed to lead-containing ingredients, which are often in powdered form. When paint is being applied by spraying or removed through scraping, abrasive blasting, dry sanding, or burning, lead particles and fumes are released that are a source of inhalational exposure [8]. Particles also settle on the skin and clothing of workers and can become a source of ingestion, as well as take-home exposure of workers' families, if facilities are not available at the workplace for changing clothes and washing. (WHO 2020)

The cost of removing existing decorative lead paint from surfaces in homes, schools and other buildings may be substantial. By contrast, the economic cost of eliminating the use of lead compounds in the production of new decorative paints is low. In fact, many manufacturers have already successfully reformulated their paint products to avoid the intentional addition of lead. According to the paint industry, the reformulation of residential and decorative paints to eliminate lead compounds is feasible, and the technical and cost impacts are manageable. Increasingly, paint producers are going public in saying that it is possible to eliminate lead compounds in all types of paint.

Increasingly, governments around the world are looking to develop laws to eliminate lead in paint. Paint manufacturers should be aware of such activities in their country or in the countries to which they are exporting their product, in order to inform their decisions for paint reformulation.

Raw materials used in paints that may contain lead are presented in the following table.

Table 1 – Raw Materials that May Contain Lead

PAINT TYPE	PIGMENTS	FILLERS	DRIERS
Oil, alkyd-based primers, intermediate and topcoats (Alkyd resins may be a source of lead because of lead catalyst used in their synthesis.)	●	●	●
Primers, other bases	●	●	
Intermediate coats, other bases		●	
Top-coats, other bases	●	●	

* For more information, please visit https://med.nyu.edu/departments-institutes/pediatrics/divisions/environmental-pediatrics/research/policy-initiatives/economic-costs-childhood-lead-exposure-low-middle-income-countries

Figure 4 - Inspection of Lead-based Paint Using and XRF Analyzer

Photo: www.istockphoto.com

It should be noted that synthetic f llers do not contain lead compounds, but f llers are often natural raw materials and may contain lead. By using these f llers, lead may be added unintentionally. Paints may also be unintentionally contaminated by lead when natural pigments, such as ferro oxides, contain lead.

There is the possibility of contaminating paint during production as well. Lead contamination occurs if the same equipment is used to produce leadfree paint that was used to produce paint that contains lead without cleaning the equipment.

There are different analytical methods for measuring lead in paint. The WHO Brief guide to analytical methods for measuring lead in pain provides an overview of the key methods, including laboratory methods, bench-top or portable X-ray fluorescence (XRF) spectrometry, and test kits (WHO 2020).

The following table presents the hazardous properties of the most commonly used paint raw materials containing lead.

Table 2 – Hazardous Properties of Lead Compounds Used in Paints

CHEMICAL/CAS NUMBER	COLOUR INDEX*	HAZARD STATEMENTS ACCORDING TO GHS
PIGMENTS (OECD 2021A)		
Lead chromate molybdate sulphate red ($PbCrO_4$ (CrH2O4.Pb) /12656-85-8	Pigment Red 104	**H350**: May cause cancer **H360 Df**: May damage fertility or the unborn child **H373**: May cause damage to organs through prolonged or repeated exposure **H400**: Very toxic to aquatic life **H410**: Very toxic to aquatic life with long lasting effects
Lead chromate ($PbCrO_4$)/ 7758-97-6	Pigment Yellow 34	
Chrome green (mixture of lead chromate and iron blue) Pigment Green 15		
Lead tetra oxide - minium (Pb_3O_4) / 1314-41-6	Pigment Red 105	**H302**: Harmful if swallowed. **H332**: Harmful if inhaled. **H351**: Suspected of causing cancer. **H360**: May damage fertility or the unborn child. **H360Df**: May damage the unborn child. Suspected of damaging fertility. **H362**: May cause harm to breast-fed children. **H372**: Causes damage to organs. **H372**: Causes damage to central nervous system, blood and kidneys through prolonged or repeated exposure by inhalation or ingestion. **H410**: Very toxic to aquatic life with long lasting effects.
Lead monoxide (PbO) /1317-36-8	Pigment Yellow 46	**H316**: Causes mild skin irritation **H341**: Suspected of causing genetic defects **H351**: Suspected of causing cancer **H360**: May damage fertility or the unborn child **H373**: May cause damage to organs through prolonged or repeated exposure (blood system, nervous system, kidney) **H413**: May cause long lasting harmful effects to aquatic life
White lead ($2PbCO_3{\times}Pb(OH)_2$) 37361-76-5	Pigment White 1	**H350**: May cause cancer **H360**: May damage fertility or the unborn child **H370**: Causes damage to organs (central nervous system, blood, kidney) **H372**: Cause damage to organs through prolonged or repeated exposure (central nervous system, blood, kidney) **H413**: May cause long lasting harmful effects to aquatic life
DRIERS (ECHA 2021A), (ECHA 2021.B)		
Lead octoate ($C_{16}H_{30}O_4Pb$) / 7319-86-0	/	**H302**: Harmful if swallowed **H332**: Harmful if inhaled **H360**: May damage fertility or the unborn child **H373**: May cause damage to organs through prolonged or repeated exposure **H400**: Very toxic to aquatic life **H410**: Very toxic to aquatic life with long lasting effects
Lead naphthenate ($C_{22}H_{14}O_4Pb$) / 61790-14-5	/	

* The Colour Index (CI) identif es each pigment by giving it a unique colour index name and colour index number (see Section 6.2).

There are many products on the market that could substitute these raw materials for paint production.


Photo: www.pixabay.com

5 SUBSTITUTION PROCESS

Law enforcement has been recognised by companies as the main driver in ensuring the substitution of hazardous chemicals. However, many companies and other organisations have gone beyond this to introduce other criteria, such as: knowledge of suppliers, organisation policy, supply chain requirements, healthcare costs, protection of workers and environmental protection, pressure from the public or pressure from workers, among others.

Substitution is a basic principle of good chemical risk management. The principle of chemical substitution states that hazardous chemicals should be systematically substituted by less hazardous alternatives or, preferably, alternatives for which no hazards have been identif ed (Olofsson 2011) Substitution usually leads to more than just the replacement of one chemical for another. The difference in the properties of the two chemicals may create a need for other changes (technical, but possibly also organisational) as well.

Substitution may include the replacement of a hazardous substance, using a technological alternative instead of the initial substance, using an organisational measure as a replacement for a hazardous substance or total product re-design.

In addition to lead compounds, there are many other very hazardous raw materials that are in use in the paint industry such as solvents (solvent naphtha, toluene), additives (plasticiser dibutyl phthalate, Formaldehyde, a preservative found in water borne paints), hexavalent chromium pigments (Zinc chromate), bromine compounds found in f re retardant paints, etc.

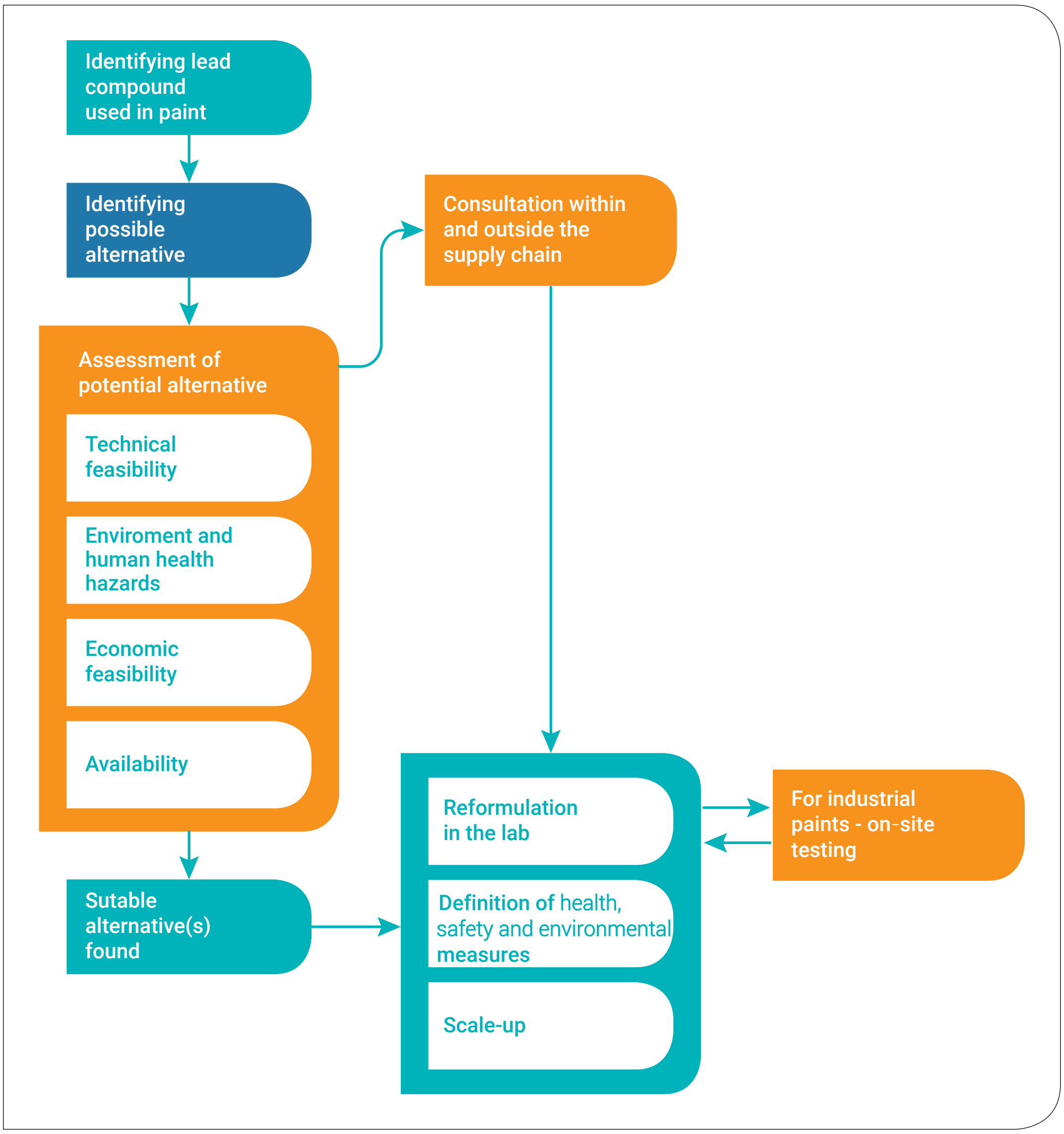
Information given in this section may assist companies in terms of further activities related to hazardous chemicals substitution.

The following f ow chart presents the steps necessary to substitute lead-containing ingredients in paints. These activities apply to any hazardous chemical for which alternatives are available on the market and whose hazardous properties are known and because of this, there is no need for any additional research in relation to these properties. This process will assist companies in their efforts to substitute lead-containing raw materials voluntarily or to either meet existing or anticipated lead concentration limits (e.g., as recommended in the Model Law or as required by such countries as Uruguay, Kenya, the Philippines and others) or to meet requirements for the phasing out of specif c lead compounds (e.g. EU REACH).

ternative substance. Information on possible alternatives may also be provided outside the supply chain.

The process of identifying alternatives begins by considering a substance's function. A detailed and specif c knowledge of the exact function for a particular

Flow chart 1 – Activities in Lead Compound Substitution



5.1 Identification of Possible Alternatives

One alternative is the use of a replacement for a hazardous substance that is able to replace the function the original substance performs.

Good communication in the supply chain is essential for identif cation and practical implementation of an al-

use, will allow the company to look for other ways of performing that same function. Consideration of how the use of an alternative may affect end products in terms of the f nal function is essential. The qualities of f nal products may need to be considered over a longer timescale. For example, some paints may need to provide resistance to weathering over a specif c product lifetime.

It is important to determine all the functions of a substance for each use (a specific industry or a specific customer, in some cases), so that possible alternatives which may be able to replace the equivalent function can be identified. Once the specific function and use conditions are precisely defined, consultation within and outside the supply chain is more successful.

Supply chain communication is an interactive process and may involve all relevant parts of the supply chain. This is important in identifying possible alternatives for all uses. Sources of information on possible alternatives within the supply chain are, for example, the company's own knowledge (product and user specifications, employee knowledge), suppliers, users, industry or professional associations. Communication within the supply chain will help the organisation to identify possible alternatives, understand technical and economic feasibility and gain information on safety and the availability of alternatives.

It can be useful to gather information on possible alternatives outside the supply chain, such as professional journals, research organisations, environmental groups, non-governmental organisations, academic institutions, databases* (i.e. SUBSPORT, REACH-IT system, Non-confidential REACH Annex XV dossier information; patent databases) or experts within the field.

5.2 Assessment of Possible Alternatives

When possible alternatives are identified, analysis is the first step in the substitution planning process (ECHA 2011).

An alternative is suitable when it:

- Provides an equivalent function to that provided by the lead compound (when pigments for topcoats are in question, a single alternative is usually not suitable, thus the original pigment would need to be substituted by more than one suitable alternative);
- results in reduced overall risks to human health and the environment, considering appropriateness and effectiveness of risk management measures for facilities;
- is technically and economically feasible; and,
- is available on the market.

The first phase of the analyses is the assessment of technical feasibility. When possible alternatives that fulfill function requirements are identified, it is necessary to define whether or not process adaptations or changes are needed. To fulfill the same function, sometimes the alternative has to be processed under different conditions (see Section 6.6.2)

If the alternative is acceptable with respect to technical feasibility, the next phase is the assessment of hazards and risks** on the environment and human health. This assessment consists of setting criteria for acceptable hazards and risks and the comparison of hazardous properties between hazardous substance (or mixture, like driers) and their possible alternatives. The comparison of similar properties and effects between substances or mixtures is not always simple or straightforward. When a comparison of hazard profiles or a lack of data raises concern, then there may be a need for a more detailed assessment.

For hazard data, key health and environmental effects of alternatives should be identified to avoid certain uncontrollable risks caused by substitution. The Safety Data Sheet (SDS) is a good source of information on chemical hazardous properties. It is meant to provide comprehensive information about a substance or mixture used as an alternative. Both employers and workers use it as a source of information on hazards, including environmental hazards, and as a source of guidance on safety precautions.

There are more sophisticated methods for alternatives assessment that can be divided into two categories (Edwards, Rossi and Civie 2016)

a. Methods that compile hazard data: those that examine the hazardous properties of chemicals must be placed in a matrix. Organisations should set their own rules for the analysis and comparison of different alternatives. These

* APPENDIX 1 – Tips for the internet search

** A risk consists of two factors, first the inherent properties of the chemical: hazard, and also the way in which the chemical is used or handled: exposure.

methods are, for example, P2OASYS*, The GHS Column Method 2017, TURI 5 Chemicals Alternatives Assessment Study High Priority**,

b. Test methods are used to analyse chemicals based on previously prioritized hazards. These include recommendations for the termination of use of certain hazardous chemicals that are very harmful. They also contain tools for the decision-making process on alternatives. The method in this category includes Green Screen for Safer Chemicals***

The main limitation of these tools is the lack of data on the hazardous properties of most chemicals in use.

An alternative may be safer (i.e., not carcinogenic, mutagenic), but it may have other hazards such as corrosivity or flammability. These hazards are easier to control and it is necessary to prescribe needed measures to manage and control them during application.

The assessment of alternatives should be repeated, as the assessment results obtained today may change as new knowledge concerning hazardous properties and risks of the chemical is acquired.

Economic feasibility identifies the lowest-cost option among a set of alternative options that all achieve the targets. An assessment would include a range of direct and tangible indirect production costs, rather than simply comparing the product price of the alternatives and the chemical being substituted.

The first step is to determine the availability and cost of identified alternatives, based on information readily available for a cost comparison. To check the viability of alternatives, it is necessary to evaluate if substitution with a specific alternative creates other costs like higher chemical consumption, increased manufacturing costs or the purchase of new equipment. It should also be kept in mind that the prices are not static and may potentially be reduced. With the rise in demand due to the ban or restriction of the use of certain chemicals, the supply of alternatives increases, leading to a drop in prices.

* For more information, please visit https://www.turi.org/Our_Work/Alternatives_Assessment/Alternatives_Assessment/Tools_and_Methods/P2OASys_Tool_to_Compare_Materials

** For more information, please visit https://www.yumpu.com/en/document/view/7083577/turi-5-chemicals-alternatives-assessment-study-high-priority

*** For more information, please visit https://www.greenscreenchemicals.org/

6 SUBSTITUTION OF LEAD PIGMENTS

It is necessary to select the right raw materials to achieve optimum paint performance such as how it is applied (i.e., by spraying, dipping...) adhesion to a specific surface, curing process, requested mechanical and/or chemical protection and decorative requirements. Coating technology is complex and includes chemical, physical, process-engineering, environmental, health and safety, and economic variables.

