IPEN
a toxics-free future

Replacement of lead pigments in solvent based decorative paints

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Background

Exposure to lead causes significant injury to human health and imposes large economic and social costs on developing countries. Children are especially sensitive to lead, and the World Health Organization (WHO) has concluded that no level of lead exposure to children is safe.

Lead in paint is a major source of lead exposure in children. When lead paints are used in homes, schools and elsewhere, childhood lead exposure pathways are created. All paints weather and wear over time. When this happens, lead from lead paint ends up in dust and soil found in and around homes and schools. Large quantities of lead-contaminated dusts are also created when old painted surfaces are scraped and sanded prior to repainting. Children get dust and soil on their hands and then ingest the lead through normal hand to mouth contact. They can also ingest lead through inhalation, by eating flaking paint chips, and by chewing on toys painted with lead paint.

Most highly industrialized countries severely restricted the lead content of paints for sale and use in their countries in the 1970's and 80's, either through maximum allowed limits or prohibition of use of lead-containing paint ingredients. In the U.S, the maximum permitted total limit for lead in decorative paint was recently lowered from 600 to 90 parts per million (ppm), emphasizing the importance of avoiding even low-level exposure.

This report was produced by Safinah Ltd on behalf of IPEN, as part of the Asian Lead Paint Elimination Project funded by the European Union. The Asian Lead Paint Elimination Project was established to eliminate lead in paint and raise widespread awareness among business entrepreneurs and consumers about the adverse human health impacts of lead-based household enamel paints, particularly on the health of children under six years old. The Project was implemented by IPEN over a period of three years (2012-2015) in seven countries (Bangladesh, India, Indonesia, Nepal, Philippines, Sri Lanka, and Thailand). While this report has been produced by Safinah Ltd and with funding from the European Union, its contents are the sole responsibility of IPEN, and can in no way be taken to reflect the views of the European Union or Safinah Ltd.

IPEN is a network of non-government organizations (NGOs) in 116 countries; most of which have developing and emerging economies. IPEN's mission is a world in which chemicals are no longer produced or used in ways that harm human health. IPEN's NGO network identifies important national issues where international policy can help protect people and the environment from toxic chemical exposure and then organizes activities that elevate and prioritize those issues within international policy arenas. Once international policy is established, IPEN mobilizes expert and financial resources to help NGOs and their national governments turn international policies into meaningful, on-the-ground change. The majority of funds IPEN raises are re-granted to NGOs in the developing world. IPEN´s goal is global lead paint elimination by the year 2020.

Contract Report for

Replacement of lead pigments in solvent based decorative paints

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1 INTRODUCTION

1. IPEN is a global network comprised of 700 participating organisations in 116 countries. As an NGO it brings together leading environmental and public health group around the world.

2. Currently IPEN has a European funded initiative to assist developing countries to remove lead from paint formulations.

3. The IPEN Asia lead paint elimination programme aims to eliminate manufacture, import, sale and use of decorative paint containing lead in 7 Asian countries.

4. While larger paint companies have the resource and capability to re-formulate, smaller paint manufactures lack the resource and sometimes the capability/expertise to undertake re-formulation work.

5. The aim of this project is to identify a suitable Paint Chemistry Expert to produce a series of reports and provide advice to assist these companies in developing lead elimination programmes.

6. IPEN has approached Safinah Ltd (Safinah) to undertake this project to provide advice in the areas of water based and solvent based decorative coatings.

7. This report deals with the replacement of lead pigments in solvent based one pack decorative paints.

2 SCOPE

8. IPEN understand that one of the main sources of lead in solvent based one pack decorative paints is the use of lead pigments.

9. They understand that there are several routes that can be taken to eliminate lead containing materials and replace them with lead free alternatives. The larger paint companies have good relationships with the major suppliers/manufacturers of the materials, and therefore receive good advice on how to make the changes.

10. Small and medium size paint companies do not have the same technical support through their supply chains as they will often purchase materials from distributors or agents, not the primary manufacturer.

11. IPEN wish to be able to provide guidance to these companies to help identify the offending materials, and how to go about replacing them in a formulation.

12. This guidance to be targeted at smaller paint manufacturers who may not have the capability to reformulate. The guidance should cover:

    a. The steps to be taken when reformulating to avoid lead pigments
    b. Possible approaches to cost-effective substitution of lead pigments
    c. Identification of suitable vendors or suppliers of the substitute ingredients. This may prove difficult so the chemical type will be provided as well rather than simply a trade name.

3 LEAD PIGMENT REPLACEMENT IN SOLVENT BASED ONE PACK DECORATIVE PAINTS

3.1 Introduction

13. Lead based pigments have been used in one pack solvent based paints as colouring pigments, extending pigments and also as anticorrosive pigments.

14. Red lead (Pb_3O_4) has been used extensively as an anticorrosive pigment but is now being replaced by less toxic anticorrosive pigmentation. White lead ($Pb(OH)_2.PbCO_3$) has been used as an extending pigment in white paints but has now been largely superseded by titanium dioxide.

15. Lead sulphochromate (PY34) Lead chromate molybdate sulphate (PR104) are yellow and red pigments that are widely used to provide a currently unique combination of good opacity and bright clean shades in paint films.

16. To date there are no single 1:1 pigment alternatives for these two pigments despite considerable research. The most successful approach has been to use a combination of organic and inorganic pigmentation can give the desired combination of properties in the final film.

