Lead Paint Reformulation
Technical Guidelines

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1. Technical Guidelines

Content

• Information on hazardous properties of lead compounds
• Substitution process
• Color theory and color index
• Dispersion process
• Alternative pigments and additives
• Assessment of alternative pigments and additives
• General information on reformulation processes
• The Technical Guidelines are developed to help address both capacity constraints and technical barriers to the substitution of lead compounds in paints

• Focus is on SMEs needs for the effective and efficient reformulation of paint
2. Colors and Paint Function
Color Theory
Color Index

• Color Index (CI) is universally accepted standard coding system for pigments
• Color Index identifies each colorant by giving the compound a unique CI name and CI number

<table>
<thead>
<tr>
<th>Abbr.</th>
<th>Pigment</th>
<th>Chemical Class</th>
<th>CI Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB</td>
<td>Pigment Blue</td>
<td>Nitrosol</td>
<td>100000—102999</td>
</tr>
<tr>
<td>PBr</td>
<td>Pigment Brown</td>
<td>Nitro</td>
<td>103000—109999</td>
</tr>
<tr>
<td>PBk</td>
<td>Pigment Black</td>
<td>Monoazo</td>
<td>110000—199999</td>
</tr>
<tr>
<td>PR</td>
<td>Pigment Red</td>
<td>Diazo</td>
<td>200000—299999</td>
</tr>
<tr>
<td>PY</td>
<td>Pigment Yellow</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

• PY 34 – lead sulphochromate
• PR 104 – lead chromate molybdate sulphate
Paint Functions: Protection
Paint Functions: Signal/Camouflage
Paint Functions: Aesthetics & Other Properties

- Decorative
- Insulation
- Conductivity
- Antibacterial
- Fire retardant
Paint Functions: Usage

- Paint is also formulated to adapt to a variety of substrates and methods of application.
• Since there are many different initial lead-containing formulations for color and other paint properties, the Technical Guidelines may only provide general information about reformulation processes

• In-depth analyses and more specific data will be provided through the pilot demonstrations in the SAICM GEF Lead Paint Project to participating companies according to their specific needs
3. Paint Raw Materials

- Resins
  - Vehicles
  - Binders
- Pigments
- Extenders
  - Fillers
- Additives
  - Driers
  - Plasticizers
- Solvents
  - Oil-based
  - Water-based
4. Lead Compounds in Paints

• Paint Raw Materials that may Contain Lead Compounds

<table>
<thead>
<tr>
<th>Type of Paint</th>
<th>Pigments</th>
<th>Extenders</th>
<th>Driers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-drying primers and topcoats</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Primers, other bases</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Primer surfacers, other bases</td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Topcoats, other bases</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

• Natural extenders or pigments (e.g., ferro oxides) may contain lead compounds, and by using them, lead compounds may be added unintentionally
## Hazardous Properties of Lead Compounds in Paints

### Pigment Chemicals

<table>
<thead>
<tr>
<th>Pigment Chemicals</th>
<th>Hazard statements according to GHS</th>
</tr>
</thead>
</table>
| Lead chromate molybdate sulphate red (PR 104) | **H350** – may cause cancer  
**H360** – may damage fertility or the unborn child  
**H373** – may cause damage to organs through prolonged or repeated exposure |
| Lead chromate (PY 34)                      | **H400** – very toxic to aquatic life  
**H410** – very toxic to aquatic life with long lasting effects |
5. Substitution Process

- Law enforcement has been recognized by companies as the main driver for hazardous chemicals substitution.
Substitution

• 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 identified
Other Hazardous Raw Materials in Paints

• In addition to lead compounds, there are many other very hazardous raw materials that are in use in paint industry, e.g.:
  • Solvents (solvent naphtha, toluene)
  • Additives (dibutyl phthalate, formaldehyde)
  • Hexavalent chromium pigment (zinc chromate)
  • Bromine compounds in fire retardant paints
Substitution Process

Identifying lead compound used in paint

Identifying possible alternative

Assessment of potential alternatives

- Technical feasibility
- Environment and human health hazards
- Economic feasibility
- Availability

Consultation within and outside the supply chain

Suitable alternative(s) found

Reformulation in the lab
Definition of HSE measures
Scale-up

For industrial paints – on site testing
Identification of Potential Alternatives

• An alternative is a possible replacement for a hazardous substance that can replace the function the original substance performs.

• It is important to determine all the functions of a substance for each use (a specific industry or a specific customer).

