Lead Replacement in the Molybdate Orange Colour Space

Peter Gee, Marketing Manager, Dr. Markus A. Meier, Marketing Manager*

Ciba Specialty Chemicals Inc., R-1045.2.09. CH4002 Basel, Switzerland.
e-mail: peter-1.gee@cibasc.com

Summary: Due to the toxicological concerns over lead and lead compounds, there has been an increased trend to replace lead based materials in paint systems. Change in this instance has been driven primarily by Legislation and regulations, however in many cases global companies wish to show a unified approach and some have taken both a positive environmental marketing approach over their competitors with Lead free paints and a positive move on labour relations.
The pigment manufactures have had the challenge to meet these requirements either from existing product ranges or to develop new pigments that are both commercially and technically viable. Due to the diverse application, systems and cost structures within General Industrial Paints no single product offers a universal solution.
The higher performing pigments generally meet the higher specifications technically but because of their chemical complexity in processing and structure fail to achieve the lower comparable costs against Molybdate Oranges. With less complex pigment structures limitations are identified within the technical area.
Additionally within the range of Molybdate Oranges differing grades are available treated to enhance temperature stability and chemical resistance or untreated to attain lower costs and increased saturation.
For this reason paint producers have the choice of a single product within the mid performance area that would act as a compromise or alternatively select three products to fulfil all requirements with the associated logistic problems on supply, stock inventory and quality testing.
Within the single product approach Pigment Orange 81 potentially offers the most flexible solution to the paint manufacturer in order to meet the volume market for **Mid performance** offering opacity, gloss, rheology, bleed resistance, good temperature stability and of great importance the ability to match the colour space occupied by Molybdate Orange.

For the multiple pigment approach:

High technical performance	Pigment Orange 73 offering higher saturation than Molybdate Orange but with associated costs.
Mid performance	Pigment Orange 81
Cost effective	Pigment Orange 34 and Pigment Orange 16 offer high saturation but limitations in durability.

 CCC 1022-1360/00/$ 17.50+.50/0

1. Introduction

Ciba Specialty Chemicals are producers of both inorganic and organic based pigments and are uniquely positioned to provide a balanced view of potential alternatives for lead replacement in line with market demands.

Within the paint market there are a number of frequently asked questions:

- Do we need to replace Lead based on current and future legislation?
- Can we replace Lead from a technical prospective?
- How much will it cost if we replace Lead?

It is our intention to provide our customers with data in order that these questions can be addressed for their specific application.

2. Chemistry and Physical Aspects of Molybdate Oranges

Composition: 25 $PbCrO_4$•4 $PbMoO_4$•1 $PbSO_4$.

Pigment Red 104, CAS Number 77605

Pigment Red 104 is primarily a bright orange, with an inorganic composition based on a solid solution of Lead chromate, Lead molybdate and Lead sulphate. Crystal form is tetragonal.

Physical data : Density 5.41 - 6.34 g/cm^3

Oil absorption 5.8 – 40 g/100g pigment,

depending on treatments and processing.

Alternative names: Scarlet Chrome, Molybdate Red, Moly Orange, Chrome Vermillion.

3. Why Replace Lead?

Molybdate Orange is effectively a mid to high performance product with a lower cost structure than organic pigments.

The primary disadvantage is related to toxicological concerns, which ultimately translate into higher costs for the complete chain from producer to end-user.

Aspects that should be considered in the selection of Lead for future applicational areas are:

a.) Impact on the environment for both aquatic and human life.

b.) Implementation of legislation for registration costs and testing may ultimately increase the raw material **cost** for paint producers.

c.) Implementation of legislation for the work place in the handling of materials will increase production **cost** for the pigment supplier.

d.) The negative marketing effect of toxic materials will lead to reduction in sales of Molybdate Orange and increase period **cost** based on the economy of scale.

e.) If legislation continues unabated then the long term **cost** of disposal of packaging materials could exceed the cost of the paint.

f.) If legislation continues and results in the ban in selective application areas then the **cost** of major claims could dramatically affect the profitability of the paint producer and their image for responsible care.