Constituents of paints are binders, solvents, pigments, f llers, and different additives. The following table provides information on task and performance requirements for pigments and extenders (Goldschmidt and Streitberger 2007).

Table 3 – Task and Performance Requirements on Pigments and Extenders

PIGMENT TASKS	REQUIREMENTS FOR PIGMENTS AND EXTENDERS	SPECIAL TASKS OF EXTENDERS
• Elective absorption • Light scattering • Optical effects by oriented ref ection or interference • UV protection • Corrosion protection	• Dispersibility • Insoluble • Lightfast and weather resistant • Heat resistant • Chemical resistant • Physiological compatible	• 'f lling' • Sandability • Improvement of mechanical technological coating properties • Improvement of anticorrosion properties

The particle size and particle size distribution of pigments affect the colour, tinting strength and hiding power of paint to a large degree. Paint properties depend on other factors related to pigments such as pigment volume concentration, choice of dispersing additives, interaction between pigment and polymer and the dispersion process. The dispersion (grinding) process affects hue, hiding power, gloss, and film appearance (i.e., haze, flooding, floating), viscosity, stability and weather resistance.

Paint reformulation can include not only substitution of lead pigment by less hazardous alternatives but may also require changes in the mill base, wetting, dispersing additives and dispersion process. In addition, substituting lead pigments in topcoats by other pigments will require adjustment of color through tinting. To address these issues, this Chapter provides information on the basic elements of the colour theory, the dispersion process, and additives for dispersion.

6.1 Colour Theory

Value, hue and chroma are standard terms used in the paint industry to describe the three dimensions of colour. Understanding these terms is necessary for successful colour adjustment. Colours can be different in one, two or all three dimensions.

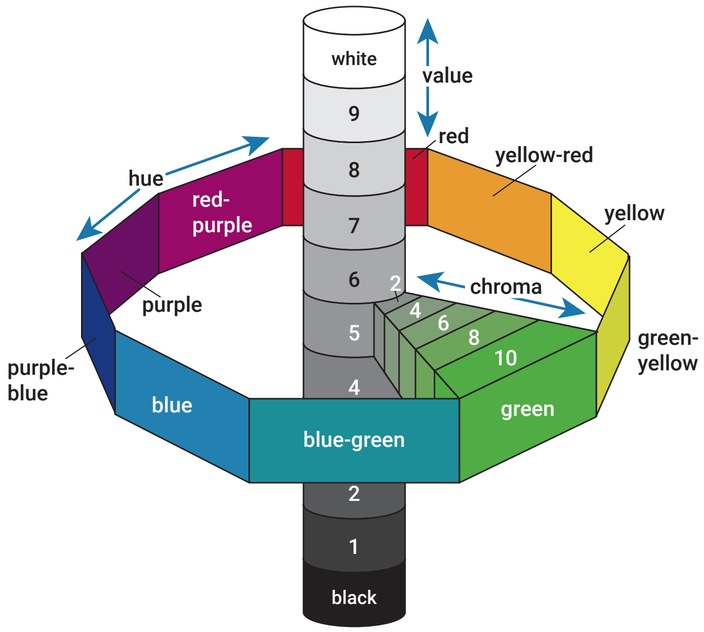
Text box 2 – Value, Hue and Chroma

Value (lightness or darkness) - this dimension refers to the degree of lightness or darkness of the colour. The value scale runs vertically through the colour sphere (Figure 5). The whitest is at the top, gradually darkening shades of grey are in the middle and black is at the bottom. The difference in value is described as a darker or lighter colour.

Hue (colour) - this dimension moves around the outer edge of the colour sphere. It moves from yellow, red, and blue (primary colours) to green.

Colours move on the hue scale - a blue can move toward redder shades and become purple or toward green shades, turning greenish blue; a red can be made either bluer (purple or maroon) or more yellow (orange); a yellow can be made redder or greener (secondary colours). Differences in hue are described i.e., as redder, or greener than another colour.

Figure 5 – Colour Sphere



Chroma (intensity, richness, saturation) - this dimension refers to a level of colour intensity and richness. It moves along the spokes that radiate outward from the central axis towards the periphery. Weak, washed-out colours with the least chroma are close to the centre of the colour sphere, while highly chromatic and the most intense colours are at the outer edge. The difference in chroma is described as more or less saturated colour.

Black, white, and grey are achromatic colours, literally colours without hue.

If we wish to produce a vibrant, intense colour, we have to use primary colours that do not contain other colours, so that they will not affect the colour we want to produce. For example, to produce intensive green, yellow and blue color should not contain red, thus only greenish yellow and greenish blue should be used; pure violets are produced with bluish reds and reddish blues, where blue and red should not contain yellow; intense orange is produced with red and yellow without any blue content, with the yellow being reddish and the red being yellowish.

White pales any colour and does not brighten it, and when added for tinting purposes, does not alter the hue.

Even a small amount of complementary colour (red and green; yellow and purple; blue and orange) starts to de-saturate the colour. The intensity of the colour (chroma) immediately begins to decrease when its complement is added.

To make a colour darker, a small amount of black is added. Adding too much black will make the colour almost black. Another way to darken a colour is to add some of the complementary colour. This produces a dark colour, richer than simply adding black.

6.2 Colour Index

The Colour Index (CI)* is the universally accepted standard coding system for pigments. It was f rst published in 1925 and is currently maintained by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists. The Colour Index identif es each colorant by giving the compound a unique Colour Index name and a Colour Index number. In the following tables the Colour Index abbreviations (Table 4) and chemical structure numbers for pigments (Table 5) are presented. For dyes, the f rst letters are A, for Acid dye and B for Basic dye.

The f rst two letters describe the general pigment colour (Table 4), and the number is the individual pigment identif er (Table 5).

Table 4 – Abbreviated Colour Index (CI) Pigment Names

ABBREVIATION	PIGMENT	ABBREVIATION	PIGMENT
PB	Pigment Blue	PBk	Pigment Black
PBr	Pigment Brown	PG	PG Pigment Green
PM	Pigment Metal	PO	Pigment Orange
PV	Pigment Violet	PR	Pigment Red
PW	Pigment White	PY	Pigment Yellow

Table 5 – Numbers Related to Pigment Chemical Structure (Selection)

CHEMICAL CLASS	CI NUMBERS	CHEMICAL CLASS	CI NUMBERS
Nitroso	100000–102999	Stilbene	400000–407999
Nitro	103000–109999	Diphenylmethane	410000–419999
Monoazo	110000–199999	Triarylmethane	420000–449999
Diazo	200000–299999	Xanthene	450000–459999

* For more information, please visit the site https://colour-index.com/

6.3 Dispersion Process

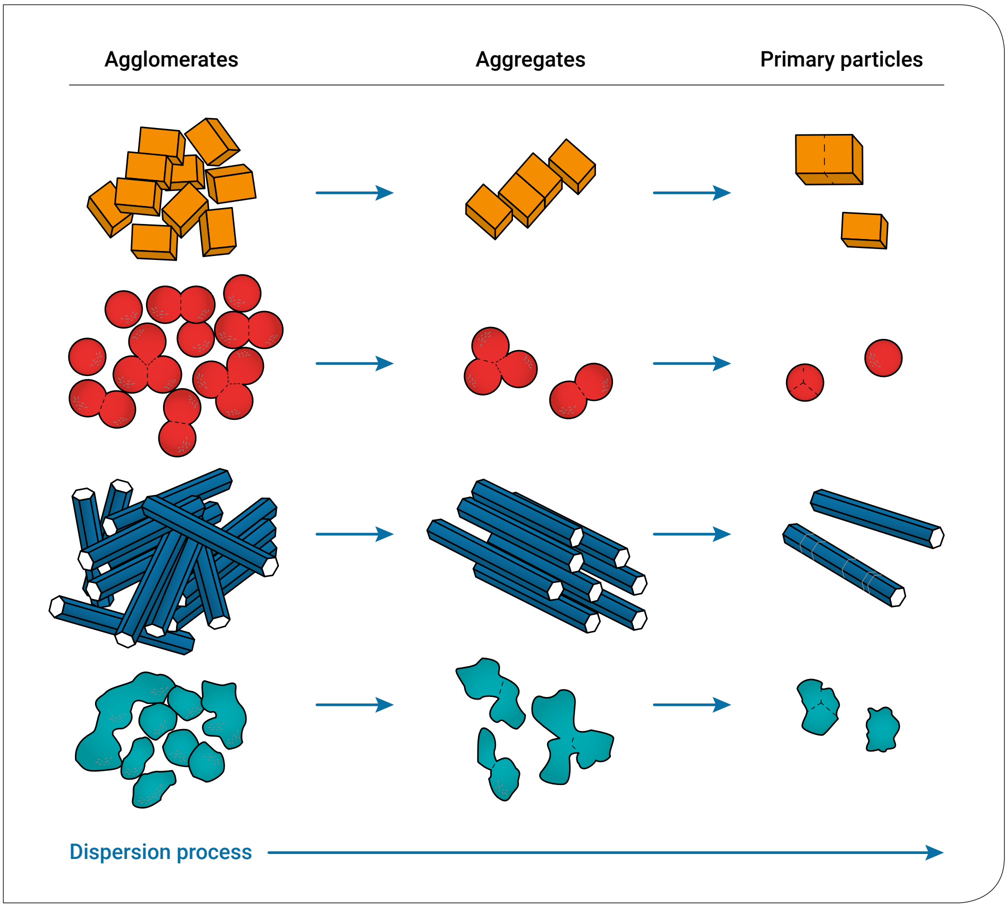
According to the EN ISO 18451-1 pigment models, there are three kinds of pigment particles, present in a pigment powder: primary particles, aggregates, and agglomerates.

The objective of the dispersion process is to produce stable and uniform dispersion of f nely divided pigment particles (primary particles and aggregates) within a vehicle (Figure 6).

The dispersion (grinding) process consists of the following three phases:

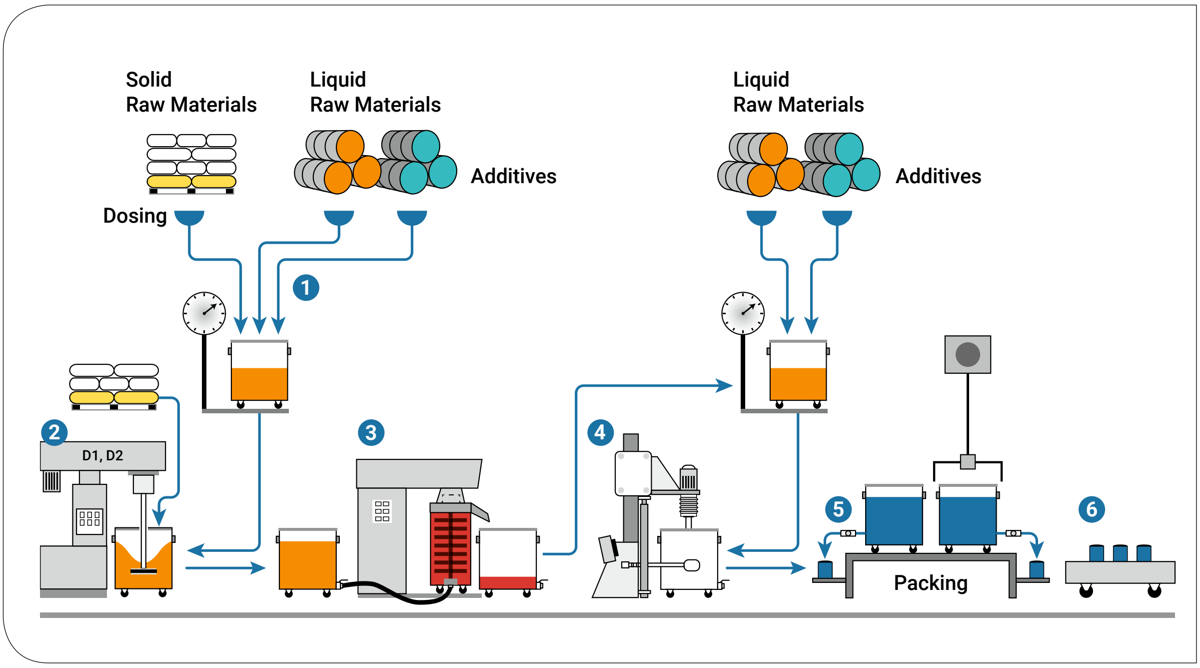
- Mechanical breakdown of agglomerates in aggregates and primary particles by mechanical forces through grinding.
- Wetting of separated particles (pigment/air or pigment/moisture interface are replaced by the pigment/medium interface) and
- Stabilisation – Prevention of reagglomeration of the particles through steric hindrance by an adsorbed polymer chain or electrostatic repulsion between particles of the same charge. Modern dispersing agents combine electrostatic and steric stabilisation mechanisms. This is usually referred to as 'electrosteric stabilisation'.

Figure 6 – Pigment Models According to the EN ISO 18451-1



The following scheme (Figure 7) demonstrates the paint production process.

Figure 7 – Paint Production Process Scheme



1. **Raw materials (resins, solvents, pigments, fillers and additives) weighing and dosing**
2. **Mixing by dissolver (pre-grinding) – wetting and mechanical breakdown of agglomerates**
3. **Grinding (dispersing) - further breakdown and stabilisation of pigment dispersion**
4. **Let down – mixing for homogenisation of pigment dispersion with a pre-prepared mixture of other liquid materials (binders, solvents, additives).**
5. **Filtration**
6. **Packing**

During paint production, monitoring is necessary to adjust the viscosity of grinding paste, temperature, f ow rate in the mill, and requested paint particle size in the course of grinding.

During the grinding operation, the sub-processes of mechanical breakdown, wetting and stabilisation do not necessarily take place in chronological order, but rather occur partly successively and partly simultaneously.

ISO 1524:2013 (Paints, varnishes and printing inks - Determination of f neness of grind) specif es a method for determining the f neness of the grind of paints by using a suitable gauge, graduated in micrometres. It is applicable to all types of liquid paints and related products, except products containing pigments in f ake form (e.g. glass f akes, micaceous iron oxides, aluminium f akes).

In addition to well-dispersed pigments, it is important to achieve effective long-term stabilisation of the pigment particles, as insufficient stabilisation may cause negative effects like colour shift, sedimentation, or changes in viscosity of the dispersion.

Highly specialised additives are needed to wet, disperse, and stabilise dry pigment powders in liquid formulations. Wetting additives accelerate the wetting of pigment agglomerates by the resin; dispersing additives improves the stabilisation of pigment dispersion. One product can often function as both the wetting and the dispersing additive. There is a signif cant difference in the wetting process between solvent-borne and water-borne systems. Wetting in solvent-borne systems is generally quite easy because of the low surface tension of organic solvents. Due to the high surface tension of water, the surface tension in water-borne systems is signif cantly higher, thus special additives are required to enable sufficient pigment wetting.

Pigment dispersion can be stabilised by def occulation or controlled f occulation. In most applications the stabilisation of the def occulated condition is desirable, but controlled f occulation is preferable in some cases.

Def occulation leads, in general, to more efficient pigment utilisation, f ow behaviour is improved, and a higher pigment loading is possible. Due to the small particle size of def occulated pigments, high gloss is obtained, and colour strength is increased. These properties are of special interest to topcoats where optimal appearance and excellent surface properties are required (i.e., in automotive paints).

Without additives, the pigment particles are in direct contact with one another as uncontrolled f occulates. In contrast, in controlled f occulates, additive molecules are always between the pigment particles, without any direct contact.

tion and paints have to be evaluated for possible undesirable effects. The primary application for controlled f occulating additives is found in primers, undercoats and in protective coating systems.

Indicators of stabilization of paints with one pigment, gloss and transparency should be considered. An indicator for mixtures, f ood/f oat-behaviour should be evaluated with the 'rub-out' and sedimentation test. Ununiformed paint f lm after rubbing indicates weakly stabilised pigment particles. The colour difference between the rubbed and the unrubbed area indicates the degree of f occulation as well as the f ooding extent.