• Once the specific function and use conditions are precisely defined, consultation within and outside the supply chain is more successful.
Assessment of Potential Alternatives (1)

- When possible alternatives that fulfill function requirements are discovered, it is necessary to define whether or not process adaptations or changes are needed.
- To fulfill the same function, sometimes the alternative must be processed under different conditions.
Assessment of Potential Alternatives (2)

This assessment consists of:

- setting criteria for acceptable hazards and risks; and

- the comparison of hazardous properties between hazardous substance (or mixture, such as driers) and their possible alternatives.

- MSDS is good source of info on chemical hazardous properties
Assessment of Potential Alternatives (2)

- The assessment of alternatives must be a process that is repeated.
- The assessment results obtained now may change as new knowledge concerning hazardous properties and risks of the chemical is acquired.
Lead Compounds Substitution

• Anticorrosive “red lead” pigment
  • Zinc chromate – contains Cr$^{6+}$
  • Zinc phosphate – free of Pb and Cr$^{6+}$; performance not good
  • Calcium (poly)phosphate – Zn-free

• Pigments for red molybdate, lead chromate topcoats
  • Wide choice of possible, non-hazardous alternatives (bismuth vanadates, iron oxides, mixed metal oxides, etc.)

• Lead additives (driers)
  • Zirconium or Strontium Octoate – octoate acids hazardous to unborn child
  • Zr or Sr neodecanoate
Assessment of Potential Alternatives (3)

- Economic feasibility identifies the lowest cost option among a set of alternative options that all achieve targets.

- Assessment would include a range of direct and tangible indirect production costs, rather than simply comparing alternatives to the chemical we would like to substitute, in terms of product price.
Assessment of Potential Alternatives (4)

- The first step is to determine the availability and cost of identified alternatives based on info readily available for a cost comparison.
- To check the viability of alternatives, it is necessary to evaluate if substitution with specific alternative creates other costs like higher chemical consumption, increased manufacturing costs or purchase of new equipment.
Reformulation technology is complex; includes variables, i.e.:
- chemical,
- physical,
- process-engineering,
- environmental,
- health & safety, and
- economic.
Reformulation

- The main practical problem in (re)formulation is the large number of components present in a paint.
6. Substitution of Lead Pigments

- 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.

<table>
<thead>
<tr>
<th>Pigment Tasks</th>
<th>Requirements for Pigments and Extenders</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Elective absorption</td>
<td>• Dispersibility</td>
</tr>
<tr>
<td>• Light scattering</td>
<td>• Insoluble</td>
</tr>
<tr>
<td>• Optical effects by oriented reflection or interference</td>
<td>• Lightfast and weather resistant</td>
</tr>
<tr>
<td>• UV protection</td>
<td>• Heat resistant</td>
</tr>
<tr>
<td>• Corrosion protection</td>
<td>• Chemical resistant</td>
</tr>
</tbody>
</table>
Dispersion/Grinding Process

- Pigments may be well dispersed, but
- Effective, long-term stabilization of the pigment particles is also important
- When lab testing is scaled up to production, comparable grinding results can be achieved only if the equivalent grinding conditions are created
Insufficient Stabilization

- Insufficient stabilization may cause negative effects, i.e.:
  - Flooding/floating
  - Gloss decrease
  - Color shift
  - Sedimentation
  - Changes in viscosity of the dispersion
  - Sagging issues
  - Levelling issues
Red Lead (PR 105)

• Indirect inhibitor
• It reacts with the acidic groups in the resin to form lead soap, which has a corrosion inhibitory effect
Alternatives to Red Lead

- Chemically active anticorrosive pigments (Zinc oxide, *zinc phosphate*, calcium phosphate and their modifications)
- Electrochemically active anticorrosive pigments (Zinc and calcium phosphates and their modifications)
- Active, cathodic protective anticorrosion pigment (Zinc dust)
- Passive anticorrosive pigments (Micaceous iron oxide, aluminium silicates)

[Corrosion mechanism diagram]
Role of Extenders

- The major ingredients present in base coats are extenders;
- Choice of extenders is also important;
- Using extenders with platy shaped particles (talc, mica, china clay) prevent water, oxygen and other chemicals from reaching the substrate as particles overlap in a film.

