

LEAD PAINT REFORMULATION TECHNICAL GUIDELINES

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CONTENT

1. Technical Guidelines Content;
2. Colours and Paint Function;
3. Paint Raw Materials;
4. Lead Compounds in Paints;
5. Substitution Process;
6. Substitution of Lead Pigments;
7. Substitution of Lead Driers

1. Technical Guidelines Content

- Information on hazardous properties of lead compounds;
- Substitution process;
- Colour theory and colour index;
- Dispersion process;
- Alternative pigments and additives;
- Assessments of alternative pigments and additives;
- General information about reformulation processes;

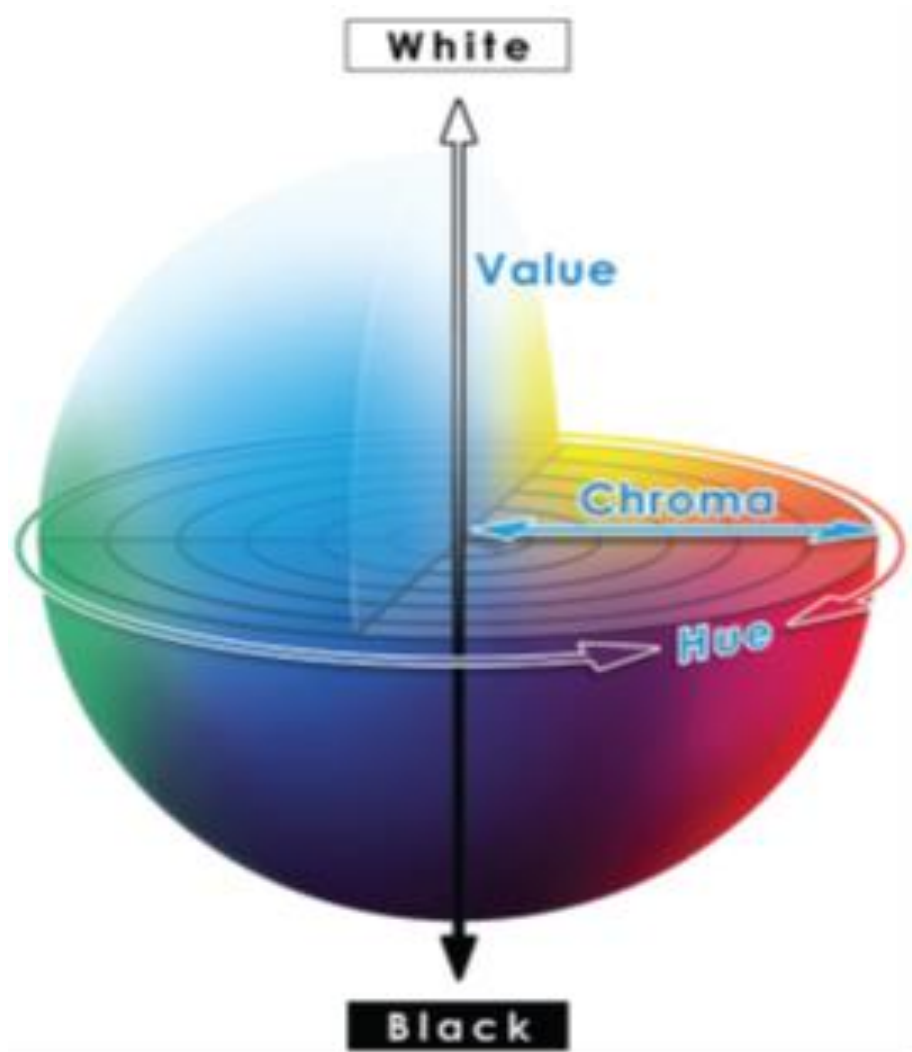
- The Technical Guidelines are developed to help address both capacity constraints and technical barriers to the substitution of lead compounds in paints
- Focus is on SMEs needs for the effective and efficient reformulation of paint.

2. COLOURS AND FUNCTIONS OF PAINT

COLOURS



Colour Theory



This Section provides tips for tinting



Colour Index

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

Abbrevi- ation	Pigment	Abbrevi- ation	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

Chemical class	CI numbers
Nitrosol	100000–102999
Nitro	103000–109999
Monoazo	110000–199999
Diazo	200000–299999

Paint Functions – Protection (1)



Paint – Signal/Camouflage Function (2)



Paint Functions (3)

- Decorative,
- Insulation,
- Conductivity,
- Antibacterial,
- Fire retardant



Paint Functions (4)

- 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 colour and other paint properties, Technical Guidelines may provide only general information about reformulation processes.
- In-depth analyses and more specific data will be provided through the pilot demonstrations in the GEF Lead Paint Project to participating companies according to their specific needs.