To carry out the sedimentation test the pigment dispersion is diluted, poured into a graduated measuring cylinder and stored for a period of time. A pigment-free layer gradually develops with f occulated systems, and this layer generally exhibits a clear boundary. In con-

Figure 8 – Dissolvers

Photo: © Kansai Helios

The controlled f occulation state forms three-dimensional network structures which lead to thixotropic (pseudoplastic or returning to a gel state quickly) f ow behaviour within the coating. Through these structures, the resting state viscosity is rather high. However, when shear forces are applied, the pigment f occulates break apart and induce lower viscosity. The f occulates can rebuild after the removal of share forces, thus rheological behaviour, as sagging and settling and excellent stability on vertical surfaces at high f lm thickness, can be achieved. Through controlled f occulation, both f ooding and f oating can also be controlled since the different pigments are bound together in the f occulates, and consequently cannot separate from the mixture. Co-f occulation may lead to gloss reduc-

trast, stable colloidal systems show a transition zone between the clear, supernatant binder solution and the pigmented phase.

When one pigment is being dispersed, the additive quantity added and grinding conditions may be optimised to achieve the best possible grind quality. When grinding several different pigments together, compromises regarding grinding parameters are necessary. Co-grinding of pigments is not recommended due to the different properties of the varying pigments in relation to the grinding process. A pigment that is difficult to grind can be substituted, if possible, or be ground separately or added as a pigment concentrate.

Too much or too little additive can be detrimental to the stability of pigment dispersion. The required quantity of wetting and dispersing additives depends on the type of pigment, as additives attach to the surface of the pigment. If the dispersant quantity is too low, then the full benef ts will not be realised. If it is too high, the thickness of the protective barrier is reduced as a result of overcrowding on the pigment surface also affecting stabilisation. The adhesion or hardness of the paint f lm may also be reduced because of the free molecules in paint f lm.

Producers provide information on the types of additive and quantities suitable for specif c types of pigments and types of paint (water- or solvent-based). However, a series of laboratory tests should be developed to optimise the dosage.

The following table recommended additive usage levels are presented (BNK, ND).

When laboratory testing is scaled up to production, comparable grinding results can be achieved only if the same grinding conditions are maintained.

6.4 Substitution of Red Lead Anticorrosive Pigment (PR 105)

Red lead pigment, minium (Pigment Red 105) is one of the oldest and most popular type of anticorrosive pigment with excellent anticorrosion properties, mainly used for metal primers. It is an indirect inhibitor and requires reaction with a selected resin system. When used in linseed oil or other oleoresins binders, it reacts with the acidic groups in the resin to form lead soap, which has a corrosion inhibitory effect.

Anticorrosive protection without chemical intervention is achieved if the diffusibility and permeability of corrosive agents such as oxygen, water and salts are signif cantly reduced by appropriate formulation. Lamellar pigments such as aluminium silicates, lamellar iron oxide or mica are best suited to achieve this property.

Table 6 – Recommended Additives Usage Level

WETTING AND DISPERSING ADDITIVE TYPE	INORGANIC PIGMENTS	ORGANIC PIGMENTS	TOTAL FORMULATION
Classical low molecular weight polymers	0.5-2% additive on pigment	1-5% additive on pigment	0.1-1% additive
High molecular weight polymers	1-10% additive on pigment	10-80% additive on pigment	0.2-3% additive

Figure 9 – Basket Mill


Photo: NCPC Jordan

The anti-corrosion performance of a primer is inf uenced by numerous factors, like resin type, relation of pigment volume concentration (PVC) to critical volume pigment concentration (CPVC), type of anti-corrosive pigment and other pigments and f llers, dispersing conditions and overall formulation of the paint. All these factors should be taken into consideration during the paint reformulation process.

The table 7 provides information on pigment alternatives to red lead pigment.

Zinc phosphate is the f rst alternative for anticorrosive lead pigment replacement. It is free of lead and hexavalent chromium; however, anticorrosion performance is not as good as with the lead pigments. A combination

Table 7 – Possible Alternatives to Lead Anticorrosive Pigment

PIGMENT TYPE	PIGMENT	MECHANISM OF ACTION
Chemically active anticorrosive pigments	Zinc oxide (ZnO). Zinc phosphate ($ZnPO_4$) Modif ed zinc phosphates Calcium phosphate Modif ed calcium phosphates	Bind corrosion stimulators such as chloride or sulphate by forming insoluble compounds and/or stabilising the pH value of a coating in contact with the corrosion medium. Therefore, slight solubility in the corrosion medium is necessary.
Electrochemically active anticorrosive pigments	Zinc chromate ($ZnCrO_3$)*, Zinc phosphate ($ZnPO_4$) Modif ed zinc phosphates Calcium phosphate Modif ed calcium phosphates	Passivate metal surfaces by forming thin layers, such as chromate or phosphate layers. Solubility and reactivity are the critical parameters of active pigments
Active, cathodic protective anticorrosion pigment	Zinc dust	A special type of active pigment that acts by cathodic protection when applied to ferrous substrates. Act as sacrif cial anodes and protect the metal substrate. The paint needs to be formulated to yield good electrical contact between substrate metal and sacrif cial pigment particles. The most important requirement that enables zinc-rich primers to afford corrosion protection is a PVC close to or above the CPVC.
Passive anticorrosive pigments	Micaceous iron oxide Aluminium silicates	Barrier pigments - act by reinforcing the paint f lm 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 f at particles which protect substrate from contact with water and electrolytes.

* Zinc chromate contains hexavalent chromium and is not a substitution option.

of Zinc phosphate and Zinc oxide is a good option to reduce price and to provide good anticorrosion properties. Zinc oxide tends to react with fatty acids present in the binder, leading to the formation of zinc soaps, which act as a barrier for corrosive agents.

Example 3 presents the formulation of an alkyd base coat with zinc phosphate. Example 4 presents the formulation of an epoxy ester base coat combined with zinc phosphate and zinc oxide (See Appendix 3 Examples of Reformulations).

Anticorrosive pigment generation based on modif ed orthophosphates and zinc polyphosphate pigments have signif cantly improved the performance efficiency of conventional zinc phosphates (Heubach 2019). Since the effectiveness of a pigment depends on a vehicle, pigment producers recommend variations of zinc phosphate for different kinds of vehicles.

Zinc is a heavy metal and the demand for zinc-free anti-corrosive paints has increased in recent years. Calcium phosphate is an alternative to standard zinc phosphate and Table 8 presents information about its suitability as an alternative substitution for red lead. Anticorrosion properties can also be achieved by using calcium magnesium orthophosphate, and modif ed calcium phosphate is a pigment alternative for long-term anticorrosion performance.

The choice of extenders is also important as the major ingredients present in base coats are extenders (about 32% in Example 3, see Appendix 3). The physical properties of extenders, such as size and shape distribution, refractive index, density, hardness, and colour, together with their crystal structure and surface chemistry gives these minerals their functionality (Paint and Coating Industry Magazine 2001). Extenders can enhance mechanical properties and anticorrosion resistance. Using extenders with platy shaped particles prevent water, oxygen, and other chemicals from reaching the substrate through particles overlapping in a f lm.

Platy talc (hydrated magnesium silicate) is a proven anti-corrosion, hydrophobic extender, limiting the penetration of water and corrosive agents into the paint f lm. It reduces corrosion and peeling and blistering of the paint f lm. Due to the particle shape and chemical inertness, talc also promotes adhesion, increasing the paint's durability.

Mica and china clay are also functional extenders which, due to their shape, improve anticorrosion properties of base coats.

Where possible, non-toxic organic additives can be used to improve the corrosion protection afforded by coatings. This combination provides for an excellent combination of performance characteristics in terms of anti-corrosion synergy (Heubach 2021).

Example 4 (Appendix 3) presents epoxy ester base coat formulation with a corrosion inhibitor.

6.4.1 Assessment of Alternatives

The colour of a red lead-based anticorrosive paint formulation is orange. No alternatives provide this colour, but because anti-corrosive paints are never applied without a topcoat that cover up the color, this requirement is not very important. The company should contact its industry customers and explain the health and environmental and possible compliance advantages over the increased costs of a new, lead-free formulation. Moreover a lower cost can be achieved by reformulation (see Appendix 3, Case study 1)

The following table presents assessments of alternatives for red lead.

Figure 10 – Packing Line

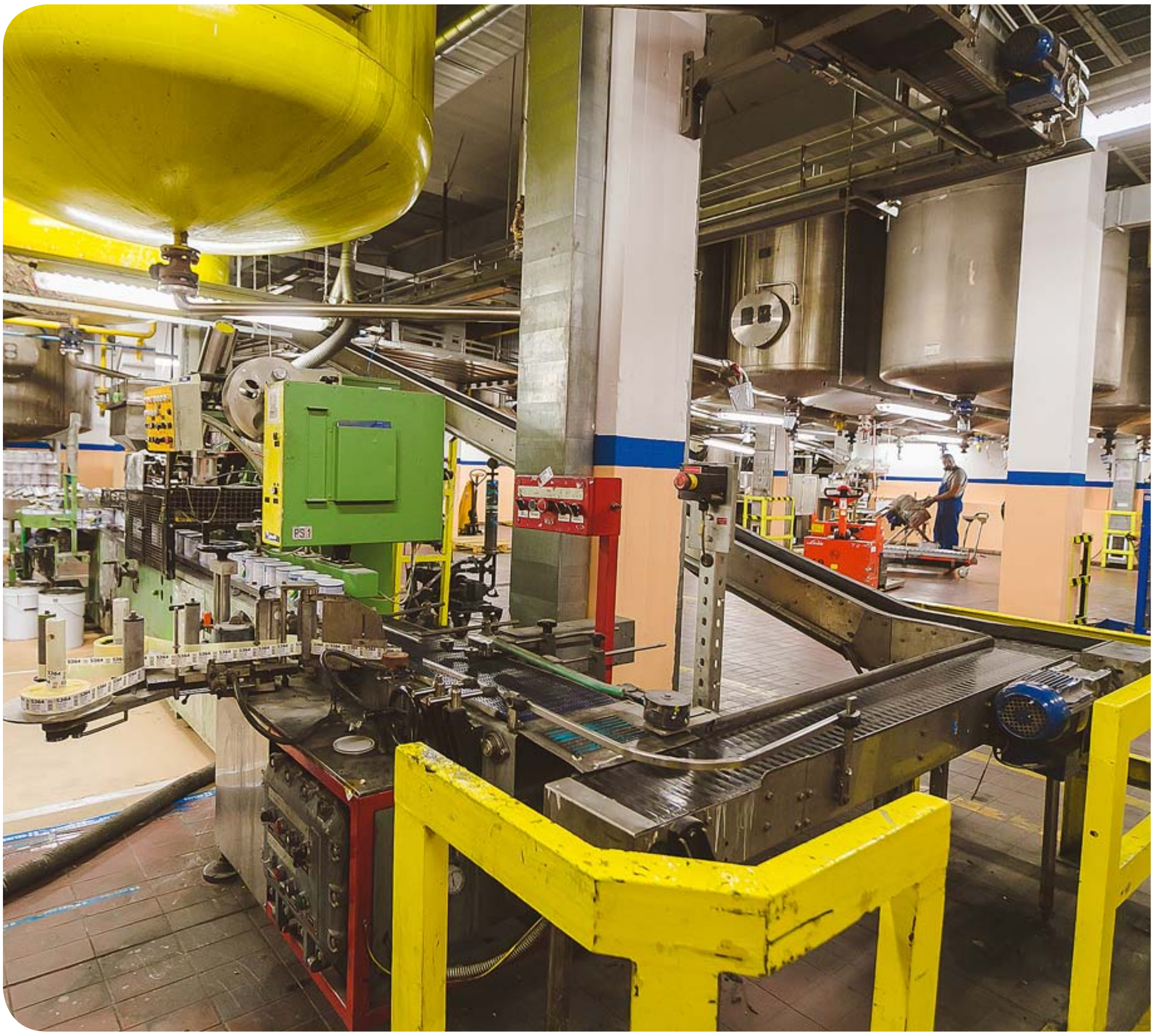


Photo: © Kansai Helios

Table 8 – Assessment of the Alternatives to PR 105

REQUEST	RED LEAD (PR 105)	ALTERNATIVE	
		ZINC ORTHOPHOSPHATE (PW 32)	CALCIUM ORTHOPHOSPHATE
Function	Excellent anticorrosion properties	Zinc phosphate and its modif cations have good anticorrosion properties. Primer colour cannot be the same, but decoration is not an important primer function.	Calcium orthophosphate and its modif cations have very good anticorrosion properties. Primer colour cannot be the same, but decoration is not an important primer function.
Production process		There is no need for changes in the production process.	There is no need for changes in the production process.
Environmental and human health hazard (OECD 2021a, ECHA 2021c and Pcimag 2001)	**H302**: Harmful if swallowed. **H332**: Harmful if inhaled. **H351**: Suspected of causing cancer state route of exposure if it is conclusively proven that no other routs of exposure cause the hazard. **H360**: May damage fertility or the unborn child. **H360Df**: May damage the unborn child. Suspected of damaging fertility. **H362**: May cause harm to breast-fed children. **H372**: Causes damage to organs. **H372**: Causes damage to central nervous system, blood and kidneys through prolonged or repeated exposure by inhalation or ingestion. **H410**: Very toxic to aquatic life with long lasting effects	**H400** - Very toxic to aquatic life **H410** - Very toxic to aquatic organisms with long lasting effects. Product is not hazardous for the human being when used properly (use of protective personal equipment).	Tricalcium phosphate does not present a hazard for human health due to its low hazard prof le. This chemical does not possess properties indicating a hazard to the environment based on its low hazard prof le (no aquatic toxicity at the limit of water solubility).
Economic feasibility		Cost-effective alternative. Depending on a product, cost may increase slightly.	Cost is higher.
Availability		There are many suppliers of Zinc phosphate on the market.	Calcium orthophosphate is available on the market.

Parallel testing of lead anticorrosive paint and reformulated paint is necessary to judge the effectiveness of substitution. Drying time, mechanical properties and testing of anti-corrosion properties is carried out. Outdoor exposure testing of anti-corrosion properties is a long-lasting process but accelerated anticorrosion tests like the Salt Spray test (ASTM B117-11 & DIN EN ISO 9227) and the Humidity test (ISO 6270-1:2017) may be conducted in cooperation with pigments producer(s).

6.5 Substitution of Lead White (PW 1)

Despite its low refractive index (1.94), basic lead carbonate pigment was used in paint formulations for many years. This pigment was successfully replaced by a more efficient titanium dioxide (PW 6) pigment with almost ten times the hiding power (Müller and Poth 2017). This formulation based on titanium dioxide pigment could contain less white pigment in the dry f lm. The difference could be covered by less expensive f llers achieving the same results.

If the substitution is carried out in the alkyd-based formulation, it is then necessary to act with care in terms of driers as white lead acts as a through drier. The quantity of the through drier in a new formulation must be increased. Zirconium and Strontium driers are recommended (see Chapter 7).

6.6 Substitution of Lead Chromate (PY 34) and Lead Chromate Molybdate Sulphate (PR 104)

Paint formulation is complex and depends on the requirements that are to be met. In addition to the vehicle, the choice of pigment plays an important role because decorative effects and technical properties are directly linked to it.

To facilitate the substitution process for companies, this section provides information on the properties of selected alternative pigments.

Economic feasibility includes many factors that are specif c to an organisation and they are not included in the assessment. Relative pigment costs are presented only.

PY 34 and PR 104 are used for properties that meet decorative performance, such as bright colours, clean colour shades and high visibility (signal function of a paint), as well as demanding technical criteria such as excellent hiding power, light and weather fastness, heat stability, in combination with non-bleeding properties.

The following table presents the technical characteristics of PY 34 and PR 104.

Table 9 – Characteristics of PY 34 and PR 104

CHARACTERISTIC	DESCRIPTION
Shade Functionality and Chroma	PY 34 – green shade to mid and red shade yellows and PR 104 from yellow to blue shade oranges.
Dispersibility	Excellent dispersibility. For certain purposes, they may be dispersed by dissolver only.
Hiding power (opacity)	Excellent f ow properties, possibility of high pigment loading which results in good hiding power.
Heat stability	Excellent heat stability. These pigments can be used at temperatures higher than 200 °C.
Bleeding	Pigments do not leach or bleed into the underlayer or into other coloured parts
Light, weather, and chemical resistance	The light fastness and weather resistance of lead chromates depend on the types used and their surface stabilisation. Most lead chromates used on the market are standard types and have excellent light and weather resistance. Poor alkali and acid resistance.