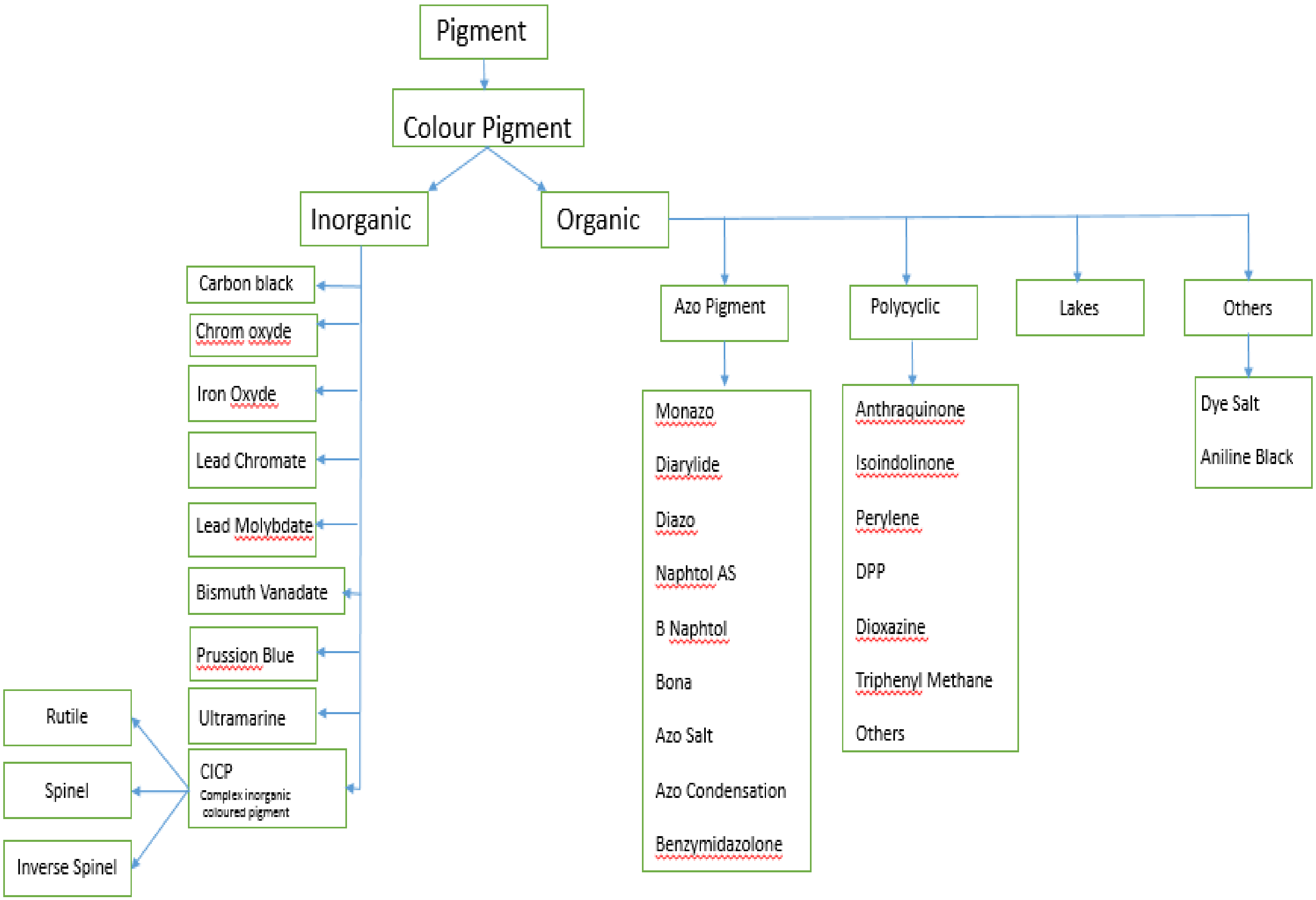
17. This report will focus primarily on the replacement of lead sulphochromate (PY34) Lead chromate molybdate sulphate (PR104) as these are by far the most commonly used lead pigments in decorative paints.

3.2 Pigments

18. Pigments are fine particle size solid materials which are insoluble in the liquid paint. Colouring pigments provide shade, strength and brightness of colour, opacity and can also give special optical effects. The pigment may have to be light fast, heat resistant and chemically resistant, depending on the intended end use.

3.3 Types of pigment

19. Pigments are divided into organic and inorganic, depending upon the chemical structure. The two classes of pigment are shown in the chart below :


Pigment
Colour Pigment
Inorganic
Organic
Carbon black
Chrom oxyde
Iron Oxyde
Lead Chromate
Lead Molybdate
Bismuth Vanadate
Prussion Blue
Ultramarine
CICP
Complex inorganic coloured pigment
Rutile
Spinel
Inverse Spinel
Azo Pigment
Polycyclic
Lakes
Others
Monazo
Diarylide
Diazo
Naphtol AS
B Naphtol
Bona
Azo Salt
Azo Condensation
Benzymidazolone
Anthraquinone
Isoindolinone
Perylene
DPP
Dioxazine
Triphenyl Methane
Others
Dye Salt
Aniline Black

21. The two main lead based colouring pigments used in paint are lead sulphochromate yellow (PY34) and lead chromate molybdate sulfate red (PR104). Formulations containing these have good weathering resistance, good opacity and give bright and clean colours.

22. In general, many formulations developed solely with inorganic pigments are comparatively dull in colour, but have good weathering performance and opacity. There are only a few inorganic pigments such as lead chromates and bismuth vanadate that give clean shades and bright colours.

23. The general properties of selected organic and inorganic pigments are tabulated below.

Organic and inorganic pigment properties			
Properties	**Inorganic pigment**	**Organic pigment**	
		Azo Type	**HPP (High Performing Pigment)**
Opacity	Excellent	Transparent	
Colouring strength	Low to average	Several times better than inorganic pigments	
Purity , Chroma	Dull	Bright	
Lightfastness	Good to Excellent	Low to average	Good to Excellent
Weather resistance	From mediocre to excellent	Mediocre	Good to Excellent
Heat resistance	normally > 500°C, not often <200°C	150 - 220 °C	200- 300°C
Bleed resistance	Excellent	Average to good	Good to Excellent
Chemical resistance	Mediocre to excellent depending upon the chemistry	Excellent except for the salt	Excellent
Pigment cost	low to average	Average	High

3.4 Colour theory

24. The aesthetics of a paint are defined by gloss, colour and opacity.

25. Gloss is primarily provided by the resin system.

26. Colour provided by the pigment(s) and is accurately defined by the following three parameters:

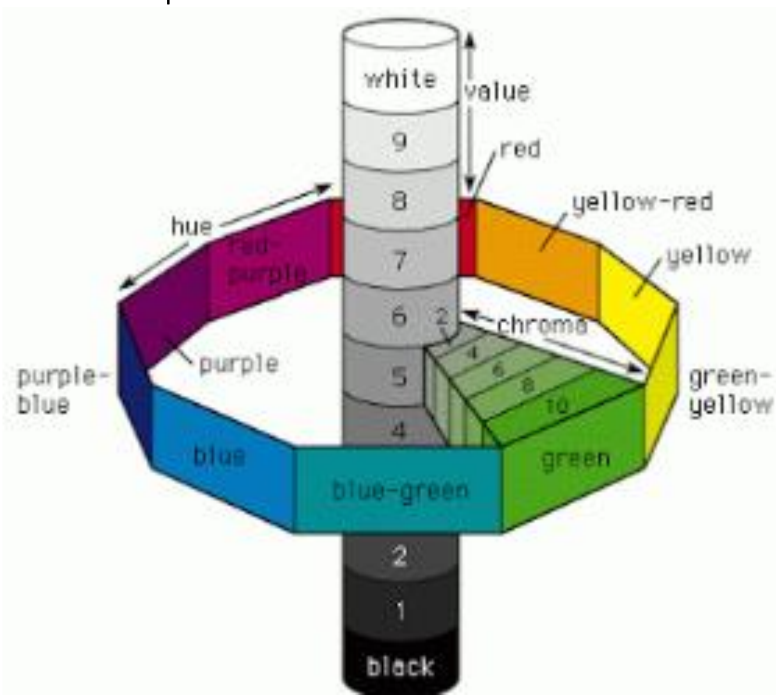
    a. Hue, which is the colour - for example, red, yellow, blue.

    b. Intensity (or chroma), which is used to describe the brightness and purity of a colour. For example, bright red or dull red.

    c. Value, which is used to describe the lightness or darkness of a colour. Value changes are obtained by adding black or white to a hue.