4. Status of Legislation – European Union

Within the European Union, Directive 98/98/EC "Adapting to technical progress for the 25th Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances" indicates the classification and labelling for lead pigments. Lead-based pigments are considered toxic and dangerous for the environment and have to be labelled with the symbols T *(Skull and cross-bones)* and N *(Dead fish/dead tree)* together with the warning phrases:

T (Skull and cross-bones)

N (Dead fish/dead tree)

- R61: May cause **harm** to the unborn child
- R33: Danger of **cumulative effects**
- R40: Possible risks or **irreversible** effect
- R50/53: Very toxic to **aquatic organism**, may cause **long-term** effects in the aquatic environment
- R62: Possible risk of impaired **fertility**
- S53: Avoid **exposure**; obtain special instruction before use
- S45: In case of accident or if you feel unwell, seek **medical advise** immediately (show the label where possible)
- S60: This material and/or its container must be disposed of as **hazardous waste**
- S61: **Avoid release to the environment**. Refer to special instruction/safety data sheet.

Further details on the white paper will be presented later.

Within the European Union selective countries have chosen to implement more stringent levels like for example Germany

5. The Evaluation of Products for the Market

For a pigment to succeed as a replacement it should certainly achieve basic requirements of opacity for thin films and bring addition benefits in the areas of colour strength coupled with durability in paler shades and chemical resistance, therefore the following pigments were examined as potential offers:

Colour Index	Chemical type
Pigment Red 104	Lead Sulfo-Chromate-Molybdate *
Pigment Orange 81	Diketo-pyrrolo-pyrrole *
Pigment Orange 61	Isoindoline *
Pigment Orange 64	Benzimidazolone *
Pigment Orange 34	Diarylide - Pyrazolone *
Pigment Orange 16	Dianisidine *
Pigment Orange 73	Diketo - pyrrolo - pyrrole *
Pigment Orange 75	Cerium Sulfide
Pigment Orange 74	Azo
Pigment Orange 69	Isoindoline
Pigment Orange 43	Perinone
Pigment Orange 67	Qunazolone
Pigment Orange 36	Benzimidazolone

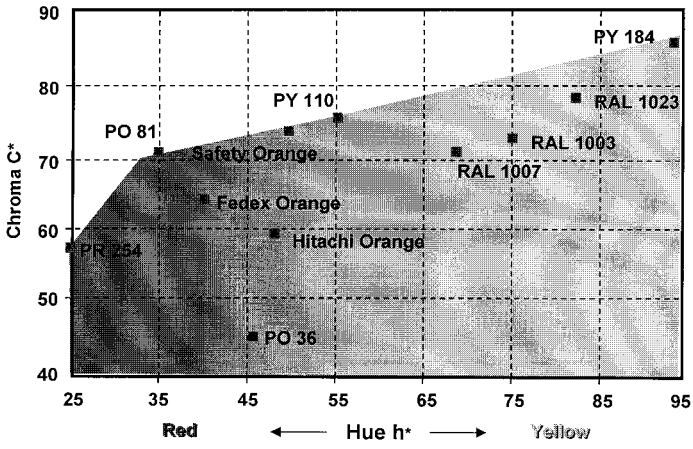
* produced by Ciba Specialty Chemicals

6. Requirements for Industrial Paints

In order to meet the requirements of the Paint maker and end user it is important to first identify the requirements for both **Paint producer and end-user**:

High saturation - Most of the shades used in Industrial paints are highly saturated for impact, Molybdate Orange covers this area well and any new pigment must cover all key shades attained by Molybdate Orange.

In addition a highly saturated product allows the paint maker great flexibility in matching and potential lower costs.


Chroma C*
90
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70
60
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25
35
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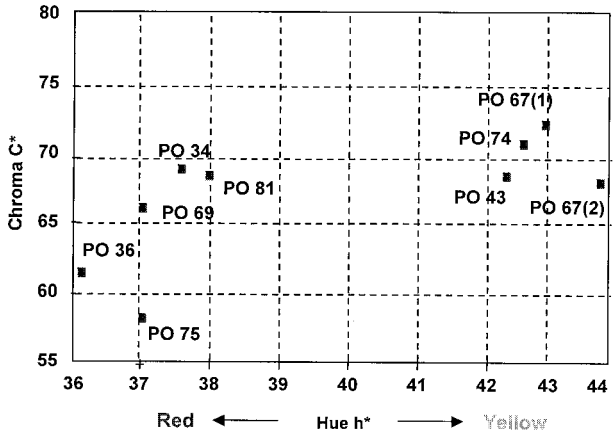
Red
Hue h*
Yellow
PY 184
PY 110
RAL 1023
PO 81
Safety Orange
RAL 1003
RAL 1007
Fedex Orange
Hitachi Orange
PR 254
PO 36