Figure 11 – Car Painting in Painting Chamber

Photo: www.pixabay.com

The substitution or withdrawal of a pigment class has a direct impact on downstream users. Formulators need to change their formulations to match the colour and technical requests. So far, there is no individual pigment alternative for an exact 1:1 replacement of specif c chrome yellow PY 34 or molybdate red PR 104 pigments. The most successful approach has been to use a combination of organic and inorganic pigmentation that can give the desired combination of properties in the f nal f lm.

There are many alternative pigments on the market and all of them have their pros and cons depending on intended use. Due to this, the assessment of alternatives is complex and based on several criteria: function (technical properties - dispersibility, heat resistance, weather resistance etc.), health, safety and environmental issues, pigment costs, and availability (see Flow chart 1).

It is necessary to be aware of the different properties, performance and cost of lead-free pigments compared to lead pigments.

6.6.1 Assessment of Possible Inorganic Pigment Alternatives

Inorganic pigments that could potentially substitute PY 34 or PR 104 are: Bismuth vanadate (PY 184), Mixed metal oxides (PY 53 and PBr 24), Iron Oxide Yellow (PY 42) and Iron Oxide Red (PR 101). There are other pigments available on the market that could be used in combination with other pigments to achieve different performance levels, such as PO 82 (tin titanium zinc oxide), PW 6 (titanium dioxide) and PY 216 (tin zinc rutile).

All inorganic pigment alternatives have different chroma and shade functionality. The best possible alternative for PY 34 is bismuth vanadate which has similar chroma and very good technical properties.

As inorganic pigments, these alternatives have similar properties to PY 34 and PR 104 regarding opacity, colour bleeding and can be used for external paint formulations due to good light and weather resistance. Heat stability up to 200 °C is also comparable to these pigments, except for PR 101 (red iron oxide), which has inferior heat resistance to PR 104.

Table 10 – Assessments of Possible Inorganic Pigment Alternatives

PIGMENT	COMPARISON WITH LEAD PIGMENTS
Possible Alternative to PY 34	
Bismuth Vanadate **PY 184**	**Function**: Very good technical properties - Durable paints with bleeding properties comparable with PY 34, excellent heat resistance. **Technical feasibility**: There is no need to change production process. **Environmental and human health hazards**: Not classif ed as hazardous to human health or the environment. **Economic feasibility**: This pigment is signif cantly more expensive, but properties are similar to the lead pigment. **Availability**: Limited sources of raw materials (Bi, V)*
Mixed metal oxides **PY 53**	**Function**: Paints are durable, but gloss retention is worse. It is not possible to achieve the same colour range. Bleeding properties and heat stability are comparable with PY 34. **Technical feasibility**: There is no need to change the production process. **Environmental and human health hazards**: Not classif ed as hazardous to human health or the environment. **Economic feasibility**: Price is similar to lead pigment prices. **Availability**: Available on the market.
Iron oxide **PY 42**	**Function**: Paints are durable. If a colour is important, this pigment is not a choice as colours are always darker and dirtier. Bleeding properties and heat stability are excellent. **Technical feasibility**: There is no need to change production process. **Environmental and human health hazards**: Not classif ed as hazardous to human health or the environment. **Economic feasibility**: Price is like lead pigment prices. **Availability**: Available on the market.
Possible Alternative to PR 104	
Iron oxide **PR 101**	**Function**: Paints are durable. If a colour is important, this pigment is not a choice as colours are always darker and dirtier. Bleeding properties are excellent, but heat stability is worse than that of PR 104. **Technical feasibility**: There is no need to change production process. **Environmental and human health hazards**: Not classif ed as hazardous to human health or the environment. **Economic feasibility**: Price is like lead pigment prices. **Availability**: Available on the market
Possible Alternative to PR 104 and PY 34	
Mixed metal oxide **PBr 24**	**Function**: Durable paints, but gloss retention is worse than that of lead pigments. The same colour range cannot be achieved. Excellent bleeding properties and heat stability. **Technical feasibility**: There is no need to change production process. **Environmental and human health hazards**: Not classif ed as hazardous to human health or the environment. **Economic feasibility**: Price is similar to lead pigment prices. **Availability**: Available on the market.

* There is an opposite opinion on pigment availability. Some companies believe that there are no availability issues with any alternative pigments.

6.6.2 Assessment of Possible Organic Pigment Alternatives

The list of organic pigments that may be alternatives to PY 34 and PR 104 is long and includes the following pigment families:

a. Azo Diarylides (e.g. PO 13, PO 34, PY 14, PY 83)
b. Azo Dianisidine (e.g. PO 16)
c. Azo Benzimidazolones (e.g. PO 36, PY 151, PY 154, PY 194)
d. Monoazo (e.g. PY 65 PY 74, PY 97)
e. Specialty Azo (e.g. PO 67)
f. Another organic alternative (e.g. PO 73, PY 110, PY 138, PY 189) and pigment
g. Diketopyrrolopyrrol Red – PR 254

There are other pigments available on the market that could be used in combination with other pigments to achieve different performance levels, such as PO3, |PO 5 (azo group), PR 112 (naphtol AS-D), PR 170 (naphtol), PY 82 (disazo-condensation), and PR 122 (quinacridone).

a. Azo Diarylides Pigment Group

The table below presents an assessment of some possible alternative pigments from this group to pigments PY 34 and PR 104.

The Azo Diarylides do not provide opacity and shade functionality. These pigments are appropriate for indoor use only because of their poor durability and gloss retention. They have poor heat stability (at over 200 °C, decomposition with generation of hazardous substances occurs).

Table 11 - Assessments of Possible Azo Diarylide Pigment Alternatives

PIGMENT	COMPARISON WITH LEAD PIGMENTS
	Possible Alternative to PY 34
PY 83 PY 14	**Function**: Durability is inferior compared to PY 34 thus paints formulated with these pigments are not suitable for outdoor use. Hiding power is lower and heat stability is poorer. Bleeding properties are good. By these pigments, only dull shades of yellow can be obtained. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: Not classif ed as hazardous to human health or the environment. **Economic feasibility**: These pigments are more expensive than PY 34. **Availability**: Available on the market.
	Possible Alternative to PR 104
PO 13 PO 34	**Function**: Durability is inferior compared to PR 104 thus paints formulated with these pigments are not suitable for outdoor use. Hiding power is lower and heat stability is poorer. Bleeding properties are good. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: Not classif ed as hazardous to human health or the environment. **Economic feasibility**: These pigments are more expensive than PR 104. Availability: Source of the raw materials for production are limited. There are a few global manufacturers.

b. Azo Dianisidine Pigment Group

This pigment group has similar properties to the Azo Diarylide pigment group.

The following table presents an assessment of PO 16 as an alternative to PR 104.

Dianisidine pigment has many of the same properties as the Diarylide pigments, but better heat stability. These pigments are not appropriate for outdoor use because of their poor durability and gloss retention.

Table 12 – Assessment of Possible Azo Dianisidine Pigment Alternative

PIGMENT	COMPARISON WITH LEAD PIGMENTS
PO 16	**Function**: Paint formulations are suitable only for indoor use because of inferior durability and gloss retention. Hiding power is lower and heat stability is poorer. Bleeding properties are good. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: No adverse f ndings were observed in the subacute oral study at the limited dose. PO 16 does not cause genotoxicity. **Economic feasibility**: This pigment is more expensive than PR 104. **Availability**: Sources of the raw materials for production are limited. There are a few global manufacturers.

c. Azo Benzimidazolones Pigment Group

Despite certain limitations, this pigment group is one of the best alternatives for PY 34 and PR 104 substitution.

The following table presents assessments of PO 36, PY 151, PY 154 and PY 194 compared to PY 34 and PR 104.

These yellow pigments are limited to green shades of yellow thus bright, high chroma shades in yellow cannot be achieved.

Table 13 – Assessments of Possible Azo Benzimidazolone Pigment Alternatives

PIGMENT	COMPARISON WITH LEAD PIGMENTS
	Possible Alternative to PY 34
PY 151 **PY 154** **PY 194**	**Function**: May be used for external paint formulations despite inferior durability and gloss retention compared to PY 34. Heat stability is comparable to this pigment. There is no colour bleeding. PY 194 is transparent and has the poorest durability of all these pigments. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: These pigments do not have adverse effects on human health or the environment. Economic feasibility: Direct cost related to pigments is higher. **Availability**: These pigments are available on the market.
	Possible Alternative to PR 104
PO 36	**Function**: This pigment may be used for outdoor paint formulations despite a bit inferior durability and gloss retention compared to PR 104. Heat stability is comparable to lead pigments. Bleeding properties are good. The colour is very close to the colour of PR 104, but little dirty. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: This pigment does not have adverse effects on human health or the environment. **Economic feasibility**: Direct cost related to pigments is higher. **Availability**: The pigment is available on the market.

d. Monoazo Pigment Group

Monoazo pigments have very poor solvent fastness, causing colour bleeding. These pigments can, for the most part, be used in water-based paints.

The following table presents assessments of these pigments compared to PY 34.

Table 14 - Assessments of the Monoazo Pigment Group as an Alternative to PY 34

PIGMENT	COMPARISON WITH LEAD PIGMENTS
PY 65 **PY 74** **PY 97**	**Function**: Because of poor durability these pigments are suitable for interior use only. Heat stability and gloss retention are also worse compared to PY 34. Bleeding occurs in solvent-based paints. These pigments are good PY 34 alternatives regarding colour. Bright green and red shade yellows can be achieved. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: These pigments do not have adverse effects on human health or the environment. **Economic feasibility**: Direct cost related to pigments is higher. **Availability**: Pigments are available on the market.

e. Specialty Azo

The following table presents assessments of PO 67 compared to PR 104.

Table 15 - Assessment of PO 67 as an Alternative to PR 104

PIGMENT	COMPARISON WITH LEAD PIGMENTS
PO 67	**Function**: This pigment may be used for outdoor paint formulations despite a bit inferior durability and gloss retention compared to PR 104. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: This pigment does not have adverse effects on human health or the environment. **Economic feasibility**: This pigment is much more expensive than PR 104. **Availability**: Limited availability.

f. Other Organic Alternatives

The further set of alternatives to PY 34 and PR 104 are organic pigments such as PO 73, PY 110, PY 138 and PY 139. This group of pigments is quite different among themselves, but all are characterised by their lack of opacity and limited chroma.

The following table presents assessments of these alternatives.

Table 16 - Assessments of Other Organic Pigments as Alternatives to PY 34 and PR 104

PIGMENT	COMPARISON WITH LEAD PIGMENTS
PO 73	**Function**: This pigment may be used for outdoor paint formulations despite a bit inferior durability and gloss retention compared to PR 104. Heat stability and bleeding properties are good. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazard**s: The pigment does not have adverse effects on human health or the environment. **Economic feasibility**: This pigment is much more expensive than PR 104. **Availability**: Limited availability.
PY 110	**Function**: The pigment is suitable for external use, as it has good durability and gloss retention. Heat stability and bleeding properties are good as well. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: This pigment does not have adverse effects on human health or the environment. Production is extremely dangerous because of intermediate products or toxic solvents. **Economic feasibility**: The pigment is much more expensive than PY 34. **Availability**: Limited availability.
PY 138	**Function**: Pigment is suitable for interior use only as durability and gloss retention are worse than those of PY 34. Heat stability and bleeding properties are good. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: This pigment does not have adverse effects on human health or the environment. Production is extremely dangerous because of intermediate products or toxic solvents. **Economic feasibility**: This pigment is much more expensive than lead pigments. **Availability**: Limited availability.
PY 139	**Function**: This pigment has worse durability and gloss retention compared to PY 34, but still can be used in external paint formulations. Heat stability and bleeding properties are good. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: This pigment does not have adverse effects on human health or the environment. **Economic feasibility**: The pigment is much more expensive than lead pigments. **Availability**: Limited availability.

g. Diketopyrrolopyrrol Red (DPP)

This pigment is used in automotive paints and has a number of very good properties, including heat stability and very good gloss retention.

The following table presents assessments of PR 254 as an alternative to PR 104.

- cover different performance levels for interior and exterior use, very high light and weather resistance.
- provide heat resistance >200 °C.
- have no bleeding issues.
- fulf l technical requirements regarding coating manufacturing equipment.

Table 17 - Assessment of PR 254 as an Alternative to PR 104

PIGMENT	COMPARISON WITH LEAD PIGMENTS
PR 254	**Function**: Heat stability and gloss retention are excellent. It is suitable for external paint formulations. Bleeding properties are good. **Technical feasibility**: There is no need for changes in the production process, but because of the inferior dispersibility of organic pigments, the grinding stage takes more time, and more energy is required. **Environmental and human health hazards**: The pigment does not have adverse effects on human health or the environment. **Economic feasibility**: The pigment is much more expensive than PR 104. **Availability**: There is a limited number of manufacturers on the market.

Pigments PY 34 and PR 104 are used in paints that can fulf l extreme durability, gloss retention, and the signal or contrast function of the colour. In the assessment of alternatives both qualitative (function, technical feasibility, EHS performance) and quantitative (economic feasibility, availability) criteria were taken into consideration.

All considered alternatives fail to fulf l some of the technical requirements that PY 34 and PR 104 fulf lled.

Lead chromate pigments are usually used in applications where not all their high-performance attributes are necessary (e.g., for indoor application). Therefore, it is not necessary to substitute these with a single pigment that has all the characteristics but rather, to f nd an alternative formulation that fulf ls specif c requirements.

The available alternative pigments and their combinations can:

- cover the entire colour space (from yellow, via orange to red);
- provide clean colour shades.
- fulf l high opacity requirements by combining organic and inorganic pigments.

6.6.3 Dry Pigment Preparations, Hybrid Pigments and Pigment Pastes

The pigment industry has developed a solution to replace PY 34 and PR 104 through customised dry pigment preparations. These pigments are a direct 1:1 substitution for PY 34 and PR 104. Pigments in preparation are selected to provide a good balance between the colorimetric properties and hiding power in the near-full-shade colour range. Pigment preparations cover ranges of yellow from green to red shade and orange from yellow to blue shade.

Hybrid pigments are a combination of a specially micronized complex inorganic colour pigmentary core particle and a pre-dispersed organic colorant attached to the surface of the core particle. Hybrid pigments are the best optimization of organic and inorganic pigment properties. They can be adjusted in colour, opacity and colour strength to match lead pigments, and are available in yellow, orange and red shade pigment preparations. Chroma enhancement of hybrid pigment technology offers great potential for formulating high-brilliance colours and paints which exhibit high performance in durability, opacity, and high gloss.

Example 5 (APPENDIX 3) provides guide formulations with hybrid pigments.

Pigment pastes are mono-pigmented concentrates with as high as possible content of a pigment and as little as possible grinding resin which is compatible with a broad range of vehicles. They can be used for tinting or for paints manufacturing.

If pigment pastes are used for f ne adjustment of the colour, small percentages of different pastes are added and grinding resin do not have inf uence on the performance of the paint that has been tinted. They could also be used as tinting enamels in lead-paint reformulation if there is no grinding equipment in a company.

Paint can also be produced of a blend of pigment concentrates (pastes) and let down with clear or white coating. In this case, greater quantities of pastes are required, and pastes have a greater inf uence on the paint performance. In this case, the requirements for pigment pastes are considerably greater.

6.6.4 Paint Reformulation with Pigments

There is not a single lead-free pigment alternative that covers all technical properties of PY 34 or PR 104. These pigments combine chroma on the level of the organic pigments and the best properties of the inorganic pigments including good hiding power, weather and light resistance, heat stability and resistance to bleeding. To achieve these properties, it is necessary to use a combination of inorganic and organic pigments in the paint reformulation. The inorganic pigments provide hiding power, while the organic pigments provide colour, chroma and tinting strength. Weather resistance depends on the organic pigments used and may be adapted to specif c requirements (see Table 18). By combining these two pigment types, the required paint performance is achievable.

The f rst stage of the reformulation process should be to def ne precisely which performance properties (function) a paint should have, in addition to colour:

- Is it for external or internal use (weather and lightfastness).
- Acceptable shade difference.
- Is there a request for heat resistance?
- Excellent hiding power at def ned f lm thickness.
- Shade and brightness of colour.
- Is bleeding acceptable (is paint use in a different-layer colour system, paint purpose).

If the paint is to be used exclusively indoors, there is no need to use expensive, high-performance, lightfast organic pigments. This helps to reduce reformulation costs.

In the following example of medium- to high-performance RAL 1021 pigmentation, the cost of pigments is approximately twice as high: the cost for a lead-based formulation is EUR 0.35 per m^2, while the cost of a lead-free formulation is EUR 0.71 per m^2 (ECHA 2014).

