The Chemistry of Color Pigments used in Manufacturing Printing Inks

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Color Pigments
Manufacturers Association

Definition of Color Pigments

- Pigments are colored, black, white or fluorescent particulate organic or inorganic solids which usually are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated.
- Pigments alter appearance by selective absorption and/or by scattering of light.
- Pigments are usually dispersed in vehicles or substrates for application, as for instance in the manufacture or inks, paints, plastics or other polymeric materials.
- Pigments retain a crystal or particulate structure throughout the coloration process.

(Safe Handling of Color Pigments, Color Pigments Manufacturers Association Inc., First Edition, 1993)

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Pigments Used in 4-Color Printing

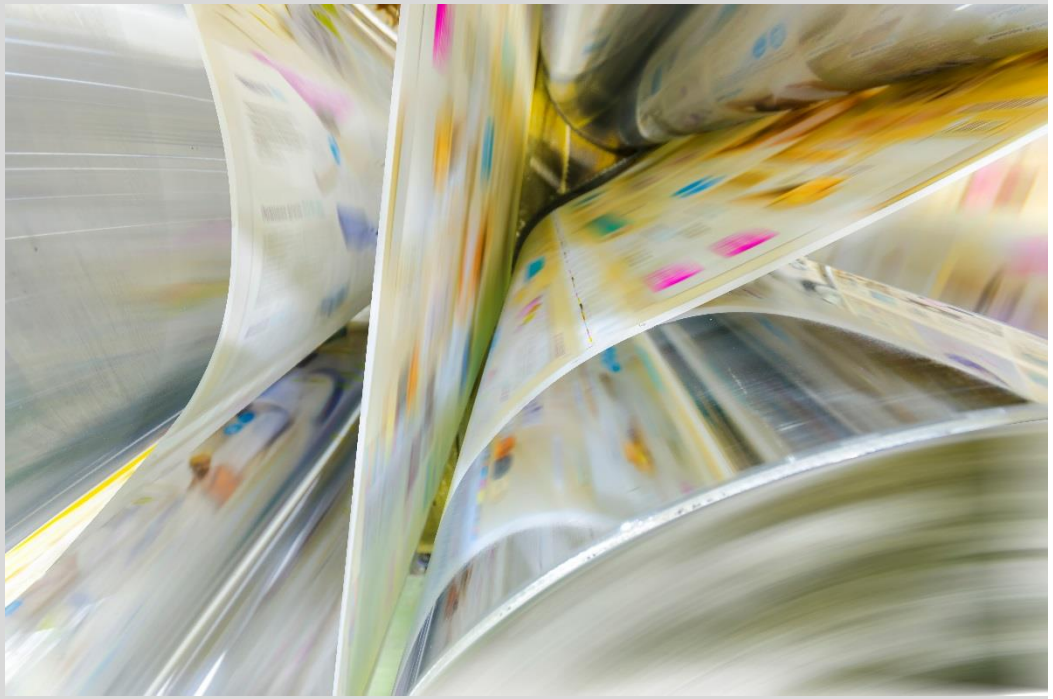
- Black (carbon black)

- Diarylide Yellow

(CI Pigment Yellow 12/ CI Pigment Yellow 14)

- Phthalocyanine Blue (CI Pigment Blue 15)

- Monoazo Red (CI Pigment Red 57:1)



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History of Color Pigments

- Carbon Black
- Diarylides–1912
- Copper Phthalocyanines –1938
- Monoazos –1900's
- Diketopyrrolopyrrole – 1970's; Latest family of pigments developed for commercial printing
- New pigments invented every 20-60 years
- Continued development of pigments for printing inks – difficult to substitute

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Color Pigments Characteristics & Customer Requirements

- ✓Chroma
- ✓Broad shade functionality
- ✓Durability/lightfastness
- ✓Opacity/transparency
- ✓Low metamerism
- ✓Dispersibilty
- ✓Heat stability
- ✓Solvent resistance
- ✓Gloss retention
- ✓Color strength
- ✓Fitness for purpose (performance level)
- ✓Regulatory status
- ✓Cost
- ✓Availability

Each pigment is **unique** to fit its intended use in commerce and **difficult to substitute**.