Chroma C*
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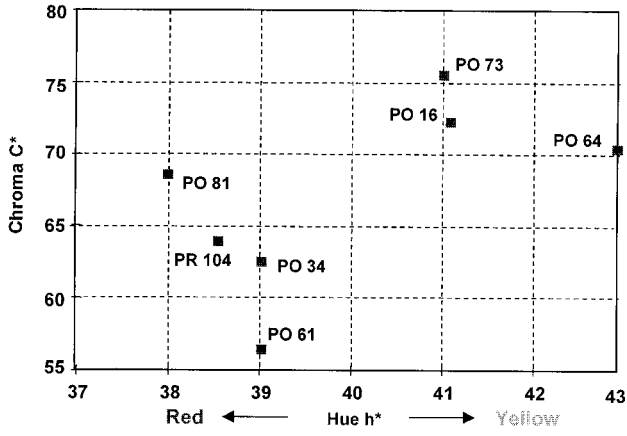
PO 67(1)
PO 74
PO 34
PO 81
PO 43
PO 67(2)
PO 69
PO 36
PO 75


Chroma C*
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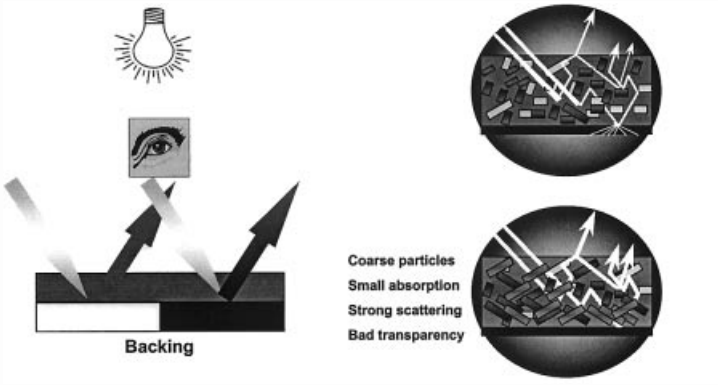
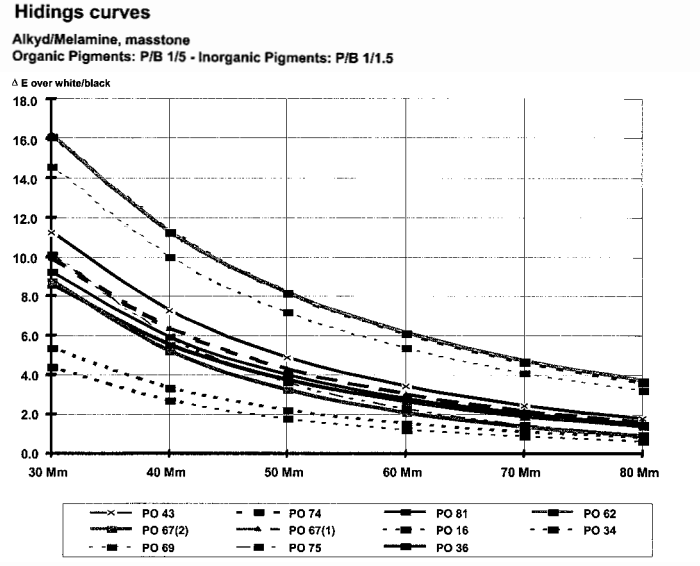
Red
Hue h*
Yellow
PO 73
PO 16
PO 64
PO 81
PR 104
PO 34
PO 61

Flow - with reduction in VOC levels there is a requirement that new pigments exhibit good rheology both for lower solvent demand and production optimisation process (higher pigment loading = lower process cost). Currently Molybdate orange clearly meets that target.

High opacity - is one of the primary benefits of Molybdate Orange allowing relatively low film thickness coupled with substrate obliteration. This has traditionally been one of the weak points in replacements with organic pigments as they generally have higher tinting strength but lower opacity.