Example 1 - RAL 1021 Lead- and Lead-free Formulations*

PIGMENT	LEAD CONTAINING FORMULATION (%W/W)	LEAD-FREE FORMULATION (%W/W)
PY 151 (organic)		81.5
PY 34 (inorganic)	85.8	
PBr 24 (inorganic)	11.0	17.7
PY 139 (organic)	0.8	0.8

In the following example of medium- to high-performance RAL 3000, the cost of pigments is approximately 30% lower due to the use of 70% of inorganic pigments in the formulation, the cost of the lead-based formulation is EUR 0.31 per m^2, while the cost of the lead-free formulation is EUR 0.20 per m^2 (ECHA 2014).

Example 2 - RAL 3000 Lead- and Lead-free Formulations

PIGMENT	LEAD CONTAINING FORMULATION (%W/W)	LEAD-FREE FORMULATION (%W/W)
PY 53 (inorganic)	21.5	61.1
PR 104 (inorganic)	63.3	
PR 254 (organic)		27.3
PR 122 (organic)	8.0	
PR 101 (inorganic)	7.2	11.6

* Color and hiding power depend on the type of paint as colorants are developing differently in different vehicles.

In the most demanding performance level, the cost for lead chromate-free formulations are 2 - 3 times higher, in the mid-performance area, they are comparable and in the good-enough area, they are more affordable (ECHA 2014).

The following table summaries the properties of alternative pigments compared to PY 34 and PR 104.

The paint reformulation process for a lead pigment substitution does not only require colour adjustment; this is just one of the paint properties which is affected by pigments.

Depending on pigment combinations in initial formulations with lead pigment and in the new formulation, replacement of a dispersant agent and the grinding process should be considered (see Section 6.3).

Table 18– Alternative Pigment Properties Compared to PY 34 and PR 104

PIGMENT	EXTERNAL USE	WORSE HEAT STABILITY*	BLEEDING
PY 184, PY 42, PR 101, PY 110, PR 254, PR 122, PW 1, PY 216, PR 122, PY53, PBr.24, PY 151, PY 154, PY 194, PO 73, PY 139	YES	NO	NO
PO 36	YES	YES	NO
PO 13, PO 34, PY 14, PY 83, PO 16, PO 155	NO	YES	NO
PY 65, PY 74, PY 97	NO	YES	YES
PO 67	YES	NO	YES
PY 138	NO	NO	NO

*Compared to PY 34, PR 104

After eliminating pigments that cannot fulf l the requested requirements, colour adjustment with selected pigments may start, considering the properties of organic and inorganic pigments.

The basic approach would be to measure the colour of paint containing lead pigment and then to use colour matching tools (software and equipment) to produce the colour match required. Pigment producers can also help by proposing starting formulations for specific colours. Persons experienced in tinting could determine needed pigments and def ne a f nal formulation through an iterative colour tinting process.

Pigments, including PY 34 and PR 104, are almost never used alone in end-use. Therefore, the factors inf uencing the choice for one or other pigment to achieve a specif c colour and desired performance properties will vary signif cantly. Each paint is specif c and therefore, it is impossible to give an exact solution, but simply providing orientation on how to approach the substitution will depend on the initial paint formulation and requirements.

In some cases, due to very good dispersibility of lead pigments, the production process includes dispersing by dissolver only. Reformulation of lead paints implies the use of organic pigment(s) thus the production process must be changed and includes grinding.

If the lead formulation contains only inorganic pigments and the lead-free contains mainly organic pigments (Examples 1, 2), the reformulation requires a new dispersant and change in the grinding process (grinding time must be prolonged).

If lead formulation contains organic pigment, it is necessary to consider changes to dispersant type and quantity, depending on the pigments in the new formulation.

In the case of organic/inorganic pigment combinations, co-grinding should be avoided due to the different properties of inorganic and organic pigments related to grinding. Co-grinding may be avoided by:

- Production of tinting enamels and its mixing to achieve the desired shade:
- Separate grinding of pigments during the process (this means grinding inorganic pigment(s), and then, on the same grinding equipment, grinding organic pigment(s) under different conditions, or vice versa). A good example of this approach is the pigment combination presented in Example 2. First Pigment PY 53 and PR 101 should be pre-dispersed and dispersed together and then PR 254 or vice versa. Grinding conditions should be adjusted for each grinding phase.
- Use of f nished pigment dispersions (universal dispersions) compatible to a wide range of vehicles.

From a practical point of view, the choice between these alternative production methods depends on quantities to be produced and capacities of equipment, but cost plays a signif cant role as well.

To achieve successful scaling-up, grinding conditions in the laboratory should be comparable to those available in the plant.

It is of extreme importance to check the stability of dispersion (see Section 6.3). If dispersion is not stabilised it could affect the colour reproducibility, cause haze or other f lm defects and have an adverse effect on weather resistance.

Weather resistance can be tested by outdoor weathering, but to get a meaningful result, a long period of exposure is needed. For this reason, artif cial weathering is performed with the help of accelerated weathering testers. Methods include accelerated weathering using a QU-V weathering tester, a Weather-O-Meter (xenon or carbon arc lamp), or a Sun test (UV light). Accelerated weathering tests may run for several thousand hours, depending on the application. It is needed to test a new formulation parallel with lead paint. During and after weathering test colour retention (or the difference compared to unexposed paints), gloss retention (or the difference in gloss compared to unexposed paints) and chalking are measured.

Sunlight contains the entire visible spectrum of light, incandescent light has more yellows, oranges while f uorescent has more violets and reds. Since painted object will more likely be seen during the daylight, it should be used to make colour evaluations. If a colour booth is used for colour comparison, it is possible to use different kinds of light sources.

Text box 3 – Light Booth

Photo: Courtesy of BYK-Gardner

To make a proper judgment on colour matching it is necessary to:

- Apply samples to be tested over a base coat.
- Allow the base coat (if it is air drying) enough time to dry.
- Apply paint samples by the same technique.
- Apply standard colour and tested colour in approximately the same thickness.
- Compare colours using light booth or daylight.

In case of pigment substitution, metamerism may occur. Metamerism is present when two objects match under one light source but fail to do so under another. The most common cause for this is when one sample contains a pigment or pigments that do not exist in the other sample. As an example, samples match under daylight but are mismatched under incandescent lighting.

Photo: www.pixabay.com

7 SUBSTITUTION OF LEAD DRIERS

This Chapter provides information on driers that are most used (lead octoate and lead naphthenate), but literature references are provided for readers seeking information on other driers or more detailed information on most used driers.

Lead drier replacement does not require complex reformulation. As a result, these guidelines provide information on the general principles of the role of driers, individual characteristics and principles of dosage and paint testing as guidelines for substitution and future formulations of air-drying paints without lead additives.

7.1 Role and Composition of Driers

Some binders, such as resins based on drying oil and modified resins, such as alkyds and epoxy esters, are cured by a crosslinking reaction that is triggered by atmospheric oxygen. During the drying process, several different stages can be identified. The first process is the physical drying of the paint. In this process, a solvent evaporates and a closed film forms through the coalescence of the binder particles. Then chemical drying (also called oxidative drying) occurs, which is a lipid autoxidation process, and means that the paint dries by oxidation of the binder compound with molecular oxygen found in the air. This process may be accelerated by driers, which act as catalysts.

Driers belong to the class of soaps that are added to air-drying coating systems to accelerate or promote the transformation from a liquid film into the solid stage within an appropriate time after application. The transformation occurs by oxidative cross-linking, a process that is catalysed by the metallic cation of the drier.

When in solution, driers, also referred to as siccatives, are organometallic compounds soluble in organic solvents and binders. The anion in the metal soap largely determines whether the drier will meet the basic, desired properties, which are:

- good solubility and high stability in various kinds of binders.
- good storage stability of the drier.
- the ability to be present in high metal concentration.
- a sufficiently low viscosity, to make the handling of the drier easier.
- the drier should have an optimal catalytic effect and,
- the best price/performance relation (Bieleman 2000).

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. The metals used for the driers in each category are listed in the following table:

Metal Carboxylates are classed as:

- Neutral
- Acidic (more commonly classed as neutral)
- Basic
- Overbased - refers to the use of CO_2, which substitutes part of the acid in a drier

7.2 Properties of Selected Driers

Lead has been widely used as a secondary drier. Secondary driers are active in the cross-linking steps of drying, they are responsible for overall drying throughout the entire paint layer. Lead drier activity as the sole drier is very low. Lead also improves the f exibility and durability of the f lm. Apart from the toxicity issue, lead driers have other disadvantages. They can give rise to precipitation in the f lm, which may cause haziness and loss of gloss. This effect can be minimised when used in combination with a calcium drier that acts as an emulsif er and improves the pigment dispersing and wetting properties. They may also cause sulphur staining, as they react with sulphur to form a black lead sulphide. During paint storage, the reaction of the lead drier with long-chain fatty acids, formed by hydrolysis of the alkyd resin, may render the lead salt insoluble.

Lead driers are used in combination with cobalt or manganese. Calcium is often also added to avoid precipitation of the lead and hazing. A typical composition for a lead-based drier combination, calculated as the metal proportions of the total resin solids in the paint, is:

Table 19 – Metals Used for Driers

PRIMARY DRIERS	SECONDARY DRIERS	AUXILIARY DRIERS
• Cobalt • Manganese • Iron • Cerium • Vanadium	• Lead • Zirconium • Bismuth • Barium • Cerium • Strontium	• Calcium • Zinc • Lithium • Potassium

The organic acids for the preparation of such metal salts are selected for their optimum compatibility with binders and their optimum solubility.

The f rst driers were based on fatty acids or rosin, which were subsequently replaced by naphthenic acid, a material obtained from crude petroleum. Due to the scarcity of naphthenic acid in modern driers, it has been replaced by branched-chain synthetic acids such as octoate acid (2-ethylhexanoic acid), isononanoic (3,5,5-trimethyl hexanoic acid) acid or neodecanoic acid (mainly 2,2,3,5-tetramethyl hexanoic acid). Synthetic acids offer low odour, enable higher metal contents and consistent quality.

- 0.05 % cobalt
- 0.5 % lead
- 0.1 % calcium

Cobalt is a primary drier, and as such, functions predominantly as a surface drier. As a simple metal soap, it shows the best effectiveness at room temperature, and it can be used in a broad range of coatings and varnishes. If used alone, cobalt may have a tendency to cause surface wrinkling and poor through-drying. For this reason, it is used in combination with other metals such as manganese, zirconium, strontium, lead, calcium, and combination driers based on these metals. If cobalt is added as a drier to an undiluted resin, great increases in viscosity may occur. Cobalt driers may be used on their own in a waterborne system but are most often combined with a drying accelerator.

Cobalt needs only to be added in very small amounts and does, therefore, tend to minimise discoloration compared to other drier metals. Furthermore, cobalt does not discolour white coatings to the same extent as other driers since the deep blue colour of cobalt counteracts the yellow of the oils and alkyd binders and thereby enhances the whiteness of the paint.

The IARC (International Agency for Research on Cancer) classif es cobalt and cobalt compounds as “possibly carcinogenic to humans” (Group 2B). Furthermore, the substance may cause a form of allergic contact dermatitis. This characteristic qualif es cobalt driers for substitution, if possible.

Alternatives to cobalt driers are vanadium, iron, and manganese driers.

Manganese is an active drier as well, though less effective than cobalt. As an accelerator of polymerisation in baking f nishes, manganese is normally more effective than cobalt. Cobalt and manganese essentially improve the surface drying of paint f lm; the low-temperature drying performance of manganese is better than that of cobalt. Coatings with manganese do not wrinkle under high-humidity conditions, as f lms with cobalt alone do. It is generally better to formulate white paints with no manganese or very low manganese content because a pink or pinkish-yellow colour develops if high manganese contents are used. Manganese also has the advantage that it does not cause baked f lms to become brittle, which happens when only cobalt is used. Additionally, in systems prone to skinning, such as urethane oil-based coatings, manganese may be used with good results. However, manganese is seldom used alone: cobalt is usually the primary drier with manganese as a useful modif er. The effect of manganese driers can be modif ed by organic drier promoters.

Vanadium driers provide both surface and through-drying of the coating f lm. A considerable disadvantage is its tendency to stain the f lm; this limits the application of vanadium in paints considerably. It seems that vanadium also tends to be particularly prone to loss-of-drying-ability issues. They can be used in solvent-borne airdrying coatings and for high solids paints. In its emulsif able form, it may be used for water-borne systems as well.

Calcium has limited effectiveness as a drier, but it is very useful in combination with active driers. Calcium keeps the f lm matrix open, which allows more oxygen into the f lm and more solvent to escape early in the drying process. It is very effective when used together with cobalt and zirconium, to promote drying under adverse weather conditions such as low temperatures and high humidity. When calcium is used as an auxiliary drier, loss of drying ability becomes less of a problem when paints are stored over longer periods. Calcium driers help to improve hardness and gloss and also reduce skin-formation and silking. Most driers are added in the let-down stage of paint manufacturing, except for auxiliary driers such as zinc and calcium, which may generally be added to the mill base due to their effectiveness as wetting and dispersing agents.

For a lead-based drier, substitution alternatives are zirconium or strontium driers.

Zirconium, like lead and rear earth metals, serves as a through drier. Zirconium is only effective in combination with primary driers. It promotes surface and thorough drying. Unlike lead, zirconium is a poor pigment-wetting and dispersing agent. Therefore, the combination with calcium is necessary. The drying properties of cobalt/zirconium/calcium combination, at ambient temperature and humidity conditions, are quite similar to that of the lead-based combination drier. However, there are some problems with respect to its performance under critical conditions, i.e. lower than 10 °C.

Strontium has the same through drying performance as Zirconium but also offers benef ts in delivering auxiliary drying characteristics, resulting in improved stored stability and reduced “loss of dry” - especially benef cial in systems that are heavily pigmented or contain a high level of additives. Strontium seems to overcome the insufficient zirconium performance and is about to be the most prominent choice for lead substitution. In addition, it is a good pigment-wetting and dispersing agent preventing haze and wrinkling. However, outdoor performance may be affected negatively when strontium is used.

Overbased Strontium driers are a cost-effective alternative providing superior drying performance and are more cost-effective than neutral grades.

It has become common practice in the coating industry to use combinations of metals. These combinations involve one or more active driers with one or more auxiliary driers. These combination driers are being offered as ready-to-use or as precomplexed driers.

Mixed driers offer many advantages over traditional single metal driers:

- Improved efficiency.
- Reduction of the quantity of raw materials.
- Reduced risk of weighing errors.
- Optimal metal proportions.
- Simplif ed production process.
- Uniform quality.

Drying Accelerators - or complexing agents are non-metallic compounds (organic ligands), which increase the activity of primary drier metals, causing more rapid drying of the coating f lm. They function by complexing with the metal atoms through forming chelates. Two different types of drying accelerators are used extensively commercially. These are 2,2´-bipyridyl and 1,10-phenanthroline. They are used in solvent-borne as well as waterborne air-drying systems. In waterborne coatings, hydrolysis of the primary drier can lead to loss of dry upon storage of the coating. In combining the primary driers with drying accelerators, some protection from hydrolysis is obtained. Loss-of-dry due to adsorption of the metal drier on the pigment surface is also, to some extent, reduced using drying accelerators.

During storage, premature and undesirable crosslinking of the binder at the atmospheric interface (surface) under the inf uence of the oxygen may occur. Anti-skinning agents can inhibit or delay these undesirable oxidative processes.

7.3 Loss of Drying Ability

Oxidative-drying paints normally tend to have longer drying time after long storage periods. The loss of drier activity is caused mainly by:

- **Chemisorption of the drier onto the pigment surface**: as opposed to physical adsorption, which is a reversible process, chemisorption leads to permanent immobilisation of the drier. Chemisorption occurs onto pigments with acidic groups on the surface, and mainly occurs with pigments with a large surface area such carbon blacks and various organic pigments. The solvent composition also affects the chemisorption process; strongest adsorption occurs with poor drier solvents, such as very polar or very nonpolar solvents. Systems with aromatic free mineral solvents are more prone to chemisorption than systems diluted with aromatic white spirit.

- **Salt formation**: the reaction product of the drier ion and the long-chain aliphatic acids - their formation is caused by hydrolysis of the binder or other ingredient and is usually not soluble in the paint material and it deposits after crystallisation which results in the loss of the drier.

