Integrated Colour Solutions

Dominion Colour Corporation

Working Together for Quality®

ISO 9001
ISO 14001

PCB’s and their Inadvertent Presence in Pigments

Mark Vincent

Agenda

- Who is DCC?
- Yellow Pigments used in Roadmarking
  - Technical requirements
  - Pigments used
  - History of pigments used – why?
  - Technical comparison of pigments used
- Pigments used in printing inks
- PCBs and their inadvertent presence in Pigments
- Options to reduce PCB content
- Conclusions

Who is DCC?

- Canadian based manufacturer of Coloured Pigments
- Manufacturing since 1946
- What we make:
  - Inorganic pigments
    - Used in the coatings and plastics markets, including traffic marking
    - Bismuth Vanadate – Pigment Yellow 184 (PY.184)
    - Lead Chromate based oranges and yellows – PY.34 and PR.104
  - Organic pigments
    - Broad range for the inks, coatings and plastics markets, including traffic marking

Yellow Pigments used in Roadmarking:

1. Technical requirements
2. Pigments used
3. History of pigments used – why?
4. Technical comparison of pigments used

Yellow Pigments used in Roadmarking

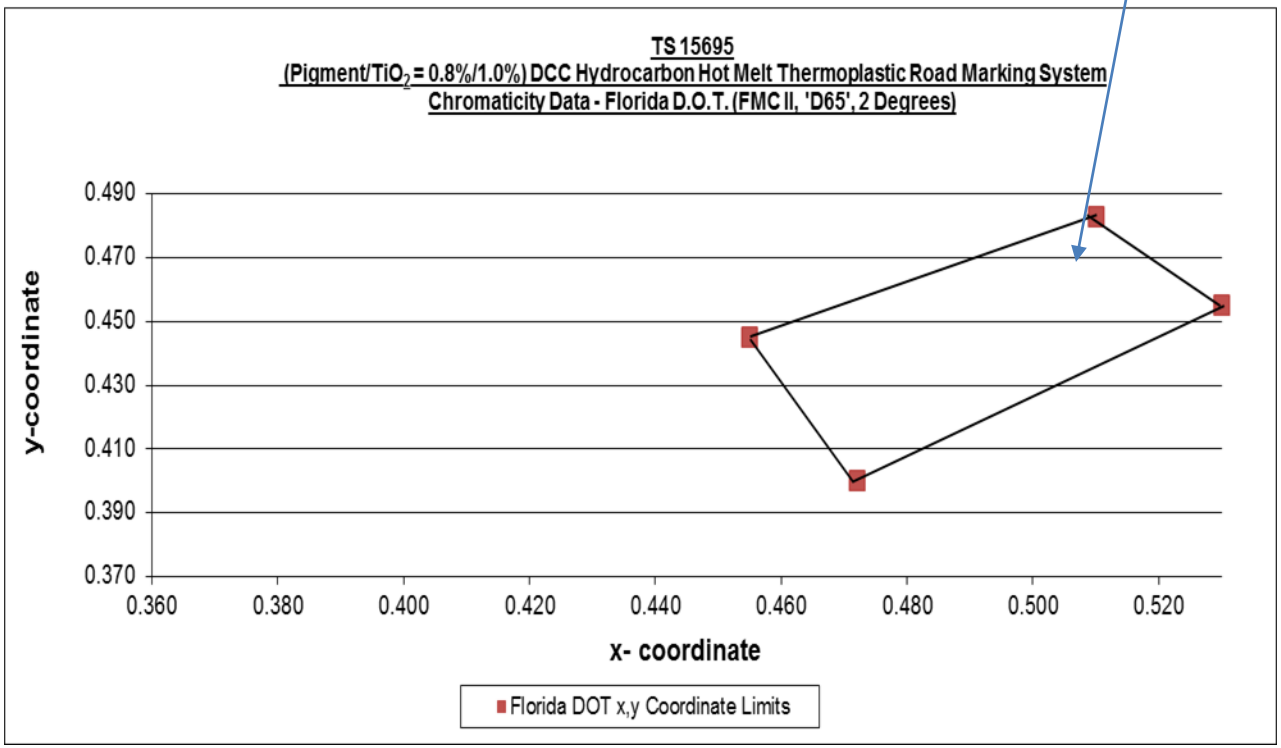
Technical Requirements

- The pigments used are selected due to the following "main" criteria:
  1. Which one fits into the strictly controlled color box
     - Dictated by the state/municipality
     - Almost all color boxes created by the state/municipality means that a "red shade yellow" is required
  2. Weatherfastness/durability
  3. Opacity/hiding
  3. Heat stability (for thermoplastic systems)
  3. Solvent resistance (for solvent based systems)

Yellow Pigments used in Roadmarking

- A colour box:

Colour must be inside box and stay inside after durability tests



Yellow Pigments used in Roadmarking

Pigments currently used

- Almost ALL pigments used in roadmarking are “red shade yellows” – dictated by the colour box
- The three main pigments used in roadmarking:
  - Lead chromate based pigments, PY.34, which has been phased out over the past decade
  - Pigment Yellow 83 (PY.83) for thermoplastic (and some solvent based)
  - Pigment Yellow 65 (PY.65) for waterbased (and some solvent based)
- Secondary pigments used are:
  - Pigment Yellow 74 for waterbased (and some solvent based)
  - Pigment Yellow 75 for waterbased (and some solvent based)

Yellow Pigments used in Roadmarking

History of pigments used and why?