27. Hue, chroma and value combined constitute the chromaticity of a colour.

28. These three parameters are illustrated below.



29. ‘Tinting’ is the adjustment of a pigment mixture within the three dimensional space to arrive at a particular colour. For the most part, this can always be done by using 4 colours and can be less than this in many cases.

30. Mixing a non-adjacent hue (for example red and yellow hue) produces an intermediate reduced chroma orange (or dull orange).

31. The opacity of a paint film is determined by the ability of the pigment to scatter incident light. This in turn is dependent on the difference between the refractive index of the pigment and that of the medium or resin system. The greater the difference in refractive index, the greater the opacity for a given pigment loading.

32. Generally, inorganic pigments such as lead sulphochromate and titanium dioxide have higher refractive indices than organic pigments and so provide greater opacity in paint films. It is for this reason that replacement of lead pigments is most easily achieved by using a combination of organic pigments for colour and brightness and inorganic pigmentation for opacity.

3.5 The Colour index system

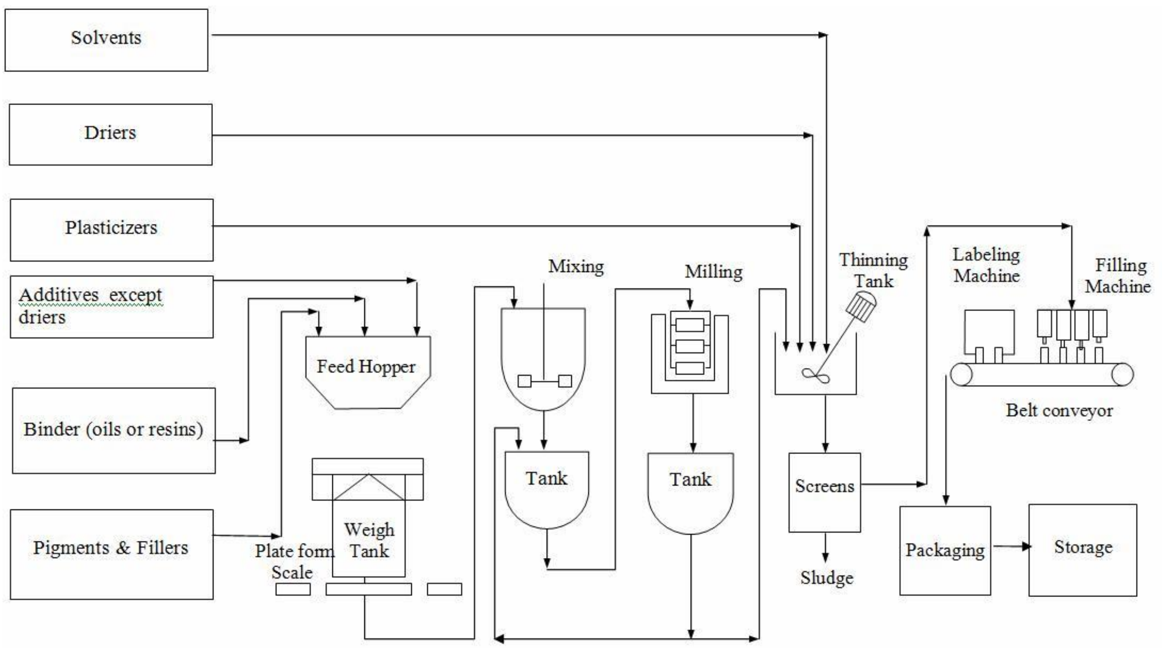
33. The colour index system is a coding system developed under joint sponsorship of the Society of Dyers and Colourists in the UK and the Association of Textile Chemists and Colorists in the USA. The colour index (CI) identifies each pigment by giving it a unique colour index name and colour index number. Hence, lead sulphochromate is PY (pigment yellow) 34 and lead chromate molybdate sulphate is PR (pigment red) 104.

34. This system enables a pigment to be uniquely identified no matter where in the world it is made or used.

3.6 Manufacture of paint and the use of tinting systems

3.6.1 Generalised manufacturing process

35. A very generalised schematic of the basic paint making process is shown below.



Gupta and Gauri / International Journal of Engineering, Science and Technology, Vol. 5, No. 4, 2013, pp. 1-13

36. It can be seen from the schematic that there is a milling stage in the process. It is at this point that the pigments are dispersed or ground to the small particle size suitable for the finished paint.

37. After dispersion, the paint is thinned down with solvent, adjusted for viscosity and solids contents and filtered.

38. If any coloured pigments were present in the initial formulation, to produce a pastel colour or off-white, then the colour may be adjusted prior to filling.

39. The precise manufacturing route of a particular paint will vary depending but they are generally made by either a 'co-grind'process or a tinting route.

3.6.2 Co-grind Process

40. Paints that sell in high volumes, such as whites, can be made via the route shown above. In this situation, the initial formulation is fixed and only small adjustments of the paint are needed before filling off for sale at the end of the process.

41. Pastel colours could also be made by this route by adding the desired pigment dispersion or tint to the white paint prior to filling off into tins.

3.6.3 Substitution in Co-grind formulations:

42. Co-grind routes are generally used for high volume white paints but it is possible that a situation may arise where the initial formulation contains the lead containing pigment. In this instance, a reasonable starting point is to replace the volume of lead pigment in the dry film by an equal volume of lead free alternative(s). In the situation where the paint contains titanium dioxide, then the lead free alternative pigment is likely to be one or more organic pigments.

43. The formulation would be worked out on paper initially, then the formulation manufactured on lab scale manufacture and the paint properties measured. The formulation is adjusted through an iterative process until the desired colour is achieved. This might be confirmed via colour matching equipment or even by experienced personnel.

3.6.4 Tinting process

44. The second, and possibly more common method used to make coloured paints is via a tinting route. This is identical in principle to the tinting systems used in paint retailers.

45. In this situation, the paint maker manufactures a small number of base paints of specific colours, essentially by the route shown in the diagram above. Depending on the end use, these bases may stored in bulk for colour adjustment when an order is confirmed. Alternatively, the paint may be filled off into smaller size tins suitable for sale at a retail outlet. These can then be tinted at point of sale to the desired colours by the addition of a range of coloured pigment dispersions.

46. The amount of tint added is generally predetermined and held within the software in the form of a ‘menu’.

47. This approach simplifies the manufacturing process and allows for a much larger range of colours to be produced.

48. Organic and inorganic pigment dispersions (or ‘tints’) are available and are compatible with a wide range of resin system chemistries. They may be referred to as ‘universal dispersions’ or ‘universal tints’ to reflect this quality.

