Printing Inks
Formulation & Manufacture

Spokane River Workshop October 2019

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Printing Ink Industry
-NAICS: 32591-

NAPIM and NPIRI

National Association of Printing Ink Manufacturers
- Formed in 1913
- Represents ~89% Domestic Production Capacity
- Ink Manufacturers and Suppliers
- Research (task forces)

National Printing Ink Research Institute
- Formed in 1947
- Funded by the Industry
- Training
- Research (task forces)
Printing Ink Industry
-NAICS: 32591-

Major Federal Regulations

• OSHA
• RCRA
• CPSA*
• CAA
• CWA
• FDCA*
Printing Ink Industry
-NAICS: 32591-

Supply Chain

RM Supplier → Ink Mfr → Printer/Converter → Brand/CPC → Consumer
Printing Ink Industry
-NAICS: 32591-
Chemical Manufacturing Sector
Mixing & Blending vs Reactions
Printing Ink Industry

-Size-

Lbs/$$

US: ~4 billion lbs/$3.8 billion
EU: ~5-6 billion lbs/?
Global: ~14 billion lbs/?

2017 exports: 182,032,011 lbs
2017 imports: 59,972,748 lbs

Sources:
- NAPIM State of the Industry Report 2017
- European Printing Ink Association Quarterly