- Historically the colour pigments used in roadmarking were based on lead chromate pigments (PY.34).
- All the technical specifications for roadmarking were written using PY.34 as the major pigment
- PY.34 is excellent technically in terms of:
  - Shade – fits into the colour box
  - Opacity
  - Night time reflectivity
  - Weatherfastness – colour does not fade
  - Heat stability – can be used in thermoplastic systems
  - Solvent resistance – can be used in solvent based systems
- When the USA states went to lead free systems the lead free alternatives have compromises in technical performance:
  - Difficulty in fitting the colour box
  - Less opaque/More transparent
  - Lack of night time reflectivity
  - Lower weatherfastness
  - Lower heat stability (some times)
  - Lower solvent resistance
- End result is very few lead free alternatives do not meet ALL the technical requirements – compromises are needed….

Yellow Pigments used in Roadmarking

Technical Comparison of Pigments used

Pigment	System Used in			Fits Colour Box	Durability	Opacity	Heat Stability	Solvent resistance
	Thermo	Water	Solvent					
PY.34	Yes	Yes	Yes	Yes	Excellent	Excellent	Excellent	Excellent
PY.74	No	Yes	Can do	Yes/No	Average	Average	Poor	Poor
PY.65	No	Yes	Can do	Yes	Average	Average	Poor	Poor
PY.75	No	Yes	Can do	Yes	Average	Average	Poor	Poor
PY.83	Yes	Yes	Yes	Yes	Above average	Above average	200C	Excellent

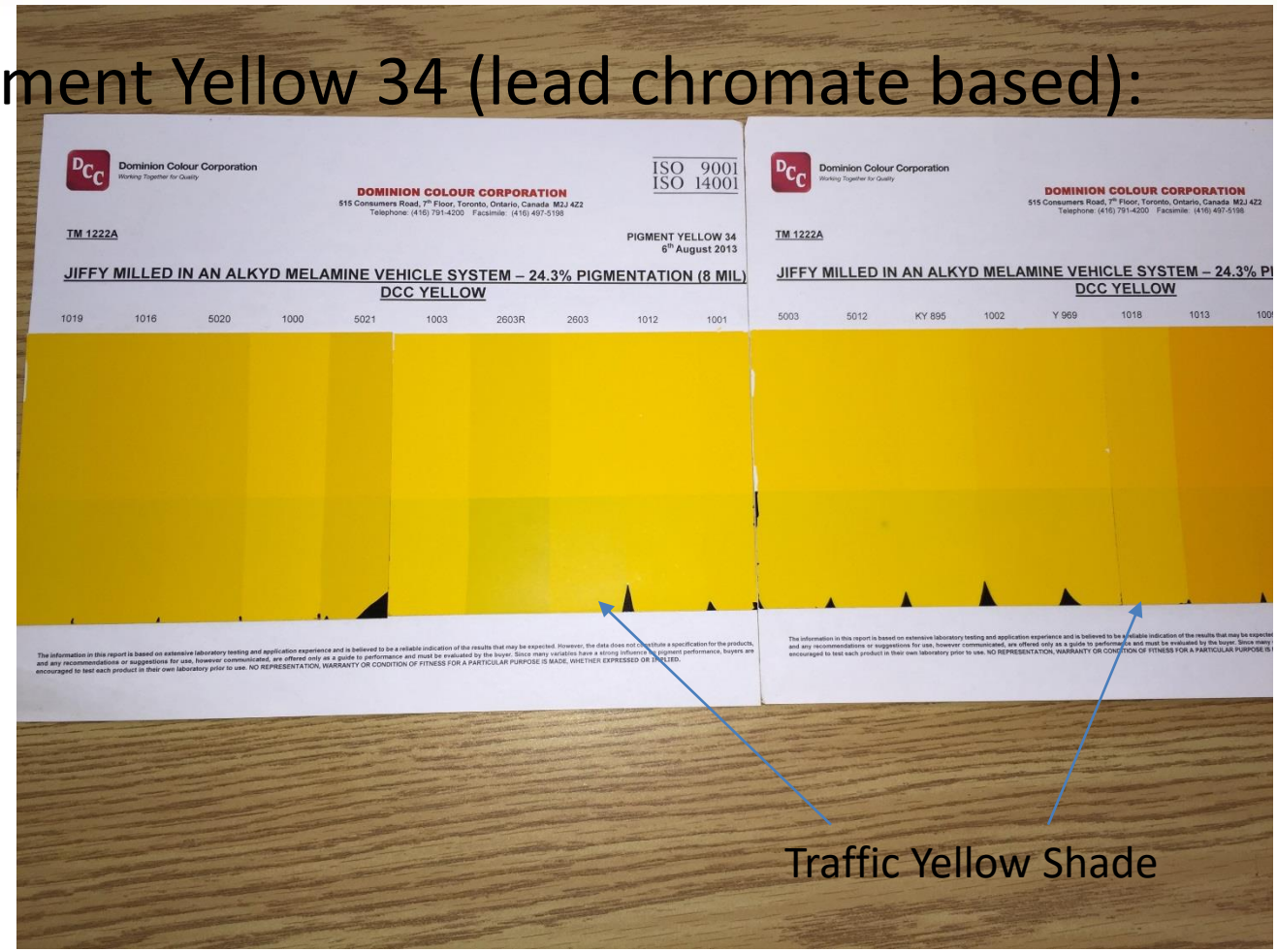
- Note:
  - All of the alternatives to PY.34 have lower technical performance
  - Selecting pigments able to meet the State specifications is very difficult