49. Paint companies do not always make their own pigment dispersions (or tints). In this case they would buy them from a specialist manufacturer who controls the formulation and colour strength of the finished pigment dispersion.

50. As a result, paint companies that buy in pigment dispersions and wish to remove lead pigments must work closely with their suppliers to achieve the desired end result.

3.6.5 Substitution in colours produced by tinting systems

51. For those colours made by a tinting system the position is more complicated. Colours are usually matched using specialised software and equipment. In this situation, all of the parameters of the various tints and bases are held in the software on the system. The colour that is to be matched is measured instrumentally, and the software devises a formulation based on the measured parameters of the base and tints to match that colour. Unfortunately, without knowing the tint strengths and the colours to match it is impossible to give any quantitative guidance.

4 REFORMULATION TECHNIQUES

4.1 General

52. As previously stated, there are no 1:1 replacements currently available for the replacement of either PY 34 or PR104.

53. It will also often be the case that paint formulations containing lead pigmentation will contain other pigments that contribute towards the final colour. For example, decorative paints will often contain titanium dioxide.

54. Because of these two factors, it is extremely difficult to give anything other than general guidance on the substitution of lead pigments as the reformulation route will be dependent on the formulation of the paint in question.

55. The resulting replacement process is possibly more complex but at the same time, almost certainly technically possible, and there may well be more than one way to achieve the desired end result.

4.2 Prioritising attributes

56. As lead pigments deliver a broad range of properties, such as opacity and bright shades, it may well be the case that formulations are over-engineered. For instance, if the formulation contains titanium dioxide, then the opacifying properties of a lead pigment are secondary to the colour shade. In such instances, replacement of the inorganic lead pigment by one or more organic pigments would be of prime importance.

57. As a result, the first stage of the reformulation process should be to decide precisely which performance properties, in addition to colour, are critical. For example, brightness of shade or opacity at typical film thicknesses. The desired balance of properties can then be reproduced by using a combination of organic and inorganic pigments.

58. By using this approach, the inorganic pigment provides the opacity (through higher refractive index) and potentially the weathering performance, whilst the organic pigment is used to obtain the desired clean colour shade.

59. Depending upon the required properties of the paint, the following generalised strategy can be used.

1. For clean shades: use organic yellow, red or orange pigments
2. For opacity: use inorganic pigments (Bismuth vanadate, CICP, or Iron oxide).
3. For opacity + clean shades: combine organic and inorganic pigments or use hybrid pigments

60. The basic approach would be to measure the colour of the paints containing lead pigments and then use colour matching tools (software and equipment) to produce the colour match required. Other performance properties such as exterior durability would help guide the choice of pigment – for example, if the paint is to be used exclusively indoors, there would be no need to use a high performance light fast pigment package. This would help reduce costs of the reformulation.

4.3 Formulation of clean shades using organic yellow, red or orange pigments

61. In situations where titanium dioxide is used as the main opacifying pigment, the choice of organic pigmentation to substitute the lead pigment will be determined by the desired level of weathering performance (interior or exterior performance) and the colour required. These are the main differentiators in performance.

62. HPP (High performance Organic pigments from the polycyclic range) can provide high level of weathering performance (comparable to inorganic pigments) but are expensive in comparison to inorganic pigments and with other organic pigments that have poor weathering performance.

4.3.1 Formulation of clean shades for interior use

63. Paints for interior use do not need to have excellent weather resistance or light fastness.

64. In this case, modified azo pigments can be used. These give good acid and base resistance but have limited weather fastness.

65. Modification of azo linkage (N=N) increases the cost and improves the weathering performance.

66. In general, their price and weathering performance increases as follows:

- Monazo - (colour range: form greenish yellow to orange)
- Disazo - (colour range: green yellow to reddish yellow, orange and red)
- B Naphtol - (colour range: orange to red)

- Naphol AS - (colour range: yellowish and medium red to brown and violet)
- Bona - (colour range: yellowish red to bluish red)
- Arylide and diarylide - (colour range: greenish yellow to orange)
- Azo Condensation - (colour range: green shade to red shade yellow)
- Benzymidazolone - (colour range: green shade yellow to red)

67. In some instances, the azo condensation or the benzymidazolone pigment can match the weathering performance of the inorganic or high performance organic pigment.

4.3.2 Formulation of clean shades for exterior use

68. When formulating paints for exterior use, the requirement is for good colour retention and weathering performance.

69. In this case, it is necessary to choose high performance organic pigments (HPP) which come mainly from the polycyclic range.

70. Depending on the colour to be used, the following pigment range can be used:

- Isolindolone - (colour range: red shade yellow)
- DPP (Diketo Pyrrolo Pyrrole) - (colour range: from orange to bluish red)
- Perylene - (colour range: red)
- Perylone - (colour range: orange)
- Quinacridone - (colour range: reddish violet and blueish red)

4.4 Formulation for opacity using inorganic pigments

71. In those formulations where lead pigments are the main opacifying pigment it may be necessary to use an alternative inorganic pigment to provide the desired opacity. The inorganic pigments typically used in formulating lead free alternatives are bismuth vanadate (PY 184), CICP (complex inorganic colour pigments) (PY 53, PBr 24, PY 164) and iron oxides (PY42,43, PR 101, 102). The choice of inorganic pigment will depend upon the strength, shade and brightness (chromaticity) of the colour required.

72. The chroma and price rank are as follows (starting from the most expensive which also has the best chroma):

Bismuth Vanadate > CICP (complex inorganic colour pigment) > Iron Oxide (red or Yellow)

73. The colour range of the three inorganic pigment is listed below;

- Bismuth Vanadate – (Colour range: greenish yellow)
- Iron Oxide - (Colour range: red and yellow)
- CICP - (Colour range: yellow, orange, green, blue and black)

74. The brightest shades are produced by bismuth vanadate or CICP's. Iron Oxides can be used in general applications but they produces dull colours by comparison with lead chromates.

75. Most of the commercial Bismuth Vanadate pigments are based on pure bismuth vanadate with monoclinic structure (PY 184) though there are still pigments based on the two phase system bismuth vanadate molybdate.

76. Pure bismuth vanadate pigments show a higher chroma than the two phase systems. Bismuth vanadate is not a complex inorganic colour pigment (CICP) but it is described as one in some cases.

Pigment type	Colour index	Comment
Bismuth vanadate	PY 184	Modified bismuth vanadates – cover colour space between green shade yellow and yellow shade orange
CICP	PY 53	Nickel antimony titanium yellow rutile (bright yellow)
CICP	PBr 24	Chrome titanate
CICP	PY 164	Titanium antimony manganese rutile
IRON OXIDE	PY 42, 43	Yellow iron oxides
IRON OXIDE	PR 101, 102	Red iron oxides

4.4.1 Formulation for opacity for exterior use

77. Any of the inorganic pigments listed above can be used in formulations for external use as they are light fast and weather resistant. The determining factor will be the desired shade of colour and chroma.