3. Paint Raw Materials

- Resins (vehicle)
- Pigments
- Extenders
- Additives
- Solvents



Flammable



Environmentally
Damaging



Irritant



Health hazard

4. LEAD COMPOUNDS IN PAINTS



Paint Raw Materials that may Contain Lead Compounds (1)

Type of paint	Pigments	Extenders	Driers
Air-drying primers and topcoats	X	X	X
Primers, other bases	X	X	
Primer surfacers, other bases		X	
Top coats, other bases	X		

Paint Raw Materials that may Contain Lead Compounds (2)

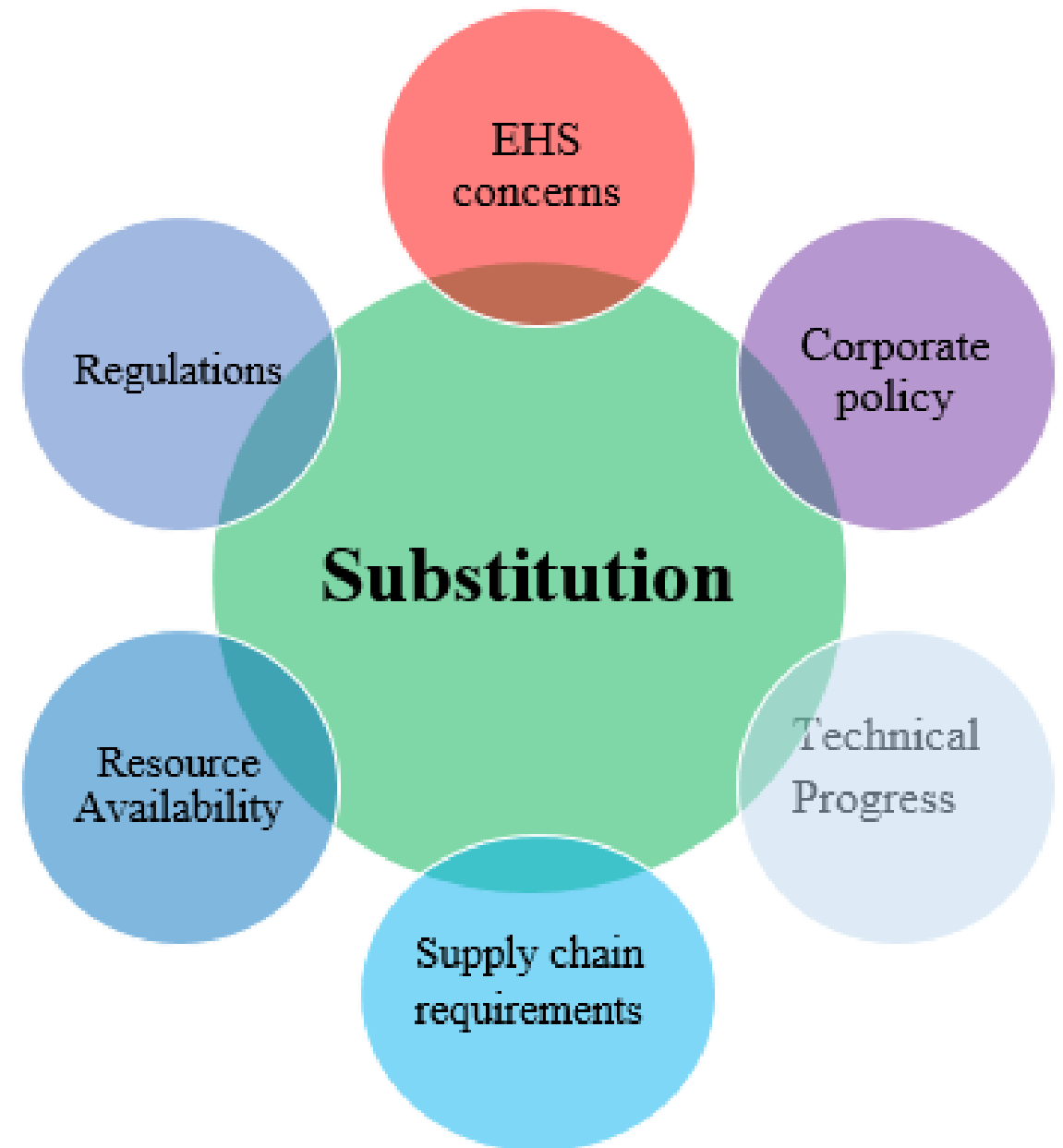
- **Natural extenders or pigments** (like ferro oxides) may contain lead compounds;
- By using these extenders or pigments, lead compounds may be added unintentionally;
- Paint may be also unintentionally contaminated if company produced lead free and lead paints (if there is no equipment cleaning between batches)

Hazardous Properties of Lead Compounds in Paints

Chemical	Hazard statements according to GHS
PIGMENTS	
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**