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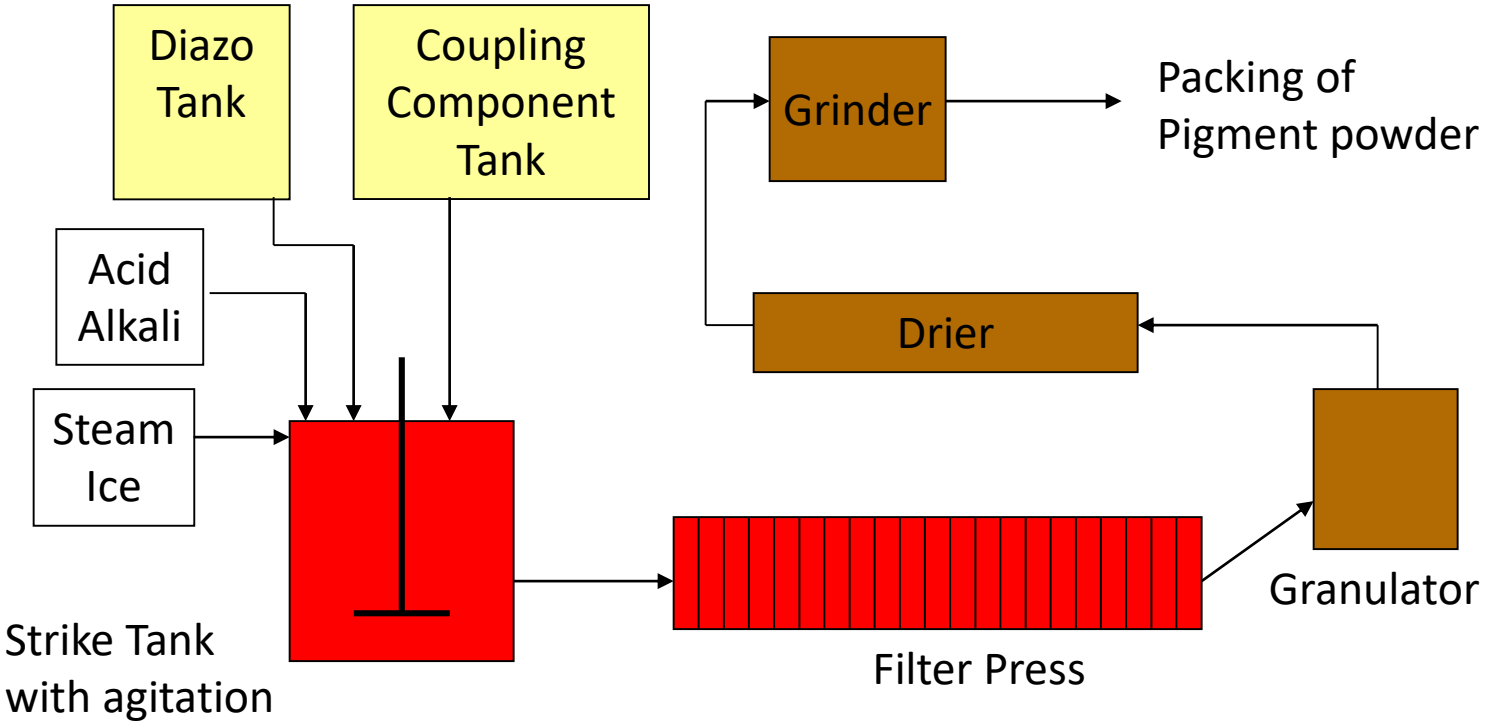
Manufacturing Process



By-products & Side Reactions

- All chemical reactions have by-products and side reactions
- Chemical hierarchy
- Improve chemical yield in theory
  - Example: remove BOD & COD from waste water
- Reduced performance characteristics due to elimination of by-products
- Some by-products governed by regulation
  - Example: chlorinated solvents

Industry Practical Solutions

- Reduced use of chlorinated solvents (byphenols)
- Modified buffers
- Process optimization/equipment design
- Sometimes “solutions” have not been the best solutions

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Sustainability

- Efficiency of energy utilization
- Efficiency of raw materials
- Examples:
  - Use of water is not efficient – energy intensive to recover; waste water regulations
  - Soy bean oil vs petroleum-based oil → solvent has limited applicability