4.4.2 Formulation for opacity interior use

78. In terms of selection for interior applications, there is nothing to differentiate these inorganic pigments apart from the actual colour and chroma required.

4.5 Formulation for clean shades and opacity

79. There may be situations when the paint must have both a clean shade and good opacity. In this case, following approaches may be used:

a. Combine organic and inorganic pigments taking into account, weathering and chroma requirements (the formulation may already contain titanium dioxide so the focus would be on producing the correct shade via organic pigments

b. Use a hybrid pigment from the pigment manufacturer. This could be a pre-prepared blend of organic / inorganic pigments

NOTE: This approach does not necessarily allow the formulator any flexibility unless they can specify the pigment blend appropriate for the end use properties.

c. Use a ‘co-finished’ or ‘hybrid’ inorganic / organic pigment. This is a proprietary mixture from the pigment manufacturer. These pigments are made using a surface treatment process to coat the surface of the inorganic pigment with a layer of organic pigment. The organic – inorganic co-finished combination acts as one pigment.

80. It is reported that the co-finished inorganic / organic pigment has better overall performance than a physical blend of organic / inorganic pigment.

4.6 Reformulation overview

81. The reformulation options are summarised in the table below. NOTE: this is for guidance only.

Performance level	require color performance	Yellow	Orange	Red
Top Performance leveL out door , processing > 200C	chroma	Isoindolinone (ie PY 110)	Isoindolinone	Isoindolinone / Perylene / Quinacridone
	opacity	Bimuth Vanadate ie (PY184)	CICP (ie PO 82)	CICP
High Performance level Highest indoor selected out door , processing > 200C	chroma	Isoindolinone (ie PY 110)	Isoindolinone (ie PO 61)	Isoindolinone / Perylene / Quinacridone
		Diazo Condensation (PY95)		Diazo Condensation (PY95)
	opacity	Bimuth Vanadate ie (PY184)	CICP (ie PO 82)	CICP
		CICP (ie PY 53)		
Mid Performance level Indoor Processing > 200C	chroma	Azo Salt (ie PY62)	Azo Salt (ie PY 62)	Bona
		Isoindoline (ie PY139)	Benzymidazolone (ie PO 64)	Monazo
				Naphtol
	opacity	CICP (ie PY 53, PB24) and TiO2 (ie PW6)	CICP (ie PO 82) and TiO2 (ie PW6)	CICP and TiO2 (ie PW6)
Mid Performance level Indoor Processing < 200C	chroma	Diarylide* (ie PY13)	Diarylide* (ie PO34)	
	opacity	CICP (ie PY 53, PB24) and TiO2	CICP (ie PO 82) and TiO2	CICP and TiO2

4.7 Green Paints

82. The above advice above has concentrated on matching colours and opacity in paints containing PY 34 and PR 104. There may be situations where PY 34 has been used in combination with a blue pigment to produce a green paint. In this situation, the same advice for substitution applies – i.e. use the yellow organic pigments for bright shades and yellow inorganic pigments for opacity, if needed.

4.8 Potential problems on reformulation

83. Whilst reformulating to lead free pigmentation, some problems may be encountered, such as:
    - Difficulty in dispersing the organic pigment
    - Pigment flocculation due to the separation of the coloured pigments
    - Settling of the paint on storage

84. Organic pigments are known to be more difficult to disperse compared to inorganic pigments and it may be necessary to use a different dispersing agent or potentially different dispersion equipment.

85. As each formulation is unique, it is not possible to give specific technical advice in this report. Instead, it is recommended that the suppliers of dispersing agents are contacted for their advice.

86. In the situation where pigment dispersions or tints are bought in by the paint company, dispersion of the organic pigment is not an issue.

87. It is possible however, that problems such as flocculation might occur. Flocculation is the re-agglomeration of previously dispersed particles and this can affect the colour of the final paint film.

88. Pigment flocculation can be assessed by means of a ‘rub up’ test. In this test, the wet paint is applied to a substrate, usually a test card. The wet paint is then rubbed with a finger. If the pigment has flocculated, the rubbed area will show up as a different colour to the surrounding un-rubbed paint.

89. To help overcome this problem, suppliers provide ’universal‘ pigment dispersions or tints which are compatible with a broad range of resin systems. The paint manufacturer should confirm with the supplier that the dispersion is compatible with the resin system in use.

90. Storage stability of a new formulation should always be checked to ensure that any settlement that does occur is within acceptable limits and can be easily re-incorporated by stirring.

5 SELECTED INDUSTRY FEEDBACK

91. In the production of this report, a number of companies were contacted and several public domain documents reviewed. Below are some comments extracted from those sources. These were selected to demonstrate the broadly held industry view that lead pigment replacement is technically possible and that there are in principle, a number of ways in which the desired paint film properties can be achieved.

92. Please note that the most active companies in terms of published data in this area are based in Europe or the USA so information from Asian suppliers is somewhat limited.

5.1 Clariant Corporation

93. Clariant Corporation promote their '70 series' range of opaque and semi opaque pigments for use in formulating lead free paints.

Pigment name	Colour index	Comment
Hansa Brilliant yellow 2GX 70	PY 74	Arylide yellow, monoazo
Novoperm Yellow 5GD 71	PY 155	Benzimidazolone yellow
Hostaperm Yellow H4G 70	PY 151	Benzimidazolone yellow 4HG
Novoperm Yellow HR 70	PY 83	Diarylide yellow HR
Novoperm Yellow M2R 70	PY 139	Isoindoline Yellow
Novoperm Orange H5G 70	PO 62	Benzimidazolone Orange H5G
Novoperm Orange HL 70	PO 36	Benzimidazolone Orange HSL
Novoperm Orange HL 70-NF	PO 36	Benzimidazolone Orange HSL
Permanent Orange 2RLD 71	PO 74	Azo
Permanent Orange RL 70	PO 34	Pyrazolone Orange
Permanent Red FGR 70	PR 112	Naphthol Red AS-D
Novoperm Red HF3S 70	PR 188	Naphthol Scarlet Lake Monoazo;
Hostaperm Red D3G 70	PR 254	Pyrrole Red
Hostaperm Red D2G 70	PR 254	Pyrrole Red
Novoperm Red F3RK 70	PR 170	Naphthol Red AS

Novoperm Red RT-172-D	PR 170	Naphthol Red AS
Hostaperm Red E28 70	PV 19	Quinacridone Violet
Hansa Yellow G-IN	PY 1	Arylamide;
Hansa Brilliant Yellow 5GX-IN	PY 74	Monoazo; Arylide; Arylamide
Dalamar Yellow YT-800-D-IN	PY 65	Arylide; Arylamide
Hansa Sacarlet RNS	PR 3	Toluidine Red
Hansa Red 2B SPL	PR 3	Toluidine Red
Hansa Red 3B-IN	PR 3	Toluidine Red
Permanent Orange G-IN	PO 13	Benzidine Orange

94. It is worth noting that the majority of their recommended lead free alternatives are also available from most other suppliers.