- **Formation of insoluble complexes**: this phenomenon typically occurs in low odour paints, diluted with pure aliphatic solvents. Complexes of different types of driers, made up of relatively short-chain aliphatic acids, such as octanoates, have only limited solubility in these solvents and tend to crystallise out. Over-basic driers are more sensitive to this effect than neutral driers. Driers consisting of longer acids such as C9-C11 are more soluble and are less prone to crystallisation in these coating systems.

- **Hydrolysis of the drier**: this process is the main reason for drying-ability loss in waterborne coating systems. In the presence of water, the drier is rapidly hydrated. Moreover, water is a good ligand for cobalt and therefore complexes cobalt easily. The formed hydrates are unstable and lead to hydrolysis of the metal soap and subsequently to insolubility of the basic metal.

Loss-of-dry ability may be avoided by the following means:

- **Selection of a drier system** that is totally compatible with the coating system. The drier should be soluble in the binder and not result in any haze formation upon storage or during the drying stage. For pigmented systems, it is recommended to carry out a compatibility test in the medium without the addition of pigment or extenders.

Figure 12 – Resin Production

Photo: © Kansai Helios

- **Introduction of a sacrificial drier in the grinding phase**. An auxiliary drier such as calcium may be used, especially when the loss of drying ability is due to the chemisorption of the primary drier onto the pigment. This approach has its limitations and cannot always be used, because if there is an overdose of the auxiliary drier, the viscosity and hardness (softening effect) as well as durability or colour resistance may be affected negatively.

- **Use a "feeder drier"** such as cobalt hydroxy naphthenate. This feeder drier is available as a paste and is insoluble in mineral spirits. These driers:
  - Replenish active metals adsorbed onto pigments (dark colours);
  - Release additional metals in a controlled manner.
  - React slowly with residual resin acidity.

7.4 Assessment of Alternatives to Lead Driers

Driers may contain components (organic solvents or drying accelerators) with undesirable health and/or environmental effects. In a substitution, it is, therefore, necessary to look upon the entire product and not just the active metallic compound. This section focuses on alternatives to lead octoate, a common drier. The synthetic acid used in lead octoate and its non-lead alternatives, octoate acid (2-ethylhexanoic acid), is now def ned as hazardous and is suspected of causing damage to the unborn child (ECHA 2021d). Non-hazardous alternatives such as driers based on isononanoic acid (3,5,5-trimethyl hexanoic acid) or neodecanoic acid (mainly 2,2,3,5-tetramethyl hexanoic acid) are recommended for use.

In the following table, an assessment of the alternatives for lead octoate, is presented.

Table 20 - Assessment of the Alternatives for Lead Octoate

REQUEST	LEAD OCTOATE*	ALTERNATIVES			
		ZIRCONIUM OCTOATE*	STRONTIUM OCTOATE**	ZIRCONIUM NEODECANATE	STRONTIUM NEODECAATE
Function	Through-drier (ECHA 2021)	Through-drier	Through-drier	Through-drier	Through-drier
Technical feasibility	Drier is added to let-down.	There is no need for changes in the production process.	There is no need for changes in the production process.	There is no need for changes in the production process.	There is no need for changes in the production process.
Environmental and human health hazard	**H226** - Flammable liquid and vapour **H302** - Harmful if swallowed **H332** - Harmful if inhaled **H410** - Very toxic to aquatic life with long lasting effects. **H360** (f,d) - May damage fertility. May damage the unborn child. **H371** - Cause damage to organs through prolonged or repeated exposure **H336** - May cause drowsiness or dizziness	**H302** - Harmful if swallowed **H304** - May be fatal if swallowed and enters airways **H318** - Causes serious eye damage **H361d** - Suspected of damaging the unborn child. **H315** - Causes skin irritation	**H302** - Harmful if swallowed **H304** - May be fatal if swallowed and enters airways **H318** - Causes serious eye damage **H361d** - Suspected of damaging the unborn child. **H315** - Causes skin irritation	**H304** - May be fatal if swallowed and enters airways	**H304** - May be fatal if swallowed and enters airways
Economic feasibility		Prices are unstable.	Strontium raw material is generally cheaper and more stable in pricing compared to Zirconium.	These driers are more expensive than driers based on other acids.	
Availability	Lead driers are available on the market, but are banned in many countries	Produced predominantly in Australia, West Africa and China, Zircon sand - the raw material for all zirconium chemicals – is in short supply due to mining restrictions, which has reduced availability and subsequently driven price increases.	There are no supply issues with Strontium and the price is stable at present.	These driers are still produced by several companies but are not widely available.	

* Environmental and human health hazards based on the SDS from the company DURA

** Ibid

7.5 Paint Reformulation with Driers

Since the oxidative-curing process is a complex reaction in which crosslinking and rupturing of bonds occur simultaneously, the dosage of driers is critical. Effective drying requires a minimum quantity of drier. Adding too much impairs f lm formation and f lm properties as metals promote continuous further oxidation, leading to embrittlement of the binder and hence of the paint.

The quantities of some driers such as organic salts of cobalt, manganese, vanadium and iron, are restricted because of the coloration of the paint f lm.

Certain pigments are also capable of accelerating oxidative drying, e.g. iron oxides (mainly transparent grades due to their large surface area), metallic zinc pigments, zinc oxides, calcium carbonates and lead pigments. Other pigments may act as inhibitors for oxidative curing, e.g. carbon blacks, ultramarine pigments and some phthalocyanine pigments. They adsorb driers on their surfaces. Thus, the amount of siccative addition must be slightly increased (Bieleman 2000).

Commercially available driers are characterised by their metal content. The technical data sheets indicate the orientation quantities of driers, including combination products. The recommendations for paints based on standard long oil alkyd resins will differ from that of a short oil alkyd or high solids coating; similarly, the nature of the oil/fatty acid and any hybridisations will change the optimal drier system. To achieve maximum performance of a paint, the formulator needs to f nd the right balance of primary, through and auxiliary driers. Specif c metals can improve def ned qualities; such as increased hardness, higher gloss, better through dry.

In the following table, recommended starting point ranges (one of the producers) are given:

Table 21 – Recommended Starting Point Ranges (Durachem ND) for Selected Driers

METAL	RANGE CALCULATED AS PERCENTAGE METAL ON RESIN SOLIDS				
	LONG OIL ALKYD	SHORT OIL ALKYD	STOVING/ BAKE	WATERBORNE	ULTRA-LOW VOC
Lead	0.50-0.80	0.35-0.70			
Zirconium	0.20-0.40	0.15-0.30		0.10-0.30	0.08-0.15
Strontium	0.20-0.40	0.15-0.30			
Cobalt	0.04-0.07	0.03-0.06	0.02-0.05	0.04-0.12	0.08-0.15
Calcium	0.15-0.30	0.10-0.20		0.05-0.10	0.15-0.45
Manganese	0.06-0.09	0.04-0.09	0.02-0.05	0.06-0.14	0.08-0.15
Vanadium	0.08-0.12	0.06-0.09			

Text box 4 – How to Calculate the Quantity of Drier Required?

Quantity of drier required is calculated using the following equation:

kg of drier = (kg of resin) x (% of resin solids) x (% of dosage)/100 x (% of metal in drier)

Example: Suppose we have a paint with an alkyd resin (50 % solids) content of 500 kg in formulation (1000 kg), and we want a 0.3 % dosage of Zirconium (18%) drier

500 x 50 x 0.3/100 x 18 = 4.2 ➡ 4.2 kg of Zirconium drier (18%) per 1000 kg of the paint should be added.

Lead cannot be simply substituted by zirconium; the ratios of cobalt and calcium also have to be adjusted. According to different sources in literature, lead driers in the formulation is substituted by 60 - 75% of Zirconium driers, calculated on metal content. The best approach would be to start with driers quantities recommended by the producer.

Zirconium driers are substituted equivalently by strontium driers, calculated on metal contentIf a strontium drier substitutes a lead drier, there is no need to change the quantities of cobalt and calcium driers.

It is necessary to test paint and adjust driers quantities to achieve the best possible result, but a general rule is to keep driers at a minimum to avoid negative effects.

If drying time and film properties comparable to the reference product (with a lead drier) is obtained, how the new formulation is influenced by storage should be investigated. Storage at an elevated temperature (40 °C for two weeks) stimulates prolonged storage, to some extent. An increase in drying time after storage indicates a loss of drying ability of the drier system. If severe phase separation or sedimentation was observed for the alternative system and this was not the case for the reference product, the alternative system is not acceptable, especially if the sample was not easily mixable again by stirring. Viscosity, gloss and hardness of the dry film should be measured before and after storage.

The table 22 provides measures used to eliminate issues connected in terms of driers.

Text box 5 – Drying Tests

After the initial drying time test, the most promising alternative drier systems should be tested on stability, viscosity, film hardness, gloss and yellowing (one month in a dark cupboard). All tests in the technical evaluation of the alternatives should be performed as comparative tests, meaning that the reference is the product containing the original lead drier system.

Figure 13 – Drying Time Recorder

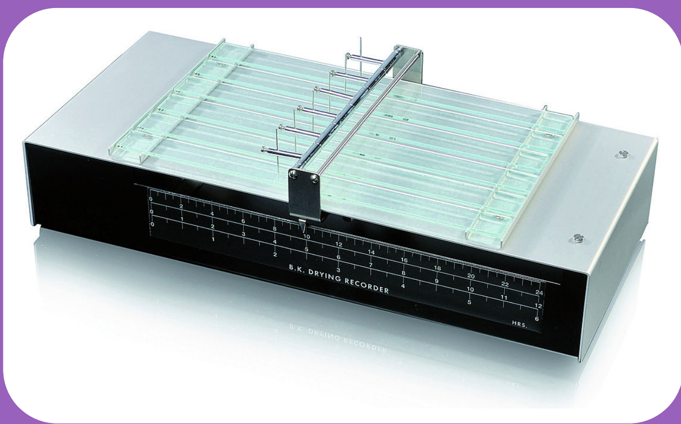


Photo: Courtesy of BYK-Gardner

Table 22 – Drier-related Troubleshooting*

DRIER RELATED TROUBLE	INCREASE OR	REDUCE OR	ADD OR	REPLACE
Film too tacky	Cobalt or Manganese		Cobalt or Potassium	
Blooming	Calcium			
After-tack	Zirconium		Iron	
Poor colour retention			Zinc	
Low gloss			Zinc	
Poor drying in high humidity			Cerium or Lanthanum	
Coating is too soft			Zinc, Cerium or Bismuth	
Loss of dry through pigment absorption	Neutral Calcium		Zinc, Iron or drying accelerator	
Loss of dry through drier precipitation	Over-based Calcium		Drying acceler ator	
Dries too slowly	All driers			
Paint has poor water resistance				Calcium with Barium or Strontium
Wrinkling	Calcium	Cobalt	Zinc	Cobalt with Manganese
In-can skinning	Anti-skin agent	Cobalt		
Poor through dry	Zirconium or Calcium	Cobalt		
Yellowing	Calcium or Lanthanum	Cerium or Manganese		
Slow surface dry	Cobalt			Calcium or Potassium
Dust entrapment	Cobalt			
Slow drying at low temperature				Calcium with Barium, Strontium or Lithium or Cobalt with Manganese
Film is too brittle	Zirconium	Cobalt		
Sulphide staining				Lead with Zirconium or Strontium
Poor pigment dispersion	Incorporate Zinc or Calcium Octoate in the mill-base			

Strontium driers are now considered to have better all-round performance compared to zirconium driers. They are a cost-effective alternative to zirconium driers providing superior drying performance in low temperatures and high humidity conditions.

* Source: Troy Corporation

Photos: www.pixabay.com

CONCLUSON

Lead is classically a chronic and cumulative toxin. Exposure to lead is a major public health and environmental concern. Infants, young children (especially those who belong to the age of 5) and pregnant women are most susceptible to the adverse effects of lead and even relatively low levels of exposure can cause serious damage to human health.

Making the switch to paint formulations without intentionally added lead raw materials is a challenge to the industry and raw material suppliers are trying to help paint manufacturers meet those challenges. Since the process began almost a decade ago, there are many raw materials on the market that could replace lead compounds in paints.

Lead anticorrosive pigment (PR 105) has excellent anticorrosive properties but could be replaced by Zinc phosphates or for better anti-corrosive performance with modif ed orthophosphates and zinc polyphosphate pigments. Further improvement in performance and environmental protection leads to Calcium phosphate and its modif cations.

PY 34 and PR 104 fulf l strict technical requests and produce clear, deep shades, however they are extremely hazardous. There is no single pigment that can replace these pigments, but with the def ned criteria that paint should fulf l, it is possible to use a combination of pigments as an alternative.

An alternative to lead driers is zirconium or strontium driers.

The following f ndings have been observed during the paint reformulation pilot test with the SMEs under the SAICM GEF project.

Text box 6 – Key Findings From Reformulation Pilot

In most of the SMEs working in the project, lead driers are not in use and all case studies are related to lead pigment substitution.

We learned during the project that lead pigments are used in solvent-based and water-borne paints

- Some small enterprises do not have all the necessary equipment to carry out paint performance testing and scale-up. Lack of grinding equipment can be addressed by using pigment pastes.
- Suppliers have less commercial interest in small markets (users) and the availability of lead-free pigments is limited (Jordan, Ecuador). This was a factor that slowed down the project in these countries, in addition to the COVID pandemic.
- All participants agreed that suppliers' technical support is important. Some of the project partners organized meeting with the project technical, which resulted in a better understanding of the reformulation process and accelerated the right pigment selection.
- SMEs successfully and significantly reduced the concentration of lead in reformulated paints – as shown in Case study 3 (Appendix 3). Lead content is reduced from 34,689 ppm in starting formulation to less than 56 ppm in reformulated alkyd paint
- Economic costs of reformulation varied. In some cases, the lead alternative raw material was less expensive lowering the cost as shown in Case study 1 (Appendix 3). In other cases, the price of the paint increased significantly.
- Companies reformulated their lead paints successfully, but further work is needed on fine-tuning of shades and cost optimization.

See appendix 3 for more information on SME case studies.

In these Guidelines, the general principles of paint reformulation have been presented. Each reformulation, due to different initial lead-containing formulations regarding colour and other paint properties, requires a specif c approach. In-depth analyses and more specific data were provided to participating companies according to their specif c needs.

According to the paint industry, the reformulation of paints to eliminate lead compounds is feasible, and the technical and cost impacts are manageable.

Lead compound elimination may also provide potential economic advantages as well. By producing or using paints without lead compounds, paint manufacturers and users (such as toy manufacturers) can ensure access to markets where lead content in paint has already been restricted.

Figure 14 – Paint Production Factory in Colombia

Photo: NCPC Colombia

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Appendices

APPENDIX 1 – TIPS FOR FINDING INFORMATION ON LESS HAZARDOUS ALTERNATIVES

When doing an internet search:

Search after:

- Substitute... (Name of a chemical that should be replaced)
- Alternative... (Name of a chemical that should be replaced)
- Name of a chemical that should be replaced… (product name, for example, paint)
- Safe/safer, green, healthier, ecological… (product name)

Include in searching:

- Chemical name + way of use (for example pigment in paints)
- Be precise as possible: sector, process, product, function
- Synonyms and identif cation numbers (CAS, EC, etc.)