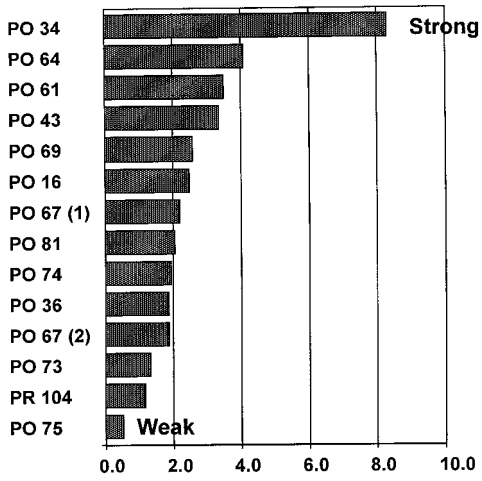
High gloss – is one of the first visual impacts on the end user, it is often to difficult achieve with organic pigments due partially to their particle size and shape, this aspect is not often noted with Molybdate Orange which generally exhibits high gloss at high pigment loadings.

Pigment	Overpaint Fastness		Gloss
	GS	Δ E	60° Angle
PO 81	**4-5**	**1.4**	**92%**
PO 73	5	0.6	87%
PO 61	5	0.5	93%
PO 64	5	0.7	93%
PO 34	4-5	1.1	90%
PO 16	4-5	1.1	73%
PR 104	5	0.7	93%
PO 75	5	0.5	87%
PO 74	2-3	8.8	90%
PO 69	5	0.7	93%
PO 43	5	0.2	74%
PO 67 (1)	2-3	9.4	93%
PO 67 (2)	2-3	9.5	92%
PO 36	5	0.5	93%

Chemical resistance - is relatively poor for traditional Molybdate Orange and the significant colour change is often observed in industrial atmospheres and in the ACE market where battery acids and hydraulic fluids are used.

Pigment	Chemical resistance			
	Acid		Alkali	
	Masstone	1/3 ISD	Masstone	1/3 ISD
PO 81	**5**	**5**	**5**	**5**
PO 73	5	5	5	5
PO 61	4-5	5	5	5
PO 64	4-5	5	1	5
PO 34	5	5	5	5
PO 16	5	5	5	5
PR 104	4	3	5	5

Intrinsic strength – becomes a more important feature in paler shades on a cost basis, within the deep shade area pigments with high intrinsic strength rely on the correct selection of an opacifying agent, a typical example being **PY184.**



Evaluated at 1/3 International Standard Depth

Durability - accepted by the industrial but generally poor in pale shades and darkening in deep shade, although certain treated grades can offer better durability. There are benefits in the use of organic / inorganic blends of pigments in this area and in line with the expected demand for longer life coatings.

Evaluation carried out on the Atlas Weather-O-Meter (CAM 7) and assessed against the ISO grey scale after a period of **1000 and 2000 hours**

Pigment	1000 hrs WOM, alkyd melamine			
PO 81	**4-5**	**1.5**	**4-5**	**0.8**
PO 73	5	0.5	5	0.5
PO 61	4	2.7	4	0.8
PO 64	3-4	2.0	1	20+
PO 34	3d	3.5	1	20+
PO 16	3d	3.4	1-2	20+
PR 104	3-4d	3.7	4	2.0
PO 75	3	4.7	1	15.0
PO 74	3-4	1.5	4-5	1.4
PO 69	4-5	0.7	4-5	1.0
PO 67 (1)	4d	2.3	3-4	3.3
PO 67 (2)	4-5d	1.4	3-4	2.8
PO 36	5	0.7	5	0.6