5.2 Vibfast Pigments PVT LTD.

95. Vibfast, based in India, recommended as starting points, their PR 228 as scarlet chrome replacement for PR104 and PY 216 as a yellow chrome replacement.

96. They also manufacture many of the pigments recommended in the Clariant literature.

5.3 Pidilite Industries Ltd.

97. Pidilite are based in Mumbai and suggested their PY74, PY 83, P 34 (fast orange MRA and HPL) as appropriate starting point organic pigments for the substitution of lead pigments.

5.4 Heubach gmbh, Germany

98. Heubach have been at the forefront of lead pigment replacement. In their ‘Third party submission’ (Document 0012-01-0012-06 Pigment Mixtures, April 8th 2014), Heubach state that:

99. *'There is not a single alternative pigment existing to exactly replace a specific PY 34 or PR 104 pigment. The solution to reformulate lead-containing paints is the smart combination of suitable organic and inorganic pigments'*

100. The typical products typically used in combination are shown in the table below.

ORGANIC PIGMENTS	INORGANIC PIGMENTS
PY 74 Arylide yellow, monoazo	PW 6 Titanium dioxide
PY 83 Diarylide yellow HR	PY 53 Nickel Antimony Titanium Yellow Rutile
PY 139 Isoindoline Yellow	PBr 24 Chrome titanate
PY 151 Benzimidazolone yellow 4HG	PY 184 Bismuth Vanadate Yellow
PY 154 Benzimidazolone Yellow 154	
PR 112 Naphthol Red AS-D	
PR 254 Pyrrole Red	

5.5 BASF SE

101. As with Heubach, BASF, one of the largest global manufacturers of pigments, have stated that they will 'comply with the defined sunset date of 21st May 2015 for PY34 and PR104 worldwide by ceasing production and use'.

102. Within the same document they also state:

The available alternative pigments are able:

- To cover the entire colour space (from yellow, via orange to red)
- To supply clean colour shades
- To fulfill high opacity requirements by combining organic and inorganic pigments
- To cover different performance levels for interior and exterior use, very high light and weather resistance
- To give heat resistance >200°C
- To have no bleeding issues
- To fulfill technical requirements regarding coating manufacturing equipment.

There is no practical need for a single lead free pigment alternative which covers all of these technical properties in one. There are many alternatives available in the concerned shade areas (yellow, orange and red) but on different performance levels.
Paint manufacturer select the alternatives according to their end user demands and specifications.

103. It is clear therefore that in the view of BASF, there is no technical reason why lead chromates cannot be substituted by lead free alternatives.

5.6 Papertex Ltd

104. The following comments regarding lead pigment replacement have been taken from correspondence with Martin Unwin from Papertex (UK distributors of Aakash Chemicals range of pigments):

a. Monoazo and Disazo pigments are generally used in the architectural paint (indoor paint) and printing ink sector as their weather fastness is limited.

b. Azo condensation pigments have a somewhat higher fastness due to their constitution

c. Benzimidazolone yellows have a higher weather resistance than both the latter types.

d. Pigments of the DPP (Diketo Pyrrolopyrrone), perylene and quinacridone type (reds to violets) have outstanding fastness properties and are used in automotive applications.

e. Dioxazine (carbonyl) violet also has excellent fastness.

f. In general for the decorative market Azo pigments are used. These are usually colouristically bright in shade.

g. In terms of opacity of a paint, this depends on the strength and shade needed. If it is a pale to medium shade then the opacity of the organic pigment is not really an issue as the paint will have Titanium Dioxide (PW 6) as an opacifier and colour strength reducer. The opacity of Ti02 is much higher than any organic pigment due to its refractive index compared to the resin binder. However, if a strong shade is required there will be little or no Ti02.

h. In terms of lead replacement the standard yellow organic pigment has been Pigment Yellow 74 – of the 2GXS type (arylide yellow) - this is the nomenclature used by most manufacturers. PY 74 is manufactured with different particle size distributions – the 2GXS type has a wide particle size distribution giving rise to improved opacity.

i. Pigment Red 112 (Naphthol red AS-D) is widely used in decorative finishes is thought to be available in different opacity modifications.

j. For oranges, one option is to mix yellow and red pigmentation but this leads to duller shades. Pigment Orange 36 (Benzimidazolone Orange SL) or 5 (Hansa Orange RN) can be used for brighter oranges – PO 5 being the brightest. Alternatively PO 62 (Benzimidazolone) can be used if higher light fastness is desired.

k. The alternative for lead replacement could be other inorganic pigments such as Iron Oxides for yellows, reds and browns (PY 42, 43, PR 101, 102). These are, of course, much duller than organic pigments but depending on the shade, have excellent fastness properties.

5.7 RAL FORMULATIONS

105. A further illustration of the technical feasibility of replacing lead pigments is shown in the following RAL formulations provided by Bruschaler Farben and BAFS SE.

106. The RAL system is a coding system originally devised in Germany in the 1920's that allows for unique identification of a colour or tint. So for example, RAL 2004 is 'pure orange', RAL 5011 is referred to as 'steel blue'.

5.7.1 Lead Free RAL formulations provided by Bruchsaler Farben

107. A set of yellow, red and orange RAL formulations has been provided below by Bruchsaler Farben. It is for guidance only and testing will still be required to confirm performance. However, it helps to demonstrate how lead free alternatives can provide suitable colour matches.

108. Clarification of the pigments being used:

- Brufasol Yellow AL30: Bismuth vanadate grade.
- PY42: Iron Oxide - Yellow
- PY 83: Diarylide - Yellow
- PY101: bisazomethine
- PR177: Anthraquinone - Red
- PR254: Pyrrole - Red
- PG7: Phthalocyanine - Green
- PB15.3: Phthalocyanine - Blue
- PO34: Pyrazolone - Orange

Safinah

- RAL 1018 (E 27040)

Brufasol Yellow AL30	59.708
Titanium dioxide	38.800
P.Y. 83	1.194
P.Y. 101	0.298

- RAL 1021 (E 27021)

Brufasol Yellow AL30	63.290
P.Y. 42	18.987
P.Y. 83	2.532
P.Y. 101	10.126
P.B. 15.3	3.165
P.G.7	1.909

- RAL 1023 (E 27023)

Brufasol Yellow AL30	95.487
P.Y. 83	1.909
P.Y. 101	2.604

- RAL 2000 (E27111)

Brufasol Yellow AL30	62.651
P.R. 177	12.048
P.Y. 83	12.048
P.Y. 101	13.253

- RAL 2004 (E 27459)

Brufasol Yellow AL30	52.175
P.O 34	27.536
P.Y. 101	5.797
Titanium dioxide	14.492

- RAL 3000 (E 27521)

Brufasol Yellow AL30	24.795
P.R. 254	24.793
P.Y. 101	25.619
Titanium dioxide	14.049
Oxid red	10.744

5.7.2 RAL lead free formulation examples provided by BASF

109. The following RAL formulations have been provided by BASF. As can been seen, the formulations for the same colour devised by BASF and Bruchsaler Farben differ, showing that it is possible to create the same colour with different pigment combinations.