Figure 15 – Start with search

Photo: www.pixabay.com

APPENDIX 2 – FORMULATIONS - EXAMPLES

NOTE 1: Examples 1 and 2 – see chapter 6.6.4 PAINT REFORMULATION

NOTE 2: Color and hiding power depend on the type of paint as colorants are developing differently in different vehicles

Example 3 - Formulation of Lead-free, Low-Cost Long-oil Alkyd Primer (ICL 2021)

RAW MATERIAL/ SUPPLIER	%WT/WT	CLASS
GRIND		
70% Long Oil Alkyd Resin	21.05	Vehicle
Mineral Spirits (odourless)/LANXESS	18.71	Solvent
Bentone 34/Omya	0.94	Thickener
Methanol/LANXESS	0.23	Solvent
Bayferrox 180 M/ Bayer	4.68	Synthetic iron oxide red pigment
HALOX® Z-PLEX 111/ICL Advanced Additives	9.35	Zinc phosphate complex (Precipitation and anodic passivation)
Mica Talc AT.1.	32.74	Filler
LET DOWN		
70% Long Oil Alkyd Resin	2.34	Vehicle
Mineral Spirits / LANXESS	8.84	Solvent
Zirconium 12% (OMG Europe)	0.28	Siccative
Cobalt 12% (OMG Europe)	0.09	Siccative
Zinc 8% (OMG Europe)	0.37	Siccative
Calcium 4% (OMG Europe)	0.19	Siccative
Skino 1 (OMG Europe)	0.19	Anti-skinning agent
TOTAL	**100**	

Example 4 – Formulation of Lead-free Industrial Epoxy Ester Base Coat

RAW MATERIAL/ SUPPLIER	%WT/WT	CLASS
GRIND		
Uranox EE4 X-50/DSM Special resins	20.00	Vehicle
Bentone 34 (10% in white spirit/ethanol, 85/5)/Omya	4.7	Thickener
Special black 100/ Orion	0.30	Pigment
Zinc oxide	4.4	Pigment
Zinc phosphate ZP 10/Heubach	11.20	Pigment
Fintalc M15/Mondo Minerals B.V.	9.00	Filler
Barytes EWO/ Sachtleben Minerals	4.40	Filler (Barium Sulphate)
Bayferrox 222 FM	1.70	Pigment
Heucorin RZ/Heubach	1.20	Organic corrosion inhibitor
LET DOWN		
Uranox EE4 X-50/DSM Special resins	14.70	Vehicle
Octa Soligen Co 6/ Borchers	0.10	Drier
Exkin II	0.20	Anti-skinning agent
Shellsol A (Shell)	12.10	Solvent
TOTAL	**100**	

This paint is fast-drying, dust-dry in 45 min, dry to handle in 2 hours, and fully cured in one day

Example 5 – Lead-free Guide Formulations (Propsector 2021)

SHADE			
RAL 1018	**%WT/WT**	**RAL 1021**	**%WT/WT**
Brufasol Yellow AL 10	59.708	Brufasol Yellow AL 10	63.290
Titanium dioxide	38.800	PY 4	18,987
PY 83	1.194	PY 83	2.532
PY 101	0.298	PY 101	10.126
		PB 15.3	3.165
		PG 7	1.909
RAL 1023	**%WT/WT**	**RAL 2000**	**%WT/WT**
Brufasol Yellow AL 30	95.487	Brufasol Yellow AL 30	62.651
PY 83	1.909	PR 177	12.048
PY 101	2.604	PY 83	12.048
		PY 101	13.253
RAL 2004	**%WT/WT**	**RAL 3000**	**%WT/WT**
Brufasol Yellow AL 30	52.175	Brufasol Yellow AL 30	24.795
PO 34	27.536	PR 254	24.793
PY 101	5.797	PY 101	25.619
Titanium dioxide	14.492	Titanium dioxide	14.049
		Oxide red	10.744

Example 6 – Lead-free Guide Formulations with Hybrid Pigments*

PIGMENT	ALTERNATIVE A	ALTERNATIVE B
(Pigment level calculated on solid binder – 23.7%)		
RAL 1003 Signal Yellow	**%WT/WT**	**%WT/WT**
TICO® Yellow 594	39.80	52.82
TICO® Yellow 622 N	24.90	25.35
HEUCODUR® Yellow 152	13.00	
HEUCODUR® Yellow 151	20.12	19.49
Iron Oxid Yellow	2.8	2.34
RAL 1004 Golden Yellow	**%WT/WT**	**%WT/WT**
TICO® Yellow 594	65.15	
HEUCODUR® Yellow 152	19.60	
Iron Oxid Yellow	15.25	
RAL 1007 Daffodil Yellow	**%WT/WT**	**%WT/WT**
TICO® Yellow 594	13.50	
TICO ®Yellow 622 N	46.79	
HEUCODUR® Yellow 251	39.70	
Carbon black	0.01	
RAL 1023 Traffic Yellow	**%WT/WT**	**%WT/WT**
TICO® Yellow 594	68.40	96.70
TICO® Yellow 622 N	3.10	3.30
HEUCODUR® Yellow 251	28.50	

* More examples can be found on the site: https://www.heubachcolor.com/f leadmin/downloads/guide_formulations/Richtformulierungen_Tico.pdf

APPENDIX 3 – CASE STUDIES OF PAINT REFORMULATION

In this section examples of successful reformulation of lead paints are presented. Pilot demonstration projects were conducted in select SMEs in seven countries over the period of 2019 to 2021.

CASE STUDY 1 – REFORMULATION OF LEAD PAINT (ALKYD ANTICORROSIVE PAINT)

Company and address: Zhejiang Yutong New Material Co., Ltd., No. 11, Shengyang Road, Shangma Industrial Park, Wenling Economic Development Zone, Zhejiang, China.

Contact person: Wu Xiaojun, R&D Manager

Number of employees: 110

Company decided to take part in this project for competitiveness, environmental awareness and social responsibility reasons.

PRODUCTION DATA

Installed capacities (t/year)	25000 t/year
Production in 2019 (t)	11000 t/year
Type of paints currently produced	solvent-based coatings, water-based industrial coatings
Type of paints that contain lead	alkyd anti-rust paint, alkyd top coat
Production of paints that contain lead in 2019 (t)	900 t/year
Consumption of raw materials that contain lead in 2018 (t)	73 t/year

SELECTION OF PRODUCT FOR REFORMULATION

Product trade name	**Anticorrosive paint**
Product type (base, use)	Alkyd resin-based, used as primer and anti-corrosive coating on steel structures above the waterline and on land
Production of this paint in 2018 (t)	2012 t
% (weight) of this product production related to lead paint production in 2018	44.7%
Reasons for this product selection	In this company, only alkyd products contain lead-containing pigments are made. By reformulating these products there will be no more lead paint in te production program.

PRODUCT REFORMULATION

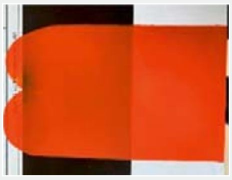
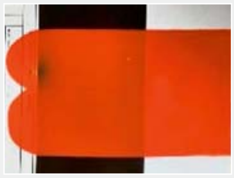
RAW MATERIAL

Lead compound to be substituted	Red lead pigment (PR 105)
Content of lead compounds in the formulation of selected product (% calculated on total formulation)	Primer: 15%; Topcoats (depend on shade); 0-20%
Total consumption of this lead compound 2019 (t)	73 t

ALTERNATIVES ASSESSMENT

Possible alternatives that were assessed	Iron Oxide Red, Iron titanium powder
Selected alternatives	Both alternatives were selected for testing
Main reason for selection of this alternative	The production process is the same as that of red lead. The alternatives do not contain heavy metals and the price is lower
Potential for implementation of these alternatives in other products (number of products and/or tons, if possible)	Used only in the selected product

RESULTS OF PARALLEL LAB TESTINGS

Request (according to technical specifications)	Lead paint (Red lead)	Paint free of lead (Iron Oxide Red)	Paint free of lead (Iron titanium powder)
Colour			
Particle size (µm)	≤60µm	≤60µm	≤60µm
Drying time	Surface 10 min Curing 6 h	Surface 10 min Curing 6 h	Surface 10 min Curing 6 h
Salt spray (300 h)	300 h	300 h	300 h
Adhesion	2	2	2
Hardness	HB	HB	HB

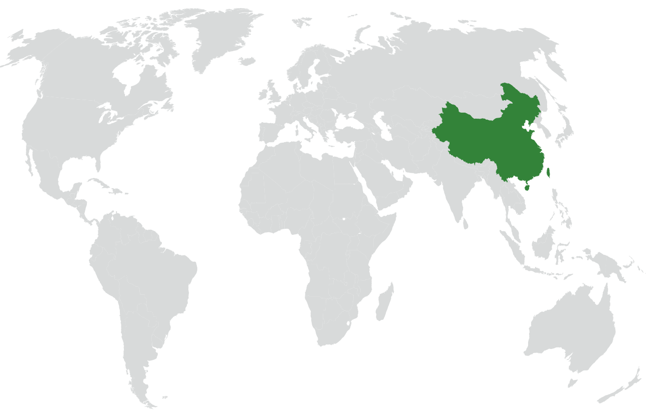
Text box 7 – Conclusion and Next Steps

- The lead-free reformulation products have similar properties on the mechanical, drying, and anti-corrosive properties compared to lead paint. Colour of product using iron oxide red is quite different but similar by using alternative of iron titanium powder.
- Reformulated products are about 10% less expensive than starting formulation.
- However, there is still challenges of clients' preference on red lead paint. It is further needed to raise awareness on the lead elimination for local regular clients and the public.

Figure 16 – Paint factory Zhejiang Yutong New Material Co. in China

Photo: NCPC China

CASE STUDY 2 – REFORMULATION OF LEAD PAINT (EPOXY FLOOR COATING)



Company, address and website: Zhejiang Tiannv Group Paint Co., Ltd., No. 150, Gaoxin West Second Road, Tongxiang Economic Development Zone, Jiaxing City, Zhejiang Province, China; www.tiannucoating.com

Contact person: Zhang Yarong, Technical Manager

Number of employees: 298

Company decided to take part in this project for competitiveness, environmental awareness, standard compliance and social responsibility reasons.

PRODUCTION DATA

Installed capacities (t/year)	120000 t/year
Production in 2019 (t)	52211 t/year
Type of paints currently produced	1) Solvent-based coatings: industrial anticorrosive coatings, pre-coated coil coatings, electronic insulation coatings, alkyd coatings, special coatings, etc. 2) Water-based industrial coatings 3) Water-based architectural coatings
Type of paints that contain lead	Paints used for colouring, such as yellow and orange
Production of paints that contain lead in 2019 (t)	15000 t/year
Consumption of raw materials that contain lead in 2018 (t)	696.5 t/year

SELECTION OF PRODUCTS FOR REFORMULATION

Product trade name	**Epoxy floor coating**
Product type (base, use)	Epoxy resin and amine curing agent are the main f lm-forming base materials, which are mainly coated on the surface of cement, concrete, stone or steel to decorate and protect the ground.
Production of this paint in 2019 (t)	860 t
% (weight) of this product production related to lead paint production in 2018	25%
Reasons for this product selection	The mandatory standard has been released for controlling hazardous substances including lead.

PRODUCT REFORMULATION

RAW MATERIAL

Lead compound to be substituted	Lead chromate - PY 34
Content of lead compounds in the formulation of selected product (% calculated on total formulation)	0%-25% depends on shade
Total consumption of this lead compound 2019 (t)	517 t
% (weight) of this product production related to lead paint production	11.2

ALTERNATIVES ASSESSMENT

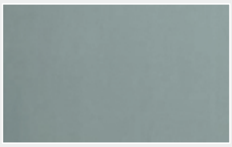
Possible alternatives that were assessed	Organic yellow, Iron oxide yellow
Selected alternative(s)	Organic yellow (PY 83, PY 74), Iron oxide yellow (PY 42)
Main reason(s) for selection of this alternative	The alternative pigments do not contain heavy metals such as lead and chromium.
Potential for implementation of this (these) alternative(s) in other products (number of products and/or tons, if possible)	Further lab test needed.

RESULTS OF PARALLEL LAB TESTINGS

Request (according to technical specifications)	Raw material to be substituted – PY 34	Alternative – Iron oxide yellow & organic yellow
Drying time	Surface 2 h, Internal 10 h	Surface 2 h, Internal 10 h
Pencil hardness(scratch)	2H	2H
Impact resistance/cm	50	50
Flexibility/mm	2	2
Cross-cut test/level	1	1
Abrasion resistance (750g/500 r)/g	0.042	0.050
Water resistance (168h)	No blistering, no falling off, f rst grade discoloration	No blistering, no falling off, f rst grade discoloration
Oil resistance (120# gasoline 168h)	No blistering, no falling off, f rst grade discoloration	No blistering, no falling off, f rst grade discoloration
Acid resistance (10%H_2SO_4, 168h)	No blistering, no falling off, f rst grade discoloration	No blistering, no falling off, f rst grade discoloration
Alkali resistance (10%NaOH, 168h)	No blistering, no falling off, f rst grade discoloration	No blistering, no falling off, f rst grade discoloration

PRODUCT REFORMULATION

RESULTS OF SCALE-UP

Request	Lead paint	Paint free of lead
Colour		
Drying time	Surface 2h, Internal 10h	Surface 2h, Internal 10h
Pencil hardness(scratch)	2H	2H
Impact resistance/cm	50	50
Flexibility/mm	2	2
Cross-cut test/level	1	1
Abrasion resistance (750g/500 r)/g	0.045	0.048
Water resistance (168h)	No blistering, no falling off, first grade discoloration	No blistering, no falling off, first grade discoloration
Oil resistance (120# gasoline 168h)	No blistering, no falling off, first grade discoloration	No blistering, no falling off, first grade discoloration
Acid resistance (10%H_2SO_4, 168h)	No blistering, no falling off, first grade discoloration	No blistering, no falling off, first grade discoloration
Alkali resistance (10%NaOH, 168h)	No blistering, no falling off, first grade discoloration	No blistering, no falling off, first grade discoloration

Text box 8 – Conclusion and Next Steps

- The lab test results are basically the same as the scale-up test results. The use of organic yellow pigments, combined with iron oxide yellow and titanium dioxide, could substitute the original lead-containing pigments for epoxy floor paints.
- The product can basically be replaced, but there are some issues:
  1) there are chroma differences and cannot be adjusted to the original color.
  2) poor shade functionality.
- The next step is to work on the improvement of shade functionality for yellow products, and to reduce costs while ensuring product quality.

Figure 17 – Paint production plant, Zhejiang Tiannv Group Paint Co., Ltd. in China

Photo: NCPC China

CASE STUDY 3 – REFORMULATION OF LEAD PAINT (YELLOW ALKYD PAINT)

Company: LIP-04*, Ecuador

Contact person: Gustavo Argoti, General Manager

Number of employees: 14

Company decided to take part in this project for the environmental awareness and social responsibility reasons.

PRODUCTION DATA

Installed capacities (t/year)	75 t/year (1200 gal/month)
Production in 2018 (t)	38 t/year production on demand
Type of paints currently produced	Alkyd enamels and architectural paints
Type of paints that contain lead	Yellow and red alkyd enamels Yellow latex architectural paints
Production of paints that contain lead in 2018 (t)	1.4 t/year (250 gal/month)
Consumption of raw materials that contain lead in 2018 (t)	0.7 t/year

SELECTION OF PRODUCT FOR REFORMULATION

Product trade name	**Bright yellow enamel**
Product type (base, use)	Alkyd enamel used as a topcoat on metal or wood surfaces.
Production of this paint in 2018 (t)	0.55 t/year
% (weight) of this product production related to lead paint production in 2018	8.0%
Reasons for this product selection	The company is very interested in having a lead-free formulation from its processes and raw materials

* Ecuadorian companies did not want their name to be published.

PRODUCT REFORMULATION

RAW MATERIAL	
Lead compound to be substituted	Medium chrome yellow (PY 34)
Content of lead compounds in the formulation of selected product (weight % calculated on total formulation)	5.73%
Total consumption of this lead compound 2018 (t)	0.29 t/year
ALTERNATIVE ASSESSMENT	
Possible alternatives that were assessed	Samples of paint colour were sent to the Mathiesen company for analysis and recommendations. The suggested alternative was a hybrid pigment from the LF line.
Selected alternative(s)	Canary Yellow LF-761
Main reason(s) for selection of this (these) alternative(s)	Similar quality characteristics of the initial product
Potential for implementation of this (these) alternative(s) in other products (number of products and/or tons, if possible)	Home use product

PRODUCT REFORMULATION

RESULTS OF PARALLEL LAB TESTINGS

Request (according to technical specifications)	Lead paint	Paint free of lead	NTE INEN 2094*
Test method and a value			
Lead content on dry base (NTE-INEN 2093)	34,689 ppm	<56 ppm	< 600 ppm Lead content in paint suggested by the Global Alliance: < 90 ppm
Specular Gloss 60° (NTE-INEN 1003)	5.4 UB	43.8 UB	Gloss type 1 and 2: Min 70 Matte type: Max 15
	The values obtained do not comply with the values def ned in the INEN 2094 Standard for a bright enamel, whereas they comply for matte or semi-matte enamel. INEN 2094 Standard is voluntary and referential in nature.		

* Ecuadorian Technical Standard INEN 2094 Paints: Synthetic alkyd air-drying enamels. Requirements; current and referential and voluntary.