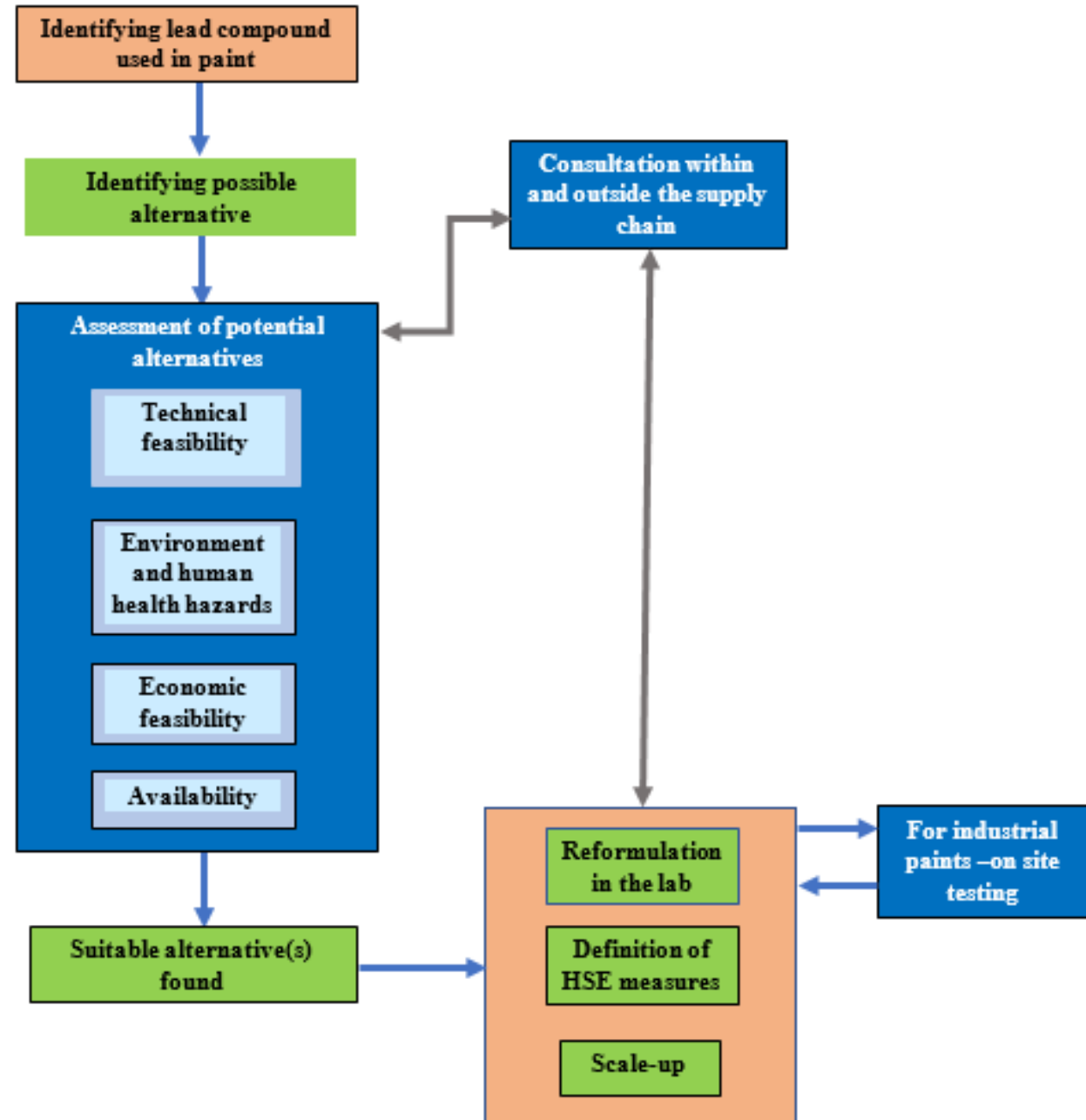
Other hazardous raw materials in paints

In addition to lead compounds there are many other very hazardous raw materials that are in use in paint industry, for example:

- solvents (solvent naphtha, toluene),
- additives (dibutyl phthalate, formaldehyde),
- hexavalent chromium pigment (Zinc chromate),
- bromine compounds in fire retardant paints



5. Substitution Process



Identification of Potential Alternatives

- An alternative is a possible replacement for a hazardous substance that is able to 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 fulfil function requirements are discovered, it is necessary to define whether or not process adaptations or changes are needed.
- To fulfil the same function, sometimes the alternative has to 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.

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 pigment Red Lead

~~Zinc chromate~~, ~~Zinc~~ phosphate?, Calcium (poly)phosphate?

Pigments for topcoats – Red molybdate, Lead chromate

There is a wide choice of possible, non-hazardous alternatives

Lead additives (driers)

Zirconium or Strontium ~~octoate~~, Zirconium or Strontium neodecanoate

Assessment of Potential Alternatives (3)



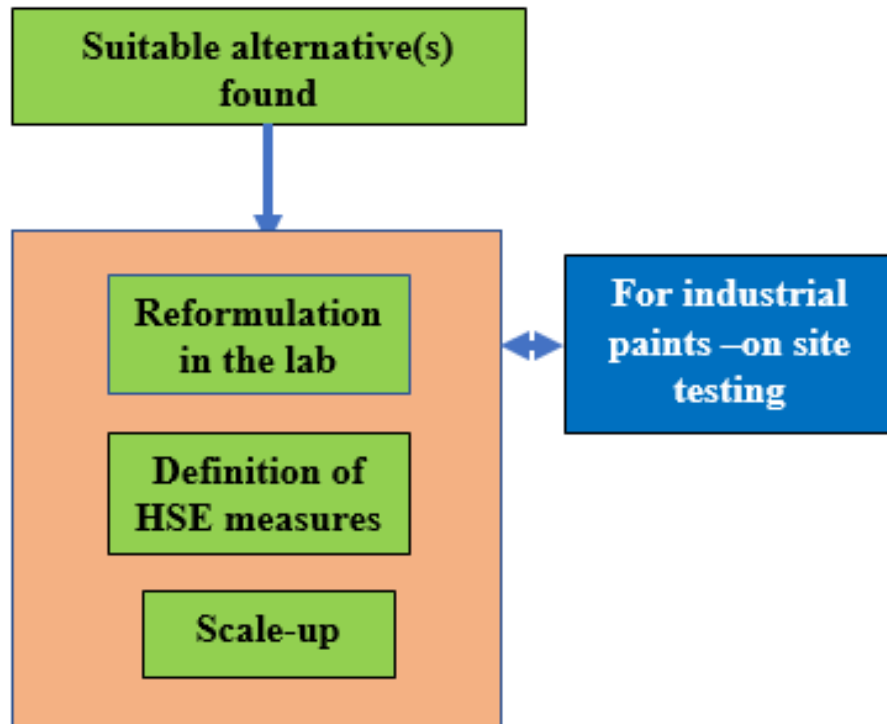
- Economic feasibility identifies the lowest cost option among a set of alternative options that all achieve the targets.
- Assessment would include a range of direct and tangible indirect production costs, rather than simply comparing alternatives to the chemical we would like to substitute, in terms of product price.