Shades of Yellow Pigments used in Roadmarking

- Pigment Yellow 34 (lead chromate based):

Shades of Yellow Pigments used in Roadmarking

- Pigment Yellow 34 (lead chromate based):



Shades of Yellow Pigments used in Roadmarking

- Organic Pigments:

Water/solvent based systems – PY.65, PY.74, PY.75, PY.83
Thermoplastic systems – PY.83

Green Shade

Red Shade

PY.74

PY.83

PY.65

PY.75

Note – the pigments are mostly "red shade"

Pigments Used in Printing Inks

Pigments Used in Printing Inks

- Printing inks split into three main areas:
  - Oil based inks
  - Solvent based inks
  - Waterbased inks
- Primary process colours used are:
  - Black, Blue, Yellow, Red
- Seconary colours:
  - Green, Orange, Violet etc
- Not all pigments used for waterbased can be used in solvent based/coil based inks and vice versa

Pigments Used in Printing Inks

- Main process colour pigments are:
  - Blacks – carbon black (PBl.7)
    - PCB content? Need to discuss with suppliers
  - Blue – copper phthalocyanine blue (PB.15:3)
  - Yellow – diarylide yellows (PY.14, PY.83)
  - Reds – metal azo reds (PR.57:1)
- Examples of secondary colours are:
  - Green – copper phthalocyanine green (PG.7)
  - Orange – diarylide orange (PO.13)
  - Violets – carbazole violet (PV.23)

PCB’s and their inadvertent presence in Pigments

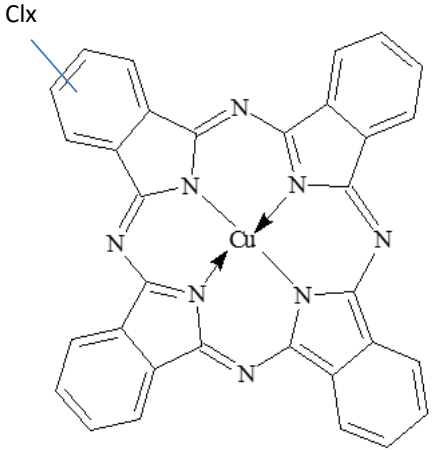
1. Blue and green
2. Diarylide pigments
    a. PCB generation in diarylide pigments (PY.83)
3. Metal azo red pigments

PCB's and their inadvertent presence in Pigments

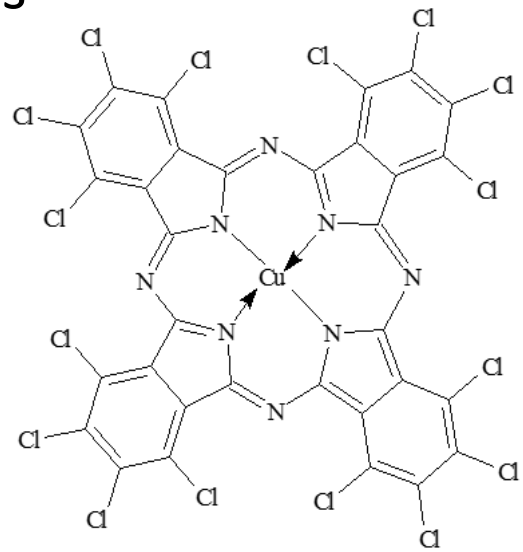
- PCB's are generated as un-intentional by-products in pigments as a result of:
  - Containing chlorine and/or
  - Being process in chlorine based solvents (e.g. dichlorobenzene)
- PCB 11 is one possible PCB in pigments
- PCB 11 is mostly an un-intentional by-product in the synthesis of diarylide yellow and orange pigments:
  - PY.13, PY.14, PY.17, PY.83, PO.13 and PO.34
- PCB 11 is found in PY.83 which is commonly used in roadmarking

Blues and Greens

- Copper Phthalocyanine is the dominant chemistry in printing inks for blue and green colours



Pigment Blue 15



Pigment Green 7

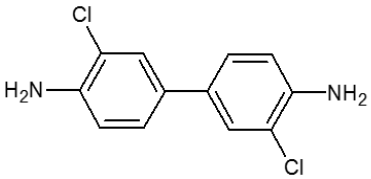
- PB.15:3 contains up to 3 Cl atoms depending on product
- PCB content can vary with manufacturer
- Typical DCC test result for PG.7 = 0.118ppm PCB