Barrier effect of lamellar pigments and extenders
Paint Reformulation

• Paint reformulation is not complex – the Guidelines provides examples of base coat formulations;

• Parallel testing of lead anticorrosive paint and reformulated paint is necessary to judge the effectiveness of substitution;

• Beside drying time and mechanical properties, anticorrosion properties must be checked
## EHS Assessment

<table>
<thead>
<tr>
<th>Request</th>
<th>Red Lead</th>
<th>Alternative</th>
</tr>
</thead>
</table>
| Environmental and human health hazard | H272 - May intensify fire; oxidiser  
H302 - Harmful if swallowed  
H332 - Harmful if inhaled  
H351 - Suspected of causing cancer  
H360 - May damage fertility or the unborn child  
H372 - Causes damage to organs through prolonged or repeated exposure  
H410 - Very toxic to aquatic life with long lasting effects | Zinc orthophosphate  
Calcium orthophosphate |
|          |          | Based on currently available data, **this product does not meet the regulatory definition of a hazardous substance**. However, good industrial hygiene practices should be used when handling. |
Lead White (PW 1)

• This pigment was successfully replaced by a more efficient titanium dioxide (PW 6) pigment with almost ten times the hiding power;
• White lead acts as a through drier;
• The quantity of the through drier in a new formulation must be increased.
Lead Chromate (PY 34) and Lead Chromate Molybdate Sulphate (PR 104)

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),

• Demanding technical criteria such as excellent hiding power, light and weather fastness, heat stability, in combination with non-bleeding properties.
Lead Chromate (PY 34) and Lead Chromate Molybdate Sulphate (PR 104)

• The Colour Index contains over 13,000 entries but currently there is no single pigment that can cover all of the properties of PY 34 or PR 104;

• These pigments are usually used in applications where not all of their high-performance attributes are necessary (e.g. for indoor application);

• It is not necessary to substitute them with a single pigment;

• It is possible to find an alternative formulation that fulfils specific requirements.
Assessment of Alternative Pigments

- Alternatives to anticorrosive red lead pigment
- Alternatives to molybdate orange and lead chromate yellow (PY 34) pigments

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Possible Alternative to</th>
<th>Colour comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth Vanadate</td>
<td>PY 34</td>
<td>Pigments have similar chroma, but PY 184 has lighter shade than PY 34 which leads to difficulty in obtaining a deeper yellow colour. These colours can be obtained by addition of other pigments.</td>
</tr>
<tr>
<td>PY 184</td>
<td>PY 34</td>
<td></td>
</tr>
<tr>
<td>Request</td>
<td>Lead chromate yellow PY 34</td>
<td>Alternative</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Function</strong></td>
<td>Excellent hiding power. Excellent bleeding properties and gloss retention, the vibrant and deep colours of PY 34 and PR 104 do not fade or become dull.</td>
<td>Durable paints, the same colour range cannot be achieved without other pigments. Excellent bleeding properties</td>
</tr>
<tr>
<td><strong>Production process</strong></td>
<td></td>
<td>There is no need for changes in the production process</td>
</tr>
</tbody>
</table>
| **Environmental and human health hazard** | **H350** – may cause cancer  
**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 | Not classified as hazardous to human health and the environment                |
| **Economic feasibility** |                                                                                          | The best alternative for PY 34, but 5 to 6 times more expansive (22 to 35 EUR per kg) |
| **Availability**  |                                                                                          | Somewhat limited; due to limited sources of raw materials (Bi, V)             |
Paint Reformulation

The first stage of the reformulation process should be to define precisely which performance properties a paint should have, in addition to colour:

• Is it for external or internal use (weather and light fastness);
• Is there request for heat resistance;
• Excellent hiding power at defined film thickness;
• Shade and brightness of colour;
• Is bleeding acceptable (is paint use in a different-layer colour system, paint purpose).
Paint Reformulation

• 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 specific requirements;

• By combining these two pigment types, the required paint performance is achievable.
# Alternative Pigment Properties Compared to PY 34 and PR 104

<table>
<thead>
<tr>
<th>Pigment</th>
<th>External Use</th>
<th>Worse Heat Stability*</th>
<th>Bleeding</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY 184, PY 42, PR 101, PY 110, PR 254</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>PY53, PBr.24, <strong>PY 151</strong>, PY 154, PY 194, PO 73, PY 139</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>PO 36</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>PO 13, PO 34, PY 14, PY 83, PO 16, PO 155</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>PY 65, PY 74, PY 97</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>PO 67</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>PY 138</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
Alternative Pigment Properties Compared to PY 34 and PR 104

PY 151 cannot reach the bright, high chroma shades of yellow as pigment is limited to green shades of yellow.

<table>
<thead>
<tr>
<th></th>
<th>PY 34</th>
<th>PY 34</th>
<th>PY 151</th>
<th>PY 34</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shade</td>
<td>Primrose shade</td>
<td>Lemon shade</td>
<td>Medium shade</td>
<td></td>
</tr>
</tbody>
</table>
Paint Reformulation

• 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

• Inorganic and organic pigments properties related to grinding are different;

• In the case of organic/inorganic pigment combinations, co-grinding should be avoided
# Paint Reformulation

RAL 1021 – Lead-free vs. Lead Containing Formulation

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Lead Containing Formulation (%w/w)</th>
<th>Lead-free Formulation (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY 151 (organic)</td>
<td></td>
<td>81.5</td>
</tr>
<tr>
<td>PY 34 (inorganic)</td>
<td>85.8</td>
<td></td>
</tr>
<tr>
<td>PBr 24 (inorganic)</td>
<td>11.0</td>
<td>17.7</td>
</tr>
<tr>
<td>PY 139 (organic)</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>
7. Substitution of Lead Driers

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.