Assessment of Potential Alternatives (4)



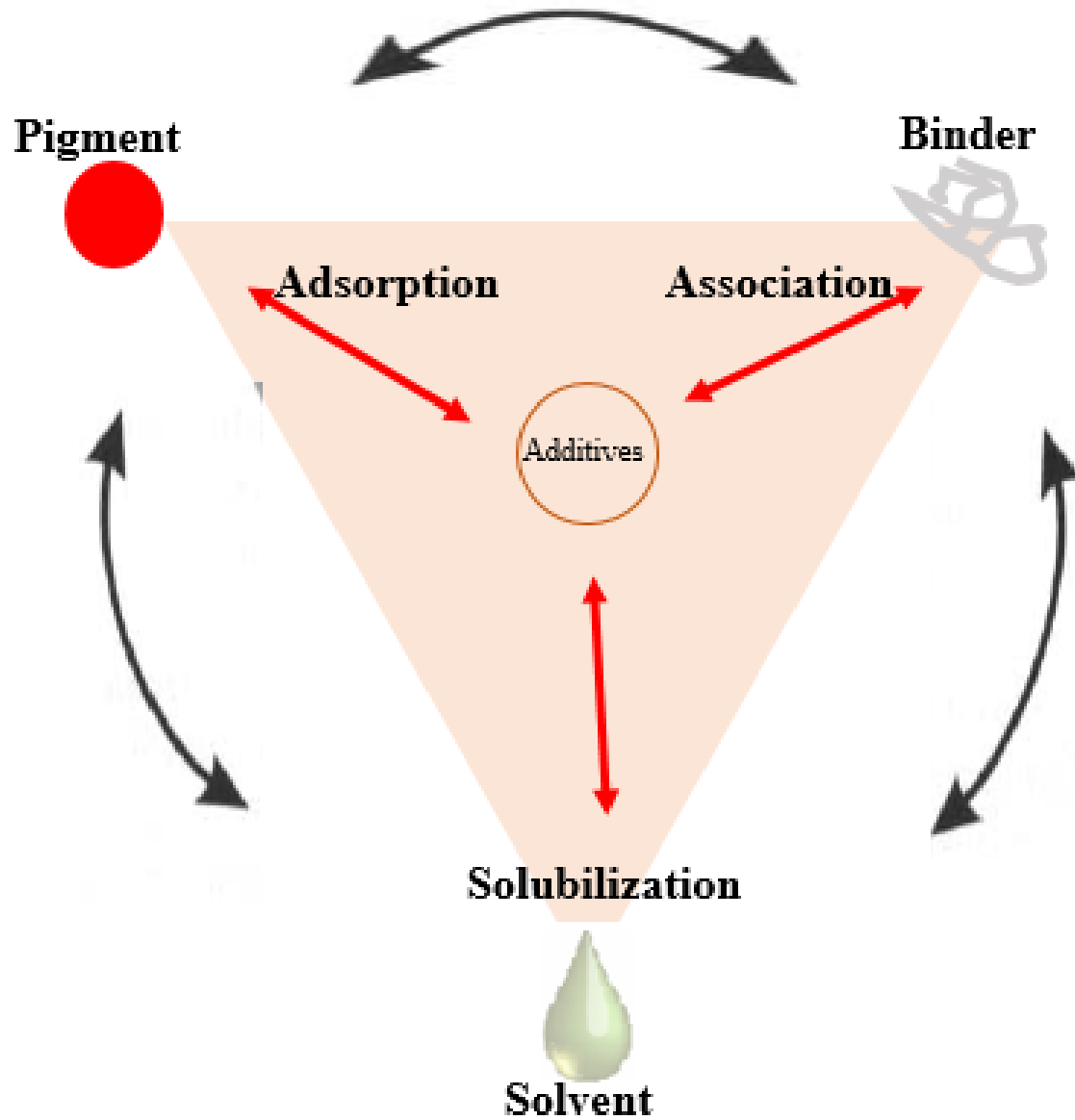
- The first step is to determine the availability and cost of identified alternatives, based on information readily available for a cost comparison

Reformulation



Coating technology is complex and includes variables, such as:

- chemical,
- physical,
- process-engineering, environmental,
- health and safety and
- economic.



The main practical problem in (re)formulation is the large number of components present in a paint