Diarylide Yellows and Oranges

- Diarylide yellows and oranges are the dominant pigments used in:
  - Printing inks (PY.14 and PY.83)
  - Thermoplastic traffic roadmarking (PY.83)

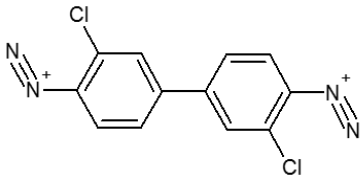
PCB's and their inadvertent presence in Diarylide Pigments

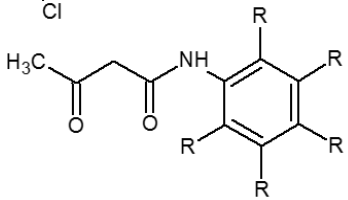
- Chemical Structure of Diarylide Pigments/PY.83



3,3'-Dichloro benzidine

NaNo2
HCl

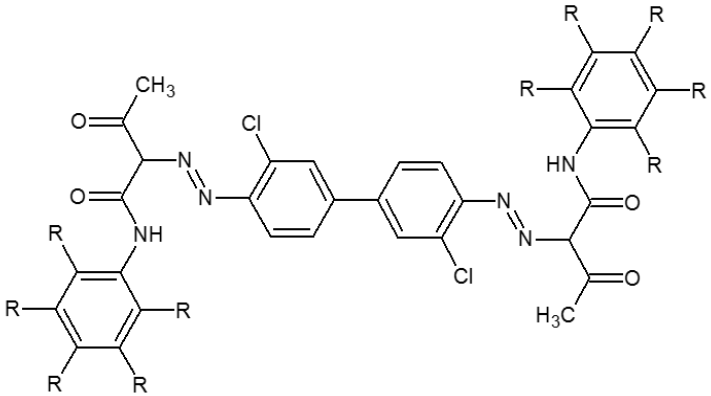




Substituted acetoacet-acetanilde

PY.13 – AAMX
PY.14 – AAOT
PY.17 – AAOA
PY.83 - AADMCA

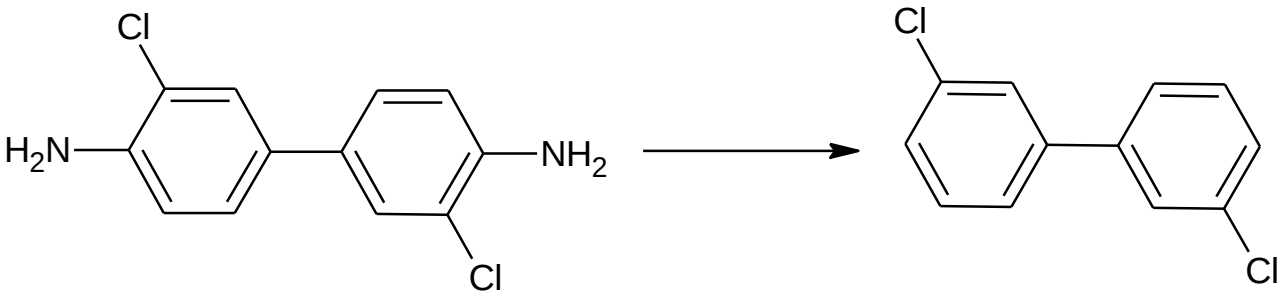
Pigment Yellow 13
Pigment Yellow 14
Pigment Yellow 17
Pigment Yellow 83