<table>
<thead>
<tr>
<th>Primary Driers</th>
<th>Secondary Driers</th>
<th>Auxiliary Driers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>Lead</td>
<td>Calcium</td>
</tr>
<tr>
<td>Manganese</td>
<td>Zirconium</td>
<td>Zinc</td>
</tr>
<tr>
<td>Iron</td>
<td>Bismuth</td>
<td>Lithium</td>
</tr>
<tr>
<td>Cerium</td>
<td>Barium</td>
<td>Potassium</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Cerium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Strontium</td>
<td></td>
</tr>
</tbody>
</table>
Lead Driers

• Secondary driers are active in the cross-linking steps of drying, they are responsible for overall drying throughout the entire paint layer;

• Lead also improves the flexibility and durability of the paint film;

• Lead driers are used in combination with cobalt or manganese.

• Calcium is often also added, to avoid precipitation of the lead and hazing.
Alternative to Lead Driers

**Zirconium driers** - Zirconium is only effective in combination with primary driers.
- It promotes surface and through drying.
- Unlike lead, zirconium is a poor pigment - wetting and dispersing agent - the combination with calcium is necessary.

**Strontium driers** – Strontium has the same through drying performance of Zirconium
- it offers benefits in delivering auxiliary drying characteristics, resulting in improved stored stability
- it is a good pigment - wetting and dispersing agent preventing haze and wrinkling
Alternative to Lead Driers

• 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.
Assessment of Alternatives

- Driers may contain components (organic solvents or drying accelerators) with undesirable health and/or environmental effects;
- It is necessary to look upon the entire product and not just the active metallic compound;
- Octoate acid (2-ethylhexanoic acid) is now defined as hazardous, it is suspected of causing damage to the unborn child.
# EHS Assessment

<table>
<thead>
<tr>
<th>Request</th>
<th>Lead octoate</th>
<th>Alternatives</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zirconium octoate</td>
</tr>
<tr>
<td>Environmental and human health hazard</td>
<td>H226 - Flammable liquid and vapour</td>
<td>H302 - Harmful if swallowed</td>
</tr>
<tr>
<td></td>
<td>H302 - Harmful if swallowed</td>
<td>H304 - May be fatal if swallowed</td>
</tr>
<tr>
<td></td>
<td>H332 - Harmful if inhaled</td>
<td>H318 - Causes serious eye damage</td>
</tr>
<tr>
<td></td>
<td>H410 - Very toxic to aquatic life with long lasting effects.</td>
<td>H315 -Causes skin irritation</td>
</tr>
<tr>
<td></td>
<td>H360(f,d) - May damage fertility. May damage the unborn child.</td>
<td>H361d - Suspected of damaging the unborn child.</td>
</tr>
<tr>
<td></td>
<td>H371 - Cause damage to organs through prolonged or repeated exposure</td>
<td></td>
</tr>
</tbody>
</table>
Paint Reformulation

• The quantities of some driers such as organic salts of cobalt, manganese, vanadium and iron, are restricted because of the coloration of the paint film;

• 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.
Paint Reformulation

- Effective drying requires a minimum quantity of drier;
- Adding too much impairs film formation and film properties as metals promote continuous further oxidation, leading to embrittlement of the binder and hence of the paint.
Paint Reformulation

• Parallel paints testing is necessary to check if reformulation is effective
• Drier systems should be tested on stability, viscosity, film hardness, gloss and yellowing.
• Storage at an elevated temperature (40°C for two weeks) stimulates, prolonged storage, to some extent.
• Drying time, viscosity, gloss and hardness of the dry film should be measured before and after storage.
Conclusion

• Lead is classically a chronic or cumulative toxin and exposure to lead is a major public health concern.

• Lead compounds are intentionally added to paint as pigments, anticorrosive, driers, and should have priority in substitution.

• Cost-effective reformulation alternatives are available on the market for all lead-containing paint ingredients.

• Lead Paint Reformulation Technical Guidelines provide information on alternatives, their assessments and reformulation processes, which helps companies to effectively substitute lead compounds.

• We will work with participating SMEs on specific reformulations, according to their needs.
THANK YOU!

Terima kasih!

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