PRODUCT REFORMULATION

RESULTS OF PARALLEL LAB TESTINGS

<table>
<tr><th>Request (according to technical specifications)</th><th>Lead paint</th><th>Paint free of lead</th><th>NTE INEN 2094</th></tr>
<tr><td>Solids by mass
(NTE-INEN 1024)</td><td>40.21 %</td><td>37.68%</td><td>Min 35%</td></tr>
<tr><td>Fineness of dispersion
(NTE-INEN 1007)</td><td>50 µm</td><td>10 µm</td><td>Max 20 µm</td></tr>
<tr><td>Waterproof
(NTE-INEN 1539)</td><td>No blistering, softening, adhesion loss, color change</td><td>No blistering, softening, adhesion loss, color change</td><td>They must not present wrinkles, blistering, color changes or any other defect visible to the naked eye.</td></tr>
<tr><td rowspan="2">Adherence (NTE-INEN 1006)</td><td><35%</td><td>65-85%</td><td rowspan="2">Gloss type: Min 90%
Matte type: Min 90%</td></tr>
<tr><td colspan="2">The values do not comply with the values def ned in INEN 2094 Standard for glossy or matte enamel.
INEN 2094 Standard is voluntary and referential in nature.</td></tr>
<tr><td>Dry time free to touch
(NTE-INEN 1011)</td><td>1.75 hours</td><td>1.9 hours</td><td>2 hours max.</td></tr>
<tr><td>Drying time when handling
(NTE-INEN 1011)</td><td>10 hours</td><td>11 hours</td><td>8 hours max.</td></tr>
<tr><td>Floatation (NTE-INEN 2088)</td><td>There is no color difference</td><td>There is no color difference</td><td>They must not present appreciable color differences.</td></tr>
<tr><td rowspan="2">Accelerated weathering resistance
(NTE-INEN-ISO 16474-3)
Exposure time: 100 hours.</td><td>• Gloss Retention 56%
• Has marked changes in color
• Does not present cracking, blistering, or loss of adherence</td><td>• Gloss Retention 36%
• Has marked changes in color
• Does not present cracking, blistering, or loss of adherencee</td><td rowspan="2">• For Type 1 paint: Minimum brightness retention of 80% of the initial value, for semi-f nal paint and Type 2, must have a minimum brightness retention of 70% of the initial value.
• It should not show cracking, blistering, loss of adhesion, or marked changes in color.</td></tr>
<tr><td colspan="2">The results obtained partially meet the requirements of the standard, since they do not meet in the brightness retention parameter and have accented color changes</td></tr>
</table>

RESULTS OF SCALE-UP

Request	Lead paint	Paint free of lead

NOTE: The project's scope to date does not include scaling tests; however, the company remains interested in performing other reformulation tests with pigments from other suppliers (e.g., Clariant and BASF), which are more accessible economically.

Text box 9 – Conclusion and Next Steps

- The reformulation test with Canary Yellow LF-761 pigment meets the company's requirements in terms of shade and hiding power.
- The Canary Yellow LF-761 pigment, provided by the Mathiesen company tested for an alkyd enamel type paint, requires the grinding process implementation for the reformulated paint that meets the required technical characteristics.
- The Canary Yellow LF-761 pigment meets the expectations in relation of the lead content required in the project, with a lead concentration on a dry basis <0.0056% (<56 ppm).
- The reformulated paint complies with most of the parameters established at the NTE INEN 2094 Paints Standard. Synthetic alkyd air-drying enamels. Requirements.
- The reformulated paint price increases by 42.20%, compared to the price of paint that the company currently has.

Figure 18 – Production of yellow alkyd paint in Ecuador

Photo: NCPC Ecuador

APPENDIX 4 – SELECTED LIST OF ISO STANDARDS FOR GENERAL TEST METHODS FOR PAINTS AND VARNISHES

These methods are for testing the performance properties of paint and do not include methods for testing lead in paint. For lead paint sampling and testing methods, see WHO Brief guide to analytical methods for measuring lead in paint, second edition. [9]

ISO 1513:2010 - Examination and preparation of test samples

ISO 1513:2010 specif es both the procedure for preliminary examination of a single sample, as received for testing, and the procedure for preparing a test sample by blending and reduction of a series of samples representative of a consignment or bulk of paint, varnish or related product.

ISO 1514:2016— Standard panels for testing

ISO 1514:2016 specif es several types of standard panels and describes procedures for their preparation prior to painting. These standard panels are for use in general methods of test for paints, varnishes and related products

ISO 1519:2011 — Bend test (cylindrical mandrel)

ISO 1519:2011 specif es an empirical test procedure for assessing the resistance of a coating of paint, varnish or related product to cracking and/or detachment from a metal or plastics substrate when subjected to bending round a cylindrical mandrel under standard conditions.

For a multi-coat system, each coat can be tested separately or the complete system can be tested.

The method specif ed can be carried out either as a "pass/fail" test, by carrying out the test with a single specif ed size of mandrel, to assess compliance with a particular requirement; or by repeating the procedure using successively smaller mandrels to determine the diameter of the f rst mandrel over which the coating cracks and/or becomes detached from the substrate.

Two types of apparatus are specif ed, type 1 being appropriate for use on test panels of thickness up to 0,3 mm, and type 2 for use on test panels of thickness up to 1,0 mm. Both types of apparatus have been found to give similar results with the same coating, but normally only one will be used for testing a given product.

ISO 1520:2006 — Cupping test

ISO 1520:2006 specif es an empirical test procedure for assessing the resistance of a coating of paint, varnish or related product to cracking and/or detachment from a metal substrate when subjected to gradual deformation by indentation under standard conditions.

For a multi-coat system, each coat may be tested separately or the complete system may be tested. The method may be carried out as follows: either as a 'pass/fail' test, by testing to a specif ed depth of indentation to assess compliance with a particular requirement; or by gradually increasing the depth of indentation to determine the minimum depth at which the coating cracks and/or becomes detached from the substrate.

ISO 1522:2006 — Pendulum damping test

ISO 1522:2006 specif es two methods of carrying out a pendulum damping test on a coating of paint, varnish or other, related, product. It is applicable to single coatings and to multicoat systems.

ISO 1524:2020 — Determination of fineness of grind

ISO 1524:2020 specif es a method for determining the f neness of grind of paints, inks and related products by use of a suitable gauge, graduated in micrometres.

It is applicable to all types of liquid paints and related products, except products containing pigments in f ake form (e.g. glass f akes, micaceous iron oxides, zinc f akes).

ISO 2409:2013 — Cross-cut test

This International Standard specif es a test method for assessing the resistance of paint coatings to separation from substrates when a right-angle lattice pattern is cut into the coating, penetrating through to the substrate. The property determined by this empirical test procedure depends, among other factors, on the adhesion of the coating to either the preceding coat or the substrate. This procedure is not to be regarded, however, as a means of measuring adhesion.

Where a measurement of adhesion is required, the method described in ISO 4624 may be used. The method is not suitable for coatings of total thickness greater than 250 μm or for textured coatings.

ISO 2431:2019 — Determination of flow time by use of flow cups

This document specif es a method for determining the f ow time of paints, varnishes and related products that can be used to control consistency.

Four f ow cups of similar dimensions, but having orif ce diameters of 3 mm, 4 mm, 5 mm and 6 mm, are specif ed. Two methods for checking the f ow cups for wear and tear are given.

Flow cups with a replaceable jet are not covered by this document as the close tolerances on the supply of the material under test to the jet are not met.

ISO 2808:2019 — Determination of film thickness

This document describes methods for measuring the thickness of coatings applied to a substrate. Methods for determining wet-f lm thickness, dry-f lm thickness and the f lm thickness of uncured powder layers are described.

ISO 2810:2004 - Paints and varnishes — Natural weathering of coatings — Exposure and assessment

ISO 2810:2004 specifies the conditions which need to be taken into consideration in the selection of the type of natural weathering and the natural weathering procedure to be used to determine the resistance of coatings or coating systems (direct weathering or weathering behind window glass).

Natural weathering is used to determine the resistance of coatings or coating systems (denoted in the following text simply by coatings) to the sun's radiation and the atmosphere. Special atmospheric influences, e.g. industrial pollution, are not taken into account.

ISO 2813:2014 — Determination of gloss value at 20°, 60° and 85°

ISO 2813:2014 specifies a method for determining the gloss of coatings using the three geometries of 20°, 60° or 85°. The method is suitable for the gloss measurement of non-textured coatings on plane, opaque substrates.

ISO 2815:2003 — Buchholz indentation test

ISO 2815:2003 describes a method for carrying out an indentation test on a single coating or multicoat system of paint, varnish or related product, using a Buchholz indentor. The length of the indentation produced is indicative of the residual deformation of the coating.

This indentation test is not suitable for products which contain a strong plasticizer.

ISO 3248:2016 — Determination of the effect of heat

ISO 3248:2016 specif es a method for determining the resistance of single coatings or multi-coat systems of paints, varnishes or related products to changes in gloss and/or colour, blistering, cracking and/or detachment from the substrate under conditions of a specif ed temperature.

This procedure is applicable to products intended for use on domestic radiators or other articles likely to be subjected to similar temperatures.

ISO 3668:2017 — Visual comparison of colour of paints

ISO 3668:2017 specif es a method for the visual comparison of the colour of f lms of paints or related products against a standard (either a reference standard or a freshly prepared standard) using artif cial light sources in a standard booth.

It is not applicable to coatings containing special-effect pigments, e.g. metallic, without previous agreement on all details of illuminating and viewing conditions

ISO 3856-1:1984 — Determination of "soluble" metal content — Part 1: Determination of lead content — Flame atomic absorption spectrometric method and dithizone spectrophotometric method

ISO 4628-1:2016 — Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance

- **Part 1: General introduction and designation system**
- **Part 2: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 2: Assessment of degree of blistering**
- **Part 3: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 3: Assessment of degree of rusting**
- **Part 4: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 4: Assessment of degree of cracking**
- **Part 5: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 5: Assessment of degree of flaking**

- **Part 6: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 6: Assessment of degree of chalking by tape method**
- **Part 7: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 7: Assessment of degree of chalking by velvet method**
- **Part 8: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 8: Assessment of degree of delamination and corrosion around a scribe or other artificial defect**
- **Part 10: Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 10: Assessment of degree of filiform corrosion**

ISO 6270-1:2017 Determination of resistance to humidity — Part 1: Condensation (single-sided exposure)

ISO 6270-1:2017 specif es a method for determining the resistance of paint f lms, paint systems and related products to conditions of condensation in accordance with the requirements of coating or product specif cations.

ISO 6270-2:2017 Determination of resistance to humidity — Part 2: Condensation (in-cabinet exposure with heated water reservoir)

ISO 6270-3:2018 Determination of resistance to humidity — Part 3: Condensation (in-cabinet exposure with heated, bubbling water reservoir)

ISO 6504-1:2019 Determination of hiding power — Part 1: Kubelka-Munk method for white and light-coloured paints

This document specif es a method for determining the hiding power (spreading rate necessary to give a hiding power of 98 %) of white or light-coloured paints. It is applicable to paint f lms having the tri-stimulus value of Y ≥ 70 and hiding power > 80 %. It is not applicable to f uorescent or metallic paints.

ISO 6504-3:2019 Determination of hiding power — Part 3: Determination of hiding power of paints for masonry, concrete and interior use

This document specif es methods for determining the hiding power given by paint coats of white or light colours of tristimulus values Y and Y10 greater than 25, applied to a black and white chart, or to a colourless transparent foil. In the latter case the tristimulus values Y and Y10 are measured over black and white panels. Subsequently, the hiding power is calculated from these tristimulus values.

ISO 6860:2006 Bend test (conical mandrel)

ISO 6860:2006 describes an empirical test procedure for assessing the resistance of a coating of paint, varnish or related product to cracking and/or detachment from a metal substrate when subjected to bending around a conical mandrel under standard conditions.

For a multi-coat system, each coat may be tested separately or the complete system may be tested.

ISO 9117-1:2009 Drying tests — Part 1: Determination of through-dry state and through-dry time

ISO 9117-2:2010 Drying tests — Part 2: Pressure test for stackability

ISO 9117-3:2010 Drying tests — Part 3: Surface-drying test using ballotini

ISO 9117-4:2012 Drying tests — Part 4: Test using a mechanical recorder

ISO 9514:2019 Determination of the pot life of multicomponent coating systems — Preparation and conditioning of samples and guidelines for testing

ISO 15528:2020 Paints, varnishes and raw materials for paints and varnishes — Sampling

APPENDIX 5 – NON-EXHAUSTIVE LIST OF SUPPLIERS*

Table 23 – Non-Exhaustive List of Suppliers as of May 2021

COMPANY	WEB SITE
PIGMENTS	
BASF Colors & Effects	www.colors-effects.com
Mathiesen	https://www.grupomathiesen.com/en/
Ferro	https://www.ferro.com
Pyosa Industrias	https://www.pyosa.com
Clariant	https://www.clariant.com/en/Business-Units/Pigments
Jiangsu Shuangle Pigment	http://www.jsshuangle.com/en
Yingze New Material	
Heubach, Ltd	https://heubachcolor.com/
Sun Chemical Corporation	https://www.sunchemical.com/pigment-products/
Ferro Corporation	https://www.ferro.com/Contact
	https://www.clariant.com/en/Business-Units/Pigments
The Shepherd Color Company	https://www.shepherdcolor.com/
Nubiola	https://www.ferro.com/nubiola
Venator	https://www.venatorcorp.com/
Dominion Colour Corporation	https://www.dominioncolour.com/
Bruchsaler Farben	https://www.bruchsaler-farben.de/en/home.html
Vijay Chemical Industries	http://vijaychemical.com/
Vibfast Pigments PVT.LTD.	http://www.vibfast.com/
Trust Chem	https://www.trustchem.eu/organic-pigments/
Resins and Chemicals PVT.LTD.	http://www.asrresin.com/pro_org_yellow.php
Special-Chem	https://coatings.specialchem.com/product/p-aarbor-colorants-corporation-naphthol-red-pigment-pr-112
Sudarshan	https://www.sudarshan.com/perch/resources/pigments-core-range-1.pdf
Milano Colori	http://www.milano-colori.com/en/plastics-rubber/pigments/organic-pigments/
Hangzhou Boray Pigments Co LTD	http://bof nepigment.com/
Hangzhou Multicolor Chemical Co LTD	http://www.multicolor-pigment.com/pid10206407/Pigment+Yellow+183.htm

* Mention of a commercial company or product in these guidelines does not imply endorsement by UNEP.

COMPANY	WEB SITE
DRIERS	
Venator	https://www.venatorcorp.com/products-and-applications/products/driers
DURA	http://www.durachem.com/home.html
American Elements	https://www.americanelements.com/
DOW	http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_090c/0901b8038090c235.pdf?f lepath=productsafety/pdfs/noreg/233-01137.pdf&fromPage=GetDoc
Comar Chemicals PVT.LTD	https://www.comarchemicals.com/index.php/en/products-en/other-organometallics-en/paint-driers-en
Blackfriar	http://www.blackfriar.co.uk/product/liquid-driers/
Matrix Universal	http://www.matrixuniversal.com/paint_driers.html
Silver Fern Chemical Inc.	http://www.silverfernchemical.com/product-lines/paint-driers/
ZINC PHOSPHATE/MODIFIED ZINC PHOSPHATE	
Shijiazhuang Xin sheng chemical co.,ltd	http://zincphosphatepigment.sell.everychina.com/p-108713315-anti-corrosion-zinc-phosphate-pigment-325-mesh-cas-7779-90-0-white-powder.html
BassTech International	http://basstechintl.com/
Numinor Chemical Industries Ltd	https://www.knowde.com/stores/numinor-chemical-industries-ltd/
Pigment Sanayi A.S	http://www.pigment.com.tr/
SNCZ Société Nouvelle des Couleurs Zinciques	https://www.societe.com/societe/societe-nouvelle-des-couleurs-zinciques-330575887.html
Dimacolor Industry Group Co., Ltd	http://www.dimacolorgroup.com/news_en.html
Heubach, Ltd	https://heubachcolor.com/
Noelson chem	http://www.noelson.com/en/index.html
Shanghai Ocen Zinc Industry Co., Ltd	https://guide31651.guidechem.com/productlist-c72-p1.html
DISPERSING AGENTS	
Byk Additives & Instruments	https://www.byk.com/en
Evonik Industries AG	https://corporate.evonik.com/en
Clariant	https://www.clariant.com/en/Business-Units/Industrial-and-Consumer-Specialties/Paints-and-Coatings
Borchers	http://www.borchers.com/index.php?id=2
Ester	https://www.esterchem.co.in/paints-inks.html
BASF	https://www.basf.com/za/en/who-we-are/sites-and-companies.html
Shah Patil & Company	http://www.shahpatilexports.in/paint_&_ink_additives.htm
Harmony Additive PVT. LTD	https://www.harmonyadditive.com/paint-dispersing-agent.html

The web site https://www.ulprospector.com/en/eu/Coatings/search may be used to f nd and contact suppliers of pigments and driers.