Pigment

PCB's and their inadvertent presence in Diarylide Pigments

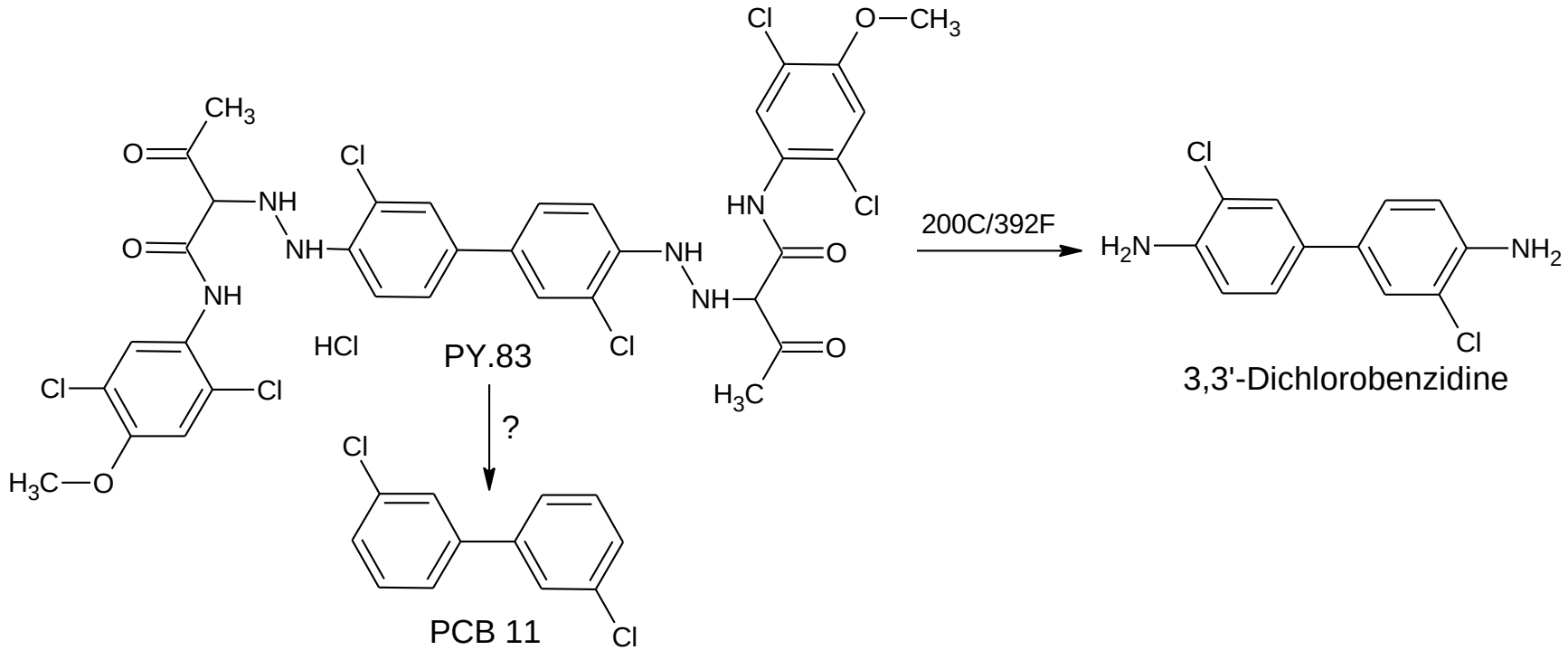
- Formation of PCB 11 in synthesis of Diarylide Pigments/PY.83
- Occurs during "diazotization" stage
  - Starting material 3,3'dichlorobenzidine (a suspect human carcinogen) breaks down to PCB 11
  - PCB 11 is retained in the final pigment



3,3'-Dichlorobenzidine PCB 11

PCB's and their inadvertent presence in Diarylide Pigments

- Other concerns regarding Diarylide Pigments/PY.83:
  - Heating >200C (392F) causes breakdown to the suspect human carcinogen 3,3' dichlorobenzidine
  - Unknown if PCB 11 can be formed at this stage?



PCB's and their inadvertent presence in Diarylide Pigments

- Typical PCB content in diarylide pigments:

Colour Index Number	Total PCB Content (ppm)	Total PCB 11 Content (ppm)
PY.13	3.8	3.6
PY.14	1.5	1.5
PY.17	1.9	1.7
PY.83	5.0	4.5
PY.83	1.2	1.2
PY.83	5.3	5.2
PY.83	2.7	2.6
PO.13	5.6	4.4
PO.34	4.2	3.7

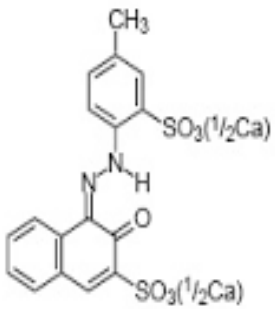
- Note in USA – 40 CFR 761 is the specific regulation that relates to PCB content in pigments. It regulates an average annual concentration of 25ppm with a maximum content of <50ppm

Diarylide Yellows and Oranges

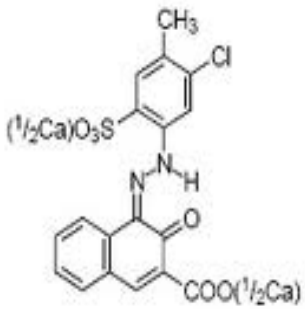
- In Germany it is being proposed that diarylide pigments be given a “water hazard” classification
  - Known as a WGK classification
  - WGK 3: severe hazard to waters
- This is due to their “possible carcinogenic potential”
- Note – diarylide pigments are not carcinogenic but it is likely the trace DCB content or “breakdown DCB” that is causing the concern
- Unknown at this time the outcome of this proposal

Metal Azo Red Pigments

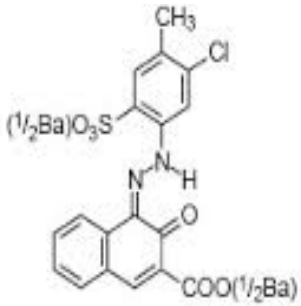
- Metal azo red pigments are the major red pigment used in printing inks
- Pigment Red 57:1 is the dominant pigment
- PR. 48:2 and PR.48:1 are the next largest in this class
- Typical PCB content ranges from 0.050 to 0.150ppm