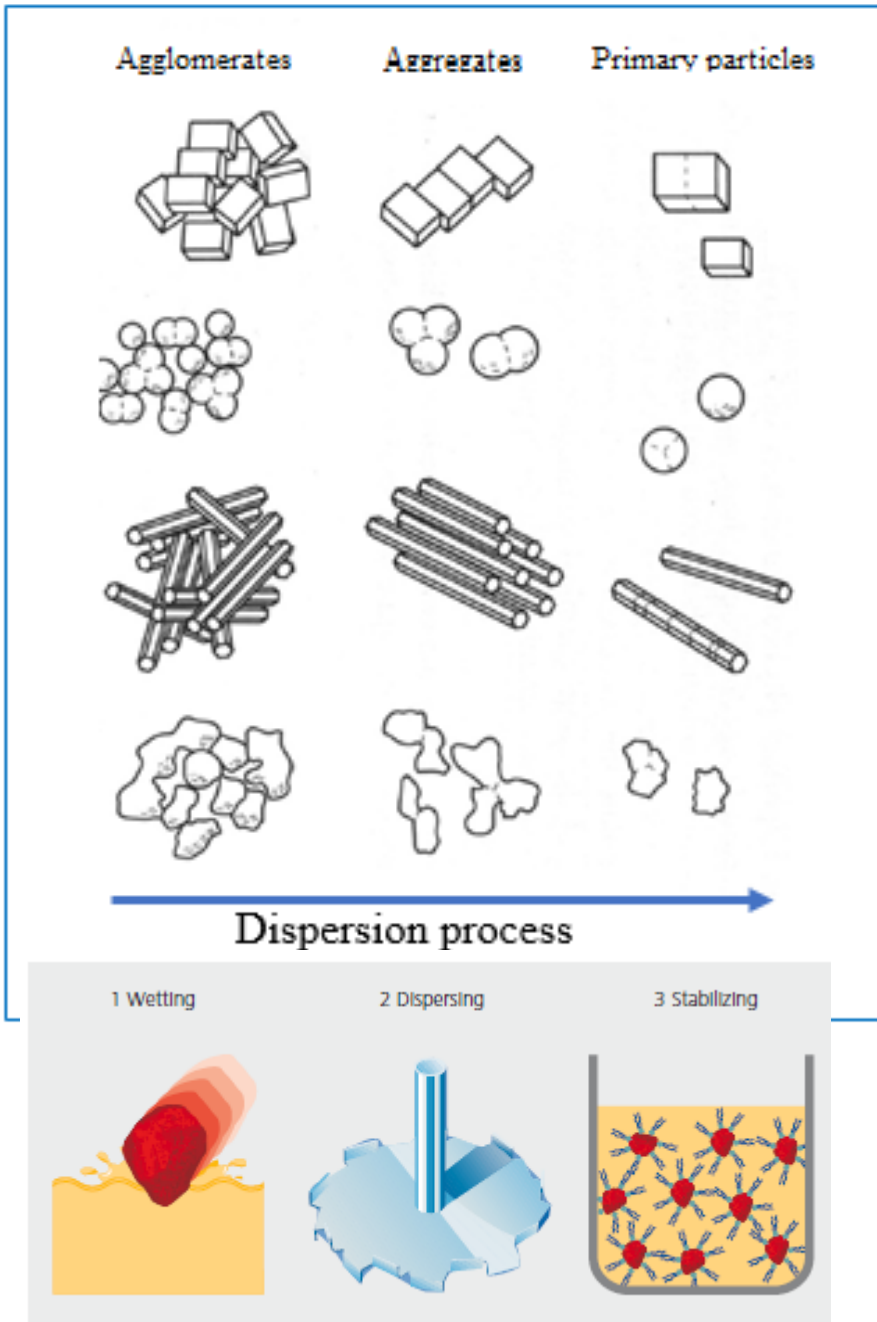
6. Substitution of Lead Pigments

Tasks of Pigments

Pigment Tasks	Requirements for Pigments and Extenders
<ul style="list-style-type: none">• elective absorption• Light scattering• Optical effects by oriented reflection or interference• UV protection• Corrosion protection	<ul style="list-style-type: none">• Dispersibility• Insoluble• Lightfast and weather resistant• Heat resistant• Chemical resistant

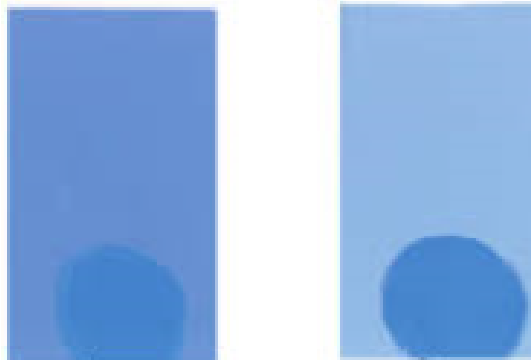
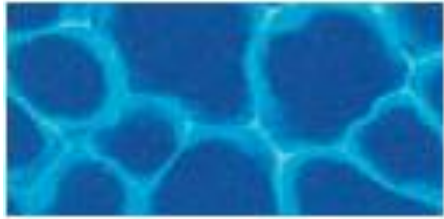
Paint properties depend on other factors related to pigments such as pigment volume concentration, choice of dispersing additives, interaction between pigment and polymer and the dispersion process.

Dispersion process



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

Insufficient Stabilisation



Insufficient stabilisation may cause negative effects, such as

- Flooding/Floating;
- Gloss decrease;
- Colour shift;
- Sedimentation;
- Changes in viscosity of the dispersion;
- Sagging issues;
- Levelling issues.