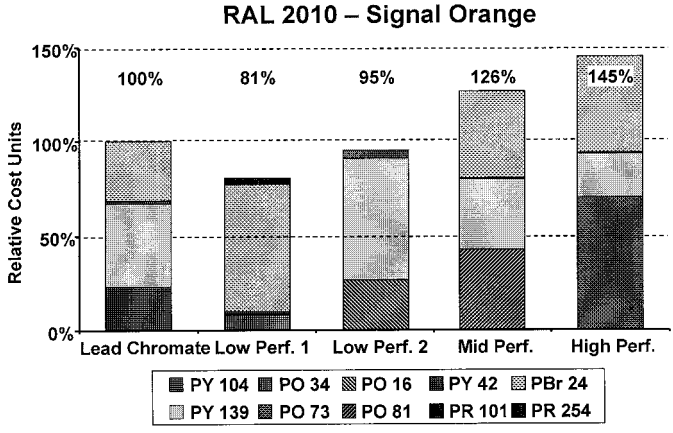
2000 hrs WOM, alkyd melamine

Pigment	Masstone		1/3 ISD	
	GS	Δ E	GS	Δ E
PO 81	**4-5**	**-**	**3-4**	**-**
PO 75	2-3	5.3	1	17.5
PO 34	3d	2.9	1	27.2
PO 74	4	2.4	3	3.7
PO 69	4	0.7	4-5	1.6
PO 43	3d	3.5	3-4	1.8
PO 67 (1)	4d	1.8	2-3	4.7
PO 67 (2)	4-5d	1.3	2	8.4
PO 36	4-5	0.6	4-5	0.7

Temperature stability - Molybdate Oranges have excellent stability within the majority of temperature-cured systems (alkyd melamine, polyesters etc.) and this becomes a prerequisite for organic and inorganic alternatives.

Cost - is currently perceived as relatively low for Molybdate Orange against organic pigments and inorganic alternatives on kilo prices.

A more cost effective approach can be taken with Value-in-use.



System suitability – Industrial paints are diverse with widely differing resins, solvents and cure temperature. Molybdate Orange currently offers an excellent compromise product in this area in order to maintain low inventories.

7. Systems for Industrial Paints

The market is extremely diverse in its requirements for chemical, durability and temperature stability with the following table (Table) indicating only a few of the many industrial systems on the market.

Table: Various paint systems used in the Industrial Paint market (Ac: Acetate)

Resin	Cure temp.	Chemical agent	Solvent	Application
Epoxy	RT	Amine catalysed	Ketone/ Ester	Outstanding alkali, anticorrosive & chemical resistant paints
Alkyd Melamine	130°C/ 30'		Xylene, Alcohol	Small machinery
Polyurethane PUR -1-pack	RT		White spirit, Xylene	Dries by oxidation or moisture cure; floor finish, trains, planes
Polyurethane PUR-2-pack (2-pack Acrylic)	RT - 80°C	Isocyanate cured	Butyl Ac/ Xylene, Butyl Ac/MEK	Trains, buses, planes (ACE)
Polyester PES - unsaturated styrene, 2-pack	RT	Peroxide catalyst	Monomer	Gel coats
Nitrocellulose N/C	RT		Alcohol, Ketone	Dries by solvent emission, repair paints, aerosols machinery
Chlorinated rubber	RT		Aromatic hydrocarbon	Dries by solvent emission, resistant to acid, alkali and water for anticorrosive, marine, line paints
Alkyd - short/medium	RT - 60°C		Xylene	Dries by oxidation & solvent evaporation, heavy machinery
Polyester PES - Melamine	130°C/ 30'		Butylglycol Ac, Solvesso	Exterior finishes
Polyester PES - Melamine	240°C/ 1'	Acid catalyst	Butylglycol Ac, Solvesso	Coil coated objects

8. Conclusion

Primary recommendations

	Pale	Deep
Classical approach	**Pigment Orange 34** **Pigment Orange 16**	**Pigment Orange 34** **Pigment Orange 16**
Technical limitations	Poor durability in pale shades	PO 16 requires additive for rheology.
Mid performance	**Pigment Orange 81**	**Pigment Orange 81**
Technical limitations	Can be system dependant and requires specific evaluation	Technically the best offer
High performance	**Pigment Orange 73**	**Pigment Orange 81**
Technical limitations	Only commercial at this point	Technically the best offer

Secondary recommendations

	Pale	Deep
Classical approach	-	-
Technical limitations	-	-
Mid performance	**Pigment Orange 61**	**Pigment Orange 64**
Technical limitations	Poor alkali fastness, low durability vs cost	Rheology requires additive, alkali fastness poor, positive – high saturation
High performance	**Pigment Orange 61**	**Pigment Orange 61**
Technical limitations	Dull shade vs cost, positive – high heat fastness and durability	Dull shade vs cost, positive – high heat fastness and durability