PR.57:1



PR.48:2



PR.48:1

Options to reduce PCB levels

Options to reduce PCB levels

- It is not possible to completely eliminate PCB's
  - Base levels for "non-PCB expecting pigments" are 0.050 to 0.150ppm
- It is possible to reduce the PCB content on in the end use but certain changes are required:
- In roadmarking three main options:
  1. Enact regulations to try and reduce PCB content in diarylide pigments for roadmarking
  2. Ban diarylides and reduce the weatherfastness requirements for roadmarking paint
  3. Ban diarylides and change the colour box to allow for greater selection of pigments

Options to reduce PCB levels in Roadmarking

1. Enact regulations to try and reduce PCB content in PY.83 for roadmarking
   a. Pros:
      i. Pigment currently known and used
      ii. Acceptable durability
      iii. Pigment fits the current technical requirements – durability, solvent resistance etc
   b. Cons:
      i. Technology to reduce PCB content currently unknown
      ii. No certainty that PCB content can be reduced
      iii. Logistically almost impossible to evaluate PCB content in every production lot (takes 3-4 weeks)
      iv. How to Police and control PCB content in every production lot used?

Options to reduce PCB levels in Roadmarking

2. Ban diarylides and reduce the weatherfastness requirements for roadmarking paint
   a. Pros:
      i. Expands the pigment selection possibilities in the red shade yellow area – e.g. PY.183 and PY.191 can then be used
      ii. Allows for the selection of pigments with lower PCB content
      iii. Maintains similar cost position
   b. Cons:
      i. Is lower weatherfastness an option? Are roadmarking paints over engineered?
      ii. Needs time to assess

Options to reduce PCB levels in Roadmarking

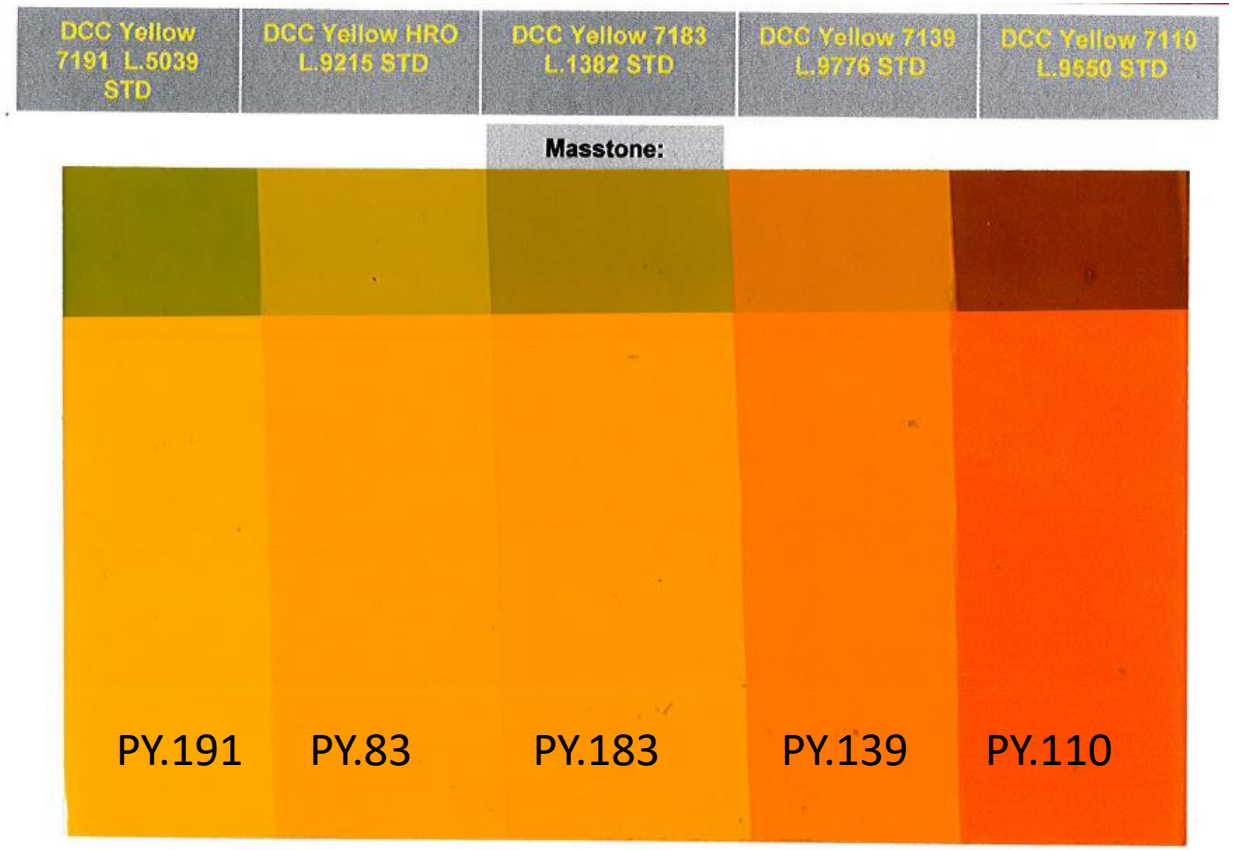
2. Ban diarylides and reduce the weatherfastness requirements for roadmarking paint.
   a. Options – PY.183/PY.191:

Pigment	System Could be used in			Fits Colour Box	Durability	Opacity	Heat Stability	Solvent resistance	PCB Content (PPM)
	Thermo	Water	Solvent						
PY.34	Yes	Yes	Yes	Yes	E	E	E	E	-
PY.83	Yes	Yes	Yes	Yes	Above average	Above average	200C	E	1-5
PY.183	Yes	Yes	Yes	Yes	Poor to average	Average	E	E	0.33
PY.191	Yes	Yes	Yes	Yes	Poor to average	Average	E	E	0.16

E = Excellent

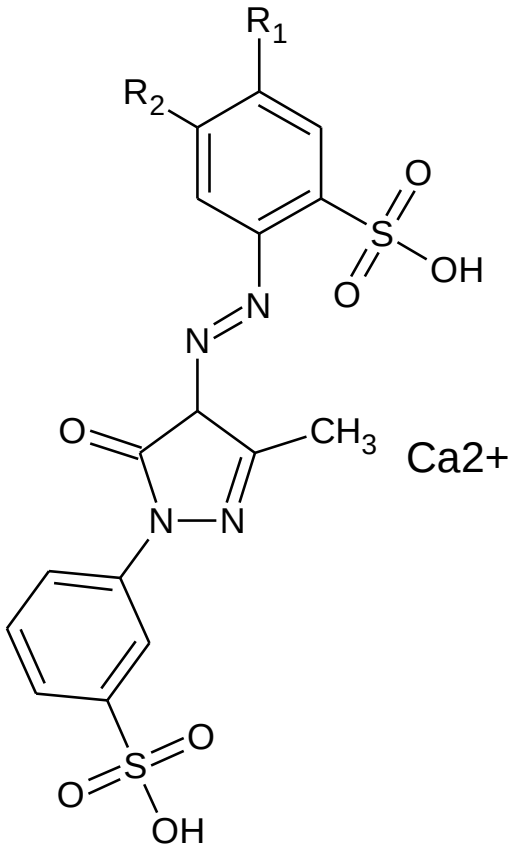
Options to reduce PCB levels in Roadmarking

2. Shade of PY.183/PY.191



Options to reduce PCB levels in Roadmarking

2. Chemical Structure of PY.183/PY.191



PY.183 – R1 = Cl, R2 = Cl

PY.191 – R1 = CH_3, R2 = Cl

Options to reduce PCB levels in Roadmarking

3. Ban diarylides and change the colour box to allow for greater selection of pigments
   a. Pros:
      i. Number of pigments to choose from expands significantly
      ii. Durability levels could be maintained
      iii. Cost position slightly higher but not massively
      iv. Allows for the selection of pigments with lower PCB content
   b. Cons:
      i. Regulatory changes needed
      ii. How easy or difficult is it to change the colour box?

Options to reduce PCB levels in Roadmarking

3. Options – examples include
   a. PY.151 shaded with PO.36
   b. PY.151 shaded with PY.110
   c. PY.154 shaded with PO.36 or PY.110
   d. PY.194 shaded with PO.36 or PY.110
   e. Bismuth Vanadate shade with PO.36 or PY.110
   f. Others…

Shades of Yellow Pigments used in Roadmarking

3. Possible options if colour box changed:
   1. PY.151 shaded with orange or PY.110
   2. PY.154 shaded with orange or PY.110
   3. PY.194 shaded with orange or PY.110
   4. And others