Red Lead (PR 104)

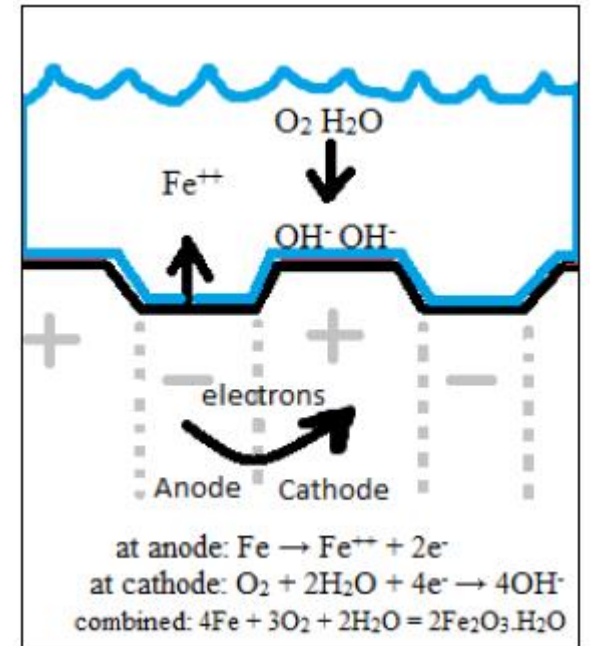


Red Lead
PR 105

- 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

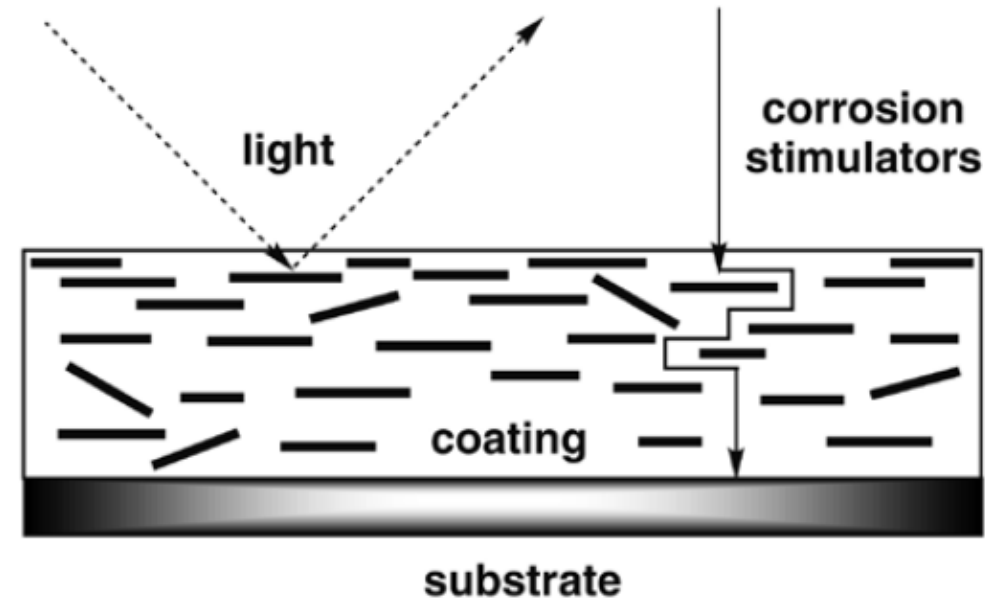
- Chemically active anticorrosive pigments (Zinc oxide, **zinc phosphate**, calcium phosphate and their modifications)
- Electrochemically active anticorrosive pigments (Zinc and calcium phosphates and their modifications)
- Active, cathodic protective anticorrosion pigment (Zinc dust)
- Passive anticorrosive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



Corrosion mechanism

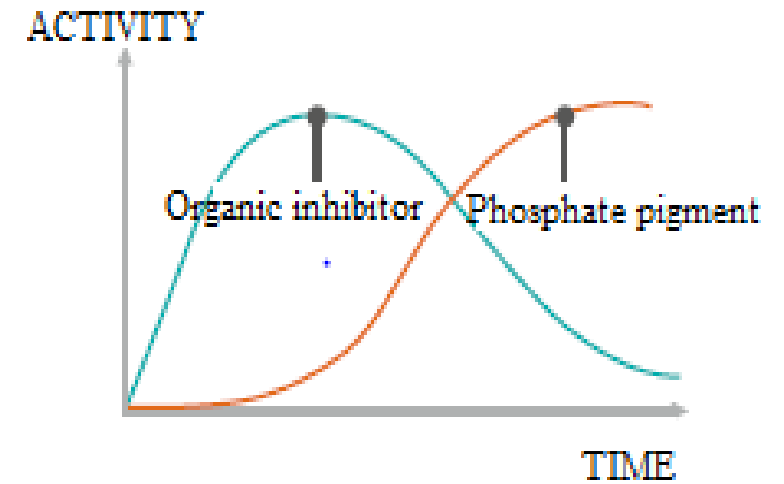
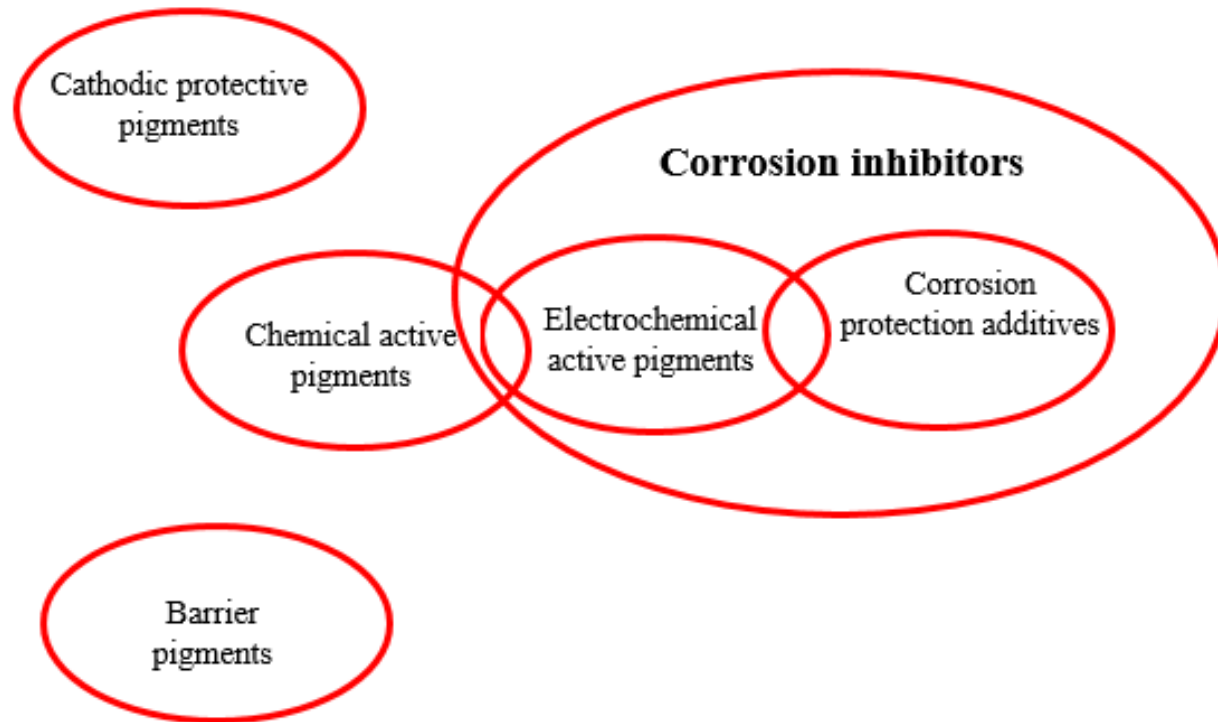
Role of Extenders