110. NOTE: An indication of relative costing has also been given below by BASF which shows that in one case it is possible to arrive at a cheaper m^2 cost. This should be treated with caution as the purchase price of pigments will vary according to geographic location, volume and commercial considerations between supplier and customer.

Pigments used in formulations
PY 151 – Benzimidazolone yellow 4HG
PY 34 – Lead sulphochromate
PBr 24 – Chrome titanate
PY 139 – Isoindoline yellow
PY 53 - Nickel Antimony Titanium Yellow Rutile
PR 104 – Lead chromate molybdate sulphate
PR 254 – Pyrrole red
PR 112 – Naphthol Red AS-D
PR 101 – Red iron oxide

111. Lead containing and lead free formulations for RAL 1021

Pigment number	Lead containing formulation (%w/w)	Lead free formulation (%w/w)
PY 151		81.5
PY 34	85.8	
PBr 24	11.0	17.7
PY 139	0.8	0.8

112. Relative costs of lead based formulation €0.35/m^2, lead free formulation €0.71/m^2

113. Lead containing and lead free formulations for RAL 3000

Pigment number	Lead containing formulation (%w/w)	Lead free formulation (%w/w)
PY 53	21.5	61.1
PR 104	63.3	
PR 254		27.3
PR 122	8.0	
PR 101	7.2	11.6

114. Relative costs of lead based formulation €0.31/m^2, lead free formulation €0.20/m^2

5.8 White Lead as an extender pigment

115. Extender pigments are incorporated into the paint formulation in order for a number of reasons, both technical and economic.

116. In addition to cost reduction, they can enhance the following properties of the paint film:

- Durability
- Rheology
- Improved application properties
- Improved physical properties (abrasion resistance, impact resistance..)
- Gloss reduction

117. Most extenders appear white as their refractive index is similar to commonly used binders. Most of the extenders occur naturally and others are produced synthetically.

118. White lead (Pb(OH)2.PbCO3,), CI number PW 1, has been used as an extender in the past but has largely been replaced by titanium dioxide (PW 6).

119. Any substitution of white lead by titanium dioxide should be carried out by replacing on a volume for volume basis in the dry film, in the first instance. As the opacity of titanium oxide is superior to that of white lead, lower levels will most likely give the desired result.

120. As a lead containing extender, white lead acts as a through drier in alkyd paints. Removal will necessitate adjustment of the drier package by replacement with strontium or zirconium driers.

6 SUMMARY AND CONCLUSIONS

121. There are no 1:1 alternatives for PY 34 (lead sulphochromate yellow) or PR 104 (lead chromate molybdate sulphate red).

122. Lead chromate pigments have been used because of their attractive cost performance benefits. However, most of the applications where lead chromates are used do not utilise all of the performance attributes of the pigment.

123. As a result, it is not necessary to have a 1:1 replacement as the desired performance attributes can be achieved by means of combinations of suitable inorganic and organic pigments.

124. As each formulation is unique and will often contain other pigments, it is not possible to be precise about the blends of replacement pigments.

125. Instead, the following general approach should be followed:

a. Define precisely the performance requirements of the paint. For example, colour, durability/light fastness (interior or exterior end use), opacity, chemical resistance, etc.

b. For clean shades formulate with organic yellow, orange and red pigments

c. For opacity, formulate with inorganic pigments (CICP, bismuth vanadate, iron oxides)

d. For opacity and clean shades formulate with a mixture of organic and inorganic pigments

126. The colour of the lead chromate containing formulation should be measured ideally instrumentally. This will then enable a closer match to the colour when using the alternative pigmentation.

127. In a co-grind formulation, it is suggested that the lead containing pigments are replaced on a volume basis in the dry film by the lead free alternatives.

128. Where tinting systems are used, the paint manufacturer should work closely with their supplier to ensure that the lead free tints supplied are capable of producing the colour and performance attributes required.

129. A suggested starting point for replacement of PY34 (Lead sulphochromate) is PY74 (Hansa Yellow, arylide yellow, monoazo yellow, CAS number 2512-29-0). Initial replacements should be carried out on a volume for volume basis.

130. A suggested starting point for replacement of PR104 (lead chromate molybdate sulphate) is PR112 (CAS Number 6535-46-2, IUPAC Name 3-hydroxy-N-(2-methylphenyl)-4-[(2,4,5-trichlorophenyl) diazenyl]-2-naphthamide).

131. Orange colours can be made by mixing red and yellow formulations based on PY74 and PR112.

132. For orange formulations with brighter shades, suggested starting point pigments are PO36 (benzimidazolone orange, CAS number 12236-62-3) and PO5 (dinitroaniline, CAS number 3468-63-1).

133. For orange shades with better light fastness, a suggested starting point is PO62 (benzimidazolone orange CAS number 52846-56-7).

134. In formulations that contain titanium dioxide along with a lead containing pigment, it may well be that the main opacifying pigment is titanium dioxide and not the lead pigment. In that instance, the emphasis would be on achieving the desired shade by adjusting the organic pigment. The pigments listed in Clariant's '70 Series' (or equivalents from other suppliers) would be good starting points for reformulation.

135. Where lead compounds have been the main opacifying pigment, then reformulation would likely entail the use of both inorganic and organic pigments to meet the required opacity and shade requirements.

136. Where white lead is used in a formulation, this should be replaced initially on a volume basis in the dry film by titanium dioxide.