Green Shade

Red Shade

PY.151 PY.194 PY.74 PY.154 PY.83 PY.65 PY.110

PY.75

Options to reduce PCB levels in Roadmarking

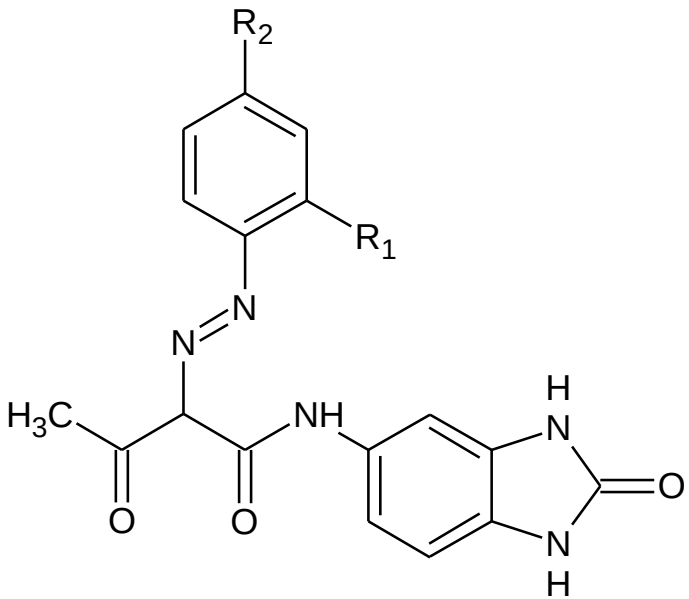
3. Options

E = Excellent

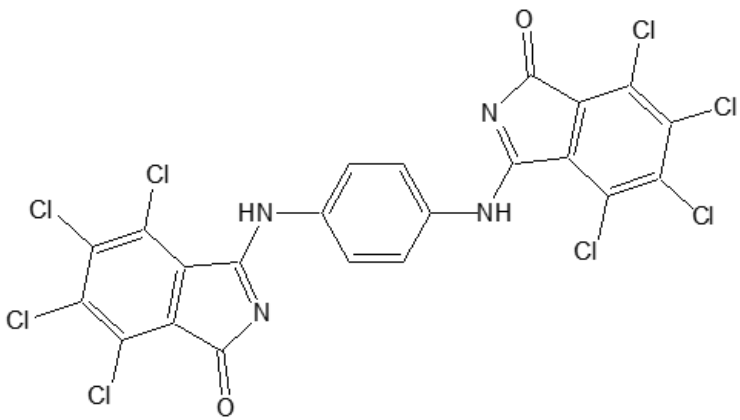
Pigment	System Could be used in			Fits Colour Box	Durability	Opacity	Heat Stability	Solvent resistance	PCB Content (PPM)
	Therm o	Water	Solvent						
PY.34	Yes	Yes	Yes	Yes	E	E	E	E	-
PY.83	Yes	Yes	Yes	Yes	Above average	Above average	200C	E	1-5
BV	Yes	Yes	Yes	No	E	E	E	E	TBD
PY.110	Yes	Yes	Yes	No	E	Average	E	E	0.1
PY.151	Yes	Yes	Yes	No	E	Above average	E	E	0.1
PY.154	Yes	Yes	Yes	No	E	Average	E	E	TBD
PY.194	Yes	Yes	Yes	No	E	Average	E	E	TBD
PO.36	Yes	Yes	Yes	No	E	E	E	E	0.2

Options to reduce PCB levels in Roadmarking

3. Options – examples include



PY.151 – R1 = COOH, R2 = H
PY.154 – R1 – CF_3, R2 = H
PY.194 – R1 = OCH_3, R2 = H
PO.36 – R1 = NO_2, R2 = Cl



PY.110

Note – high Cl content but low PCB

Options to reduce PCB levels in Printing Inks

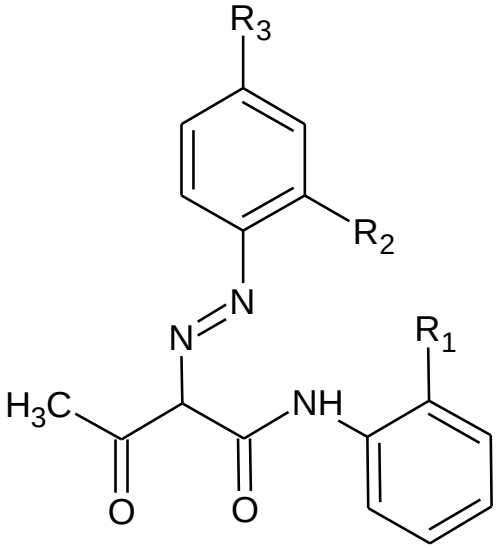
- In printing inks more research is required:
  - Are the PCBs from paper recycling coming from the pigments?
  - What is the impact of the recycling process/chemicals on the pigments:
    - Will the diarylide yellows/orange and the blue/green pigments degrade to PCB's under these conditions?
  - Are higher PCB containing blues and greens being used in printing inks?
    - As shown DCC's PG.7 contains 118ppb of PCB
    - So results show that low PCB containing blue and green is possible

Options to reduce PCB levels in Printing Inks

- Yellows in printing inks:
  - Replace PY.14 with PY.74 or PY.155
    - Both green shade yellows
    - Both already used in printing inks to some extent
    - No potential risk of breakdown to DCB or PCB
    - BUT higher cost structure
  - Typical PCB content:
    - PY.14 – 1.5ppm
    - PY.83 – 1.2 to 5.2ppm
    - PY.74 – 0.1ppm
    - PY.155 – <0.1ppm

PCB's and their inadvertent presence in Pigments

- Chemical Structure of PY.74



PY.74 – R1 = OCH_3, R2 = OCH_3, R3 = NO_2

Note:

1. No chlorine in the molecule
2. Small molecule leading to poor solvent and heat resistance
3. Cannot be used in thermoplastic systems and many solvent systems
4. Note no chlorine atoms in the molecule so PCB level expected
5. Issue not expected to be in water (and some solvent) based systems if PY.74 is used

Conclusions

Conclusions

1. PCB's are present in diarylide (PY.83) pigments
2. Diarylides are important pigments in roadmarking and printing inks
3. PY.83 is an important pigment in roadmarking
   a. Currently there are no real options to replace PY.83 unless:
      a. Durability requirements are changed or
      b. Colour box is changed
4. In printing inks:
   a. Research needed to assess impact of recycling process on blue, green and diarylides
      a. Chemical breakdown occurring?
   b. Potential to replace diarylides yellows with PY.74, PY.155 however cost structure will increase

Dominion Colour Corporation

Working Together for Quality