- 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

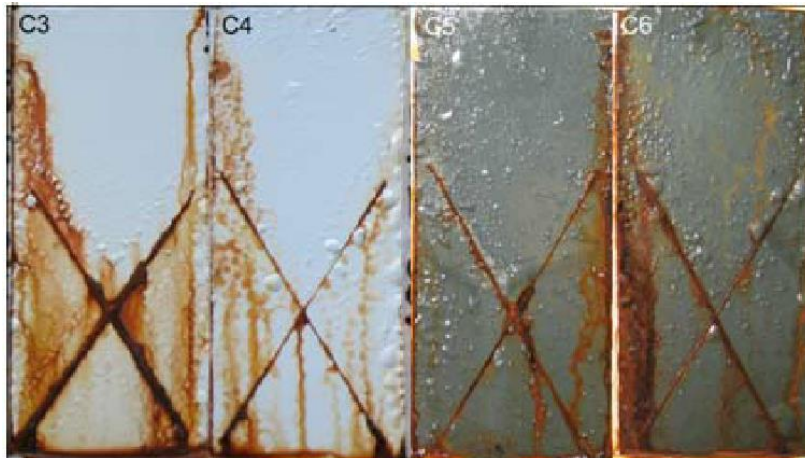
Corrosion Inhibitors



Anticorrosive Synergy

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

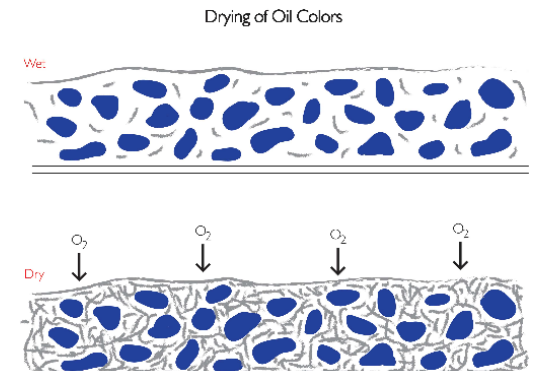


EHS Assessment

Request	Red Lead	Alternative	
		Zinc orthophosphate	Calcium orthophosphate
Environmental and human health hazard	<p>H272 - May intensify fire; oxidiser</p> <p>H302 - Harmful if swallowed</p> <p>H332 - Harmful if inhaled</p> <p>H351 - Suspected of causing cancer</p> <p>H360 - May damage fertility or the unborn child</p> <p>H372- Causes damage to organs through prolonged or repeated exposure</p> <p>H410 - Very toxic to aquatic life with long lasting effects</p>	<p>H 410 Very toxic to aquatic organisms with long lasting effects.</p> <p>Product is not hazardous for the human being when used properly (use of protective personal equipment).</p>	<p>Based on currently available data, this product does not meet the regulatory definition of a hazardous substance.</p> <p>However, good industrial hygiene practices should be used when handling.</p>

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

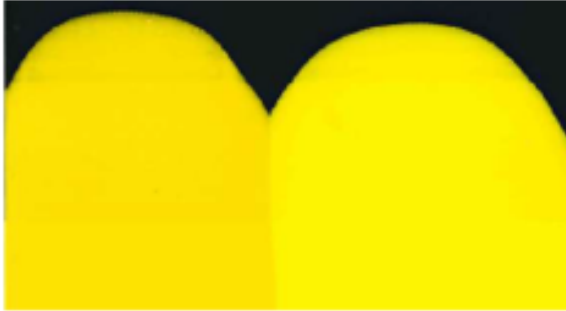
- Decorative performance, such as bright colours, clean colour shades and high visibility (signal function of a paint),
- Demanding technical criteria such as excellent hiding power, light and weather fastness, heat stability, in combination with non-bleeding properties.



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.

Alternative Pigments Assessment (1)

Pigment	Possible Alternative to	Colour comparison
Bismuth Vanadate PY 184	PY 34	<p>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.</p> <p>PY 34 PY 184</p> 

Alternative Pigments Assessment (2)

Request	Lead chromate yellow PY 34	Alternative
		PY 184
Function	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.	Durable paints, the same colour range cannot be achieved without other pigments Excellent bleeding properties
Production process		There is no need for changes in the production process
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 expensive (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).

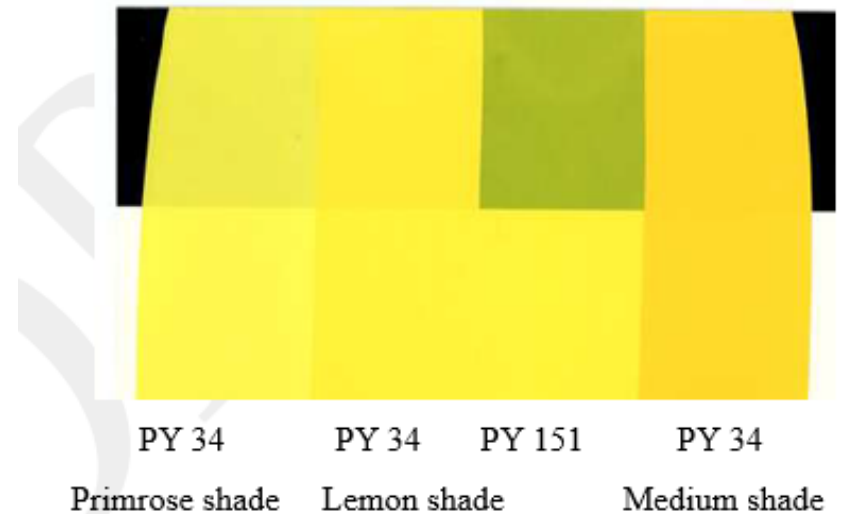
Paint Reformulation

- 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

Pigment	External Use	Worse Heat Stability*	Bleeding
PY 184, PY 42, PR 101, PY 110, PR 254	Yes	No	No
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

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



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

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

7. Substitution of Lead Driers

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.

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

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.

Alternatives to Lead Driers

1. **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.
2. **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

Alternatives 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

Request	Lead octoate	Alternatives			
		Zirconium octoate	Strontium octoate	Zirconium neodecanate	Strontium neodecanate
Environmental and human health hazard	H226 - Flammable liquid and vapour				
	H302 - Harmful if swallowed	H302 - Harmful if swallowed	H302 - Harmful if swallowed		
	H332 - Harmful if inhaled				
	H410 - Very toxic to aquatic life with long lasting effects.	H304 - May be fatal if swallowed and enters airways	H304 - May be fatal if swallowed and enters airways		
	H360(f,d) - May damage fertility. May damage the unborn child.	H318 - Causes serious eye damage	H318 - Causes serious eye damage	H304 - May be fatal if swallowed and enters airways	H304 - May be fatal if swallowed and enters airways
	H371 - Cause damage to organs through prolonged or repeated exposure	H361d - Suspected of damaging the unborn child.	H361d - Suspected of damaging the unborn child.		
	H336 - May cause drowsiness or dizziness	H315 - Causes skin irritation	H315 - Causes skin irritation		

Paint Reformulation

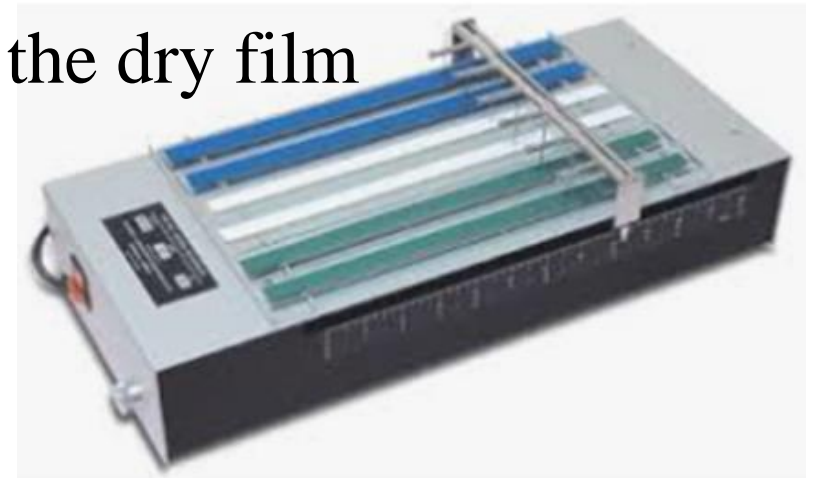
- The quantities of some driers such as organic salts of cobalt, manganese, vanadium and iron, are restricted because of the coloration of the paint film;
- Certain pigments are also capable of accelerating oxidative drying, e.g. iron oxides (mainly transparent grades due to their large surface area), 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. Exposure to lead is a major public health concern;
- Lead compounds should have priority in substitution;
- There are many pigments and driers available on the market that may effectively substitute lead compounds;
- Lead Paint Reformulation Technical Guidelines provides information about alternatives, their assessments and reformulation processes. This helps companies to effectively substitute lead compounds;
- We will work with participating SMEs on specific reformulations, according to their needs

THANK YOU!

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