7 RAW MATERIAL MANUFACTURERS

137. A non-exhaustive list of pigment manufacturers is shown below:

VIBFAST PIGMENTS PVT. LTD./ VIBFAST PIGMENTS (100% EXPORT ORIENTED UNIT)
(A GOVERNMENT OF INDIA RECOGNIZED EXPORT HOUSE)
C-1,91/6,G.I.D.C. ,Behind Bank of India
Phase - I ,VATWA
AHMEDABAD, GUJARAT
INDIA
PHONE :+91 79 25830667/32920774
FAX : +91 79 25893014
MOB : +919099948515
URL : www.vibfast.com
EMAIL : int.mkt@vibfast.com

Pidilite Industries Ltd.
Industrial Products Division, Pigment Department,
2nd Floor, Marketing Building
Ramkrishna Mandir Road, Andheri (E)
Mumbai 400059
Tel: +91-22 2835 7000/7516
Web: www.Pidilite.com

Sudarshan Chemical Industries Ltd.
162 Wellesley Road,
Pune - 411 001.
India.
Tel: 91-20 - 26058888 / 26058046 / 26226200.
Fax: 91-20 - 26058222.
CIN: L24119PN1951PLC008409

Vijay Chemical Industries
Plot No. R-422, MIDC,
Thane - Belapur Road,
Rabale, Navi Mumbai - 400701.
India.
Contact : 91-22-2769 1192/3408
Fax : 91-22-2764 1803
http://vijaychemical.com/Contact_Us

Kolorjet Chemicals Pvt Ltd.
Contact Person :
Bharat Mehta (Manager)
B / 5, Rajratna Industrial Estate,
Liberty Garden Road, Malad West
Mumbai (India) – 400064
+(91) - (22) – 28826803

Clariant Chemicals (India) ltd.
Kolshet Road
Sandoz Baug
Thane – 400 607
Tel: +91-22 25315211
Web: www.PIGMENTS.CLARIANT.COM
Web: www.CLARIANT.IN

Registered office for BASF Group Companies in India
BASF India Limited
1 st Floor, VIBGYOR Towers,
Plot No. C - 62, 'G' Block,
Bandra-Kurla Complex, Mumbai - 400 051
Phone: +91 22 6661 8000
Fax: +91 22 6758 2753

BASF
100 Park Avenue
Florham Park,
NJ 07932
USA
Tel: +1 973 245-6000

Bruchsaler Farbenfabrik GmbH & Co. KG
Talstraße 37
D-76646 Bruchsal (Germany)
Tel.: +49 7251 9754-0
Fax: +49 7251 15953
Web: www.bruchsaler-farben.de
Email: dyckerhoff@bruchsaler-farben.de

Heubach GmbH

Heubachstraße 7,
38685 Langelsheim,
Germany
Tel: +49 (0) 5326 520
Web: *www.heubachcolor.de*

Chromaflo Technologies Europe B.V
Nusterweg 98
6136 KV Sittard
Netherlands
Tel: +31 (0) 46 4570100
Web: www.chromaflo.com

Huntsman Pigments (UK) Limited – (formerly Rockwood pigment)
Liverpool Road East
Kidsgrove, Stoke-on-Trent
Staffordshire, ST7 3AA
United Kingdom
Tel.: +44 (0)1782 794400
Fax: +44 (0)1782 787338
e-mail: color_uk@huntsman.com
Web: www.**huntsman**.com/**pigments**/

NUBIOLA Group
Gran Via de les Corts Catalanes, 648, 1º
08010 Barcelona
Spain
Tel. +34 (0) 933 435 750
Fax. +34 (0) 933 435 783
Mobile +34 (0) 666 569 765
Web: www.nubiola.com

Papertex
The Rectory,
Burnsall,
BD23 6BP,
United Kingdom.
Tel: +44 (0)1756 649033
Email:munwin@papertex.co.uk
Web: www.papertex.co.uk

Ferro Global Headquarters
6060 Parkland Blvd.
Suite 250
Mayfield Heights, OH 44124
USA
Tel: (216) 875-5600
Web: www.ferro.com

The Shepherd Colour Company
4539 Dues Drive
Cincinnati, OH 45246
USA
Tel: 513-874-0714
Fax: 513-874-5061
Email: MRyan@shepherdcolor.com
Web: http://www.shepherdcolor.com/

Aakash Chemicals
561 Mitchell Road
Glendale Heights, IL
60139 USA
Tel: (630)-469-3838
info@aakashchemicals.com

138. A non-exhaustive list of dispersing agent manufacturers is given below:

Evonik Industries AG
Rellinghauser Straße 1—11
45128 Essen
Germany

+49 201 177-01
+49 201 177-3475
info@evonik.com

BYK-Gardner GmbH

Lausitzer Strasse 8
82538 Geretsried
Germany

Tel +49 8171 3493-0
Fax +49 8171 3493-140

info.BYK.Gardner@altana.com
www.byk.com

7.1 Search Engine

139. In order to find and contact suitable pigment or drier manufacturer, the following website may be used: www.ulprospector.com/

140. Colour Index of all pigments can be found at :

http://www.artiscreation.com/

8 RELEVANT DOCUMENTS

141. BASF SE: Third Party Submission of Information on Alternatives for Applications for Authorisation:
Substance Lead sulfochromate yellow (C.I. Pigment Yellow 34)
Lead Chromate molybdate sulphate red (C.I. Pegment Red 104)
(Consultation number :0012-01 to 0012-06 (Mixtures of organic and inorganic pigments)
08-04-2014

http://echa.europa.eu/documents/10162/18074545/a4a_comment_385_1_attachment_en.pdf

142. BASF SE: Third Party Submission of Information on Alternatives for Applications for Authorisation:
Substance Lead sulfochromate yellow (C.I. Pigment Yellow 34)
Lead Chromate molybdate sulphate red (C.I. Pegment Red 104)
(Consultation number :0012-07 to 0012-12 (Mixtures of organic and inorganic pigments)
08-04-2014

http://echa.europa.eu/documents/10162/18074545/a4a_comment_371_1_attachment_en.pdf

143. Heubach GmbH: Third Party Submission of information on alternatives for applications for authorisation
[0012-01 – 0012-06] [pigment mixtures] [April 8th, 2014]

http://echa.europa.eu/documents/10162/18074545/a4a_comment_392_1_attachment_en.pdf

144. Heubach GmbH: Third Party Submission of information on alternatives for applications for authorisation
[0012-07 – 0012-10] [pigment mixtures] [April 8th, 2014]

http://echa.europa.eu/documents/10162/18074545/a4a_comment_397_1_attachment_en.pdf

145. VdMi-Comment on evaluation of alternatives
0012-01 to 0012-12 2014-April-08

http://echa.europa.eu/documents/10162/18074545/a4a_comment_465_1_attachment_en.pdf

146. DCC Maastricht B.V. OR (only representative)
C.I. Pigment Yellow 34 (PY34) and C.I. Pigment Red 104 (PR104)
Industrial application of coatings containing C.I. Pigment Yellow 34 and C.I. Pigment Red 104 on metal surfaces of non-consumer items

http://echa.europa.eu/documents/10162/82332401-05e0-4125-a302-2db2c8e969ee

147. Technical Paper: Lead Chromate Replacement, Dr Jurgen Ott, Heubach GmbH, European Coatings Journal March 2015

148. Technical Paper: Lead is Dead, Mark Ryan, TheShepherd Color Co., European Coatings Journal March 2013

http://www.shepherdcolor.com/Blog/Lead%20is%20Dead%20ECJ_2013_03.pdf

149. BASF – Handbook on basic of coating Technology by Goldschmidt.

150. Protective Coatings – fundamental of chemistry and composition by Clive H. Hare.