Exposure to Color Pigments

- Inherently not bioavailable
- Virtually insoluble (as demonstrated by water and octanol partition coefficient)
- Not toxic in their intended uses
- In final use, pigments are encapsulated in resins of ink, coatings and plastics→ no exposure of concern and not readily bioavailable (humans, animals, and the environment)
- Dust handling controls – limited release into the environment
- Waste stream removal

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Organic Pigments: Tested & Used Safely in Commerce

✓Used in products and in commerce for decades

- Diarylide pigments in commerce in North America since WWII
- Phthalocyanine pigments in commerce in North America since the late 1930's

✓Tested and safe in intended applications and continue to be used in commerce

✓Governments in US, Canada and the EU have regulated the safe uses of organic pigments through extensive studies and any substitution of these safe organic pigments would have to be evaluated by the government to meet the safety levels already established

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Toxicological Data & Demonstrated Safety for Diarylide Pigments

- 1978 Study of the National Toxicological Program - no evidence of carcinogenicity for diarylide yellow in two year chronic toxicity study.
- 1990's Organisation for Economic Co-Operation and Development Screening Information Dataset Dossier - diarylide pigments do not present a hazard to the environment due to their low hazard profile.
- 2010 Registration, Evaluation, Authorisation and Restriction of Chemicals Dossier – safe for use in EU commerce in the pigment's indented use.
- 2010 US EPA Benzidine Dyes Action Plan : "In reviewing the benzidine congener-based pigments, EPA believes that the presence of pigments in such consumer products as printing inks, paints, plastics, and textiles was unlikely to present an exposure concern, because the pigments are not bioavailable and are not absorbed into the body"
- 2014 Final Canada Assessment :"Based on the information presented in this screening assessment, it is concluded that the five diarylide yellow pigments (CAS RNs 5102-83-0, 5567-15-7, 6358-85-6, 78952-70-2 and 90268-24-9) considered in this assessment do not meet the criteria under paragraph 64(a) or (b) of CEPA 1999, as they are not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends."

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Toxicological Data and Demonstrated Safety for Phthalocyanine Pigments

- 2005 Organisation for Economic Co-Operation and Development (OECD) Screening Information Dataset Dossier - low priority chemical due to low hazard profile.

- 2010 Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Dossier - safe for use in EU commerce in the pigment's intended use.

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Environmental Compliance

- Intentional production of PCBs banned by EPA under the Toxic Substances Control Act (TSCA) of 1976
- Inadvertent production of PCBs during the manufacturing process in products restricted to levels of 50 parts per million by federal and international standards
- Monochlorobiphenyl and dichlorobiphenyl, including PCB 11, largely unregulated outside of the United States
- Pending National Toxicology Program (NTP) toxicity study for PCB 11

Table 1. Summary of sources, reservoirs, releases, exposures and priorities.

Source	Legacy reservoir of PCBs	Annual releases of PCBs (kg/yr)	Potential exposure pathways and concerns
Historic uses			
transformers	100-200 kg	< 2	Accidental spills, which are identified and cleaned up.
large capacitors	20 metric tons	10 to 80	Accidental spills, which are identified and cleaned up.
lamp ballasts	100-350 metric tons	400 to 1,500	Continual release of lower concentrations, with high concentrations released when the ballast fails.
small capacitors	1-35 metric tons	3 to150	Disposal in landfills from a variety of old appliances.
other closed uses		unknown	
caulk	87 metric tons	160	Continual release of lower concentrations into the air, with high concentrations released when materials are disturbed.
other open uses		unknown	
Current generation			
pigments and dyes	N/A	0.02 to 31[a]	Continual release of lower concentrations, with higher concentrations released during recycling.
other inadvertent generation	N/A	900	Concerns about both continual releases and potential large releases.
residential waste burning	N/A	199	Released to air and already addressed by current regulations.
commercial marine vehicles	N/A	0.4	Released to air and already addressed by current regulations.

a. This estimate is for PCB-11, although additional congeners are present.

- 2015 PCBs Chemical Action Plan describes pigments as a very small contributor (at most 1%) of PCBs (see Table 1)

- Washington Department of Ecology study of PCBs in consumer products concluded none of the analyzed products (mostly yellow and green) exceed 1ppm

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Conclusions

- Unique color pigments chemistries have evolved over a considerable period of time
- Color pigment manufacturing processes are highly efficient and minimize by-products
- Each pigment is unique to fit its intended use in commerce and difficult to substitute

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Thank you!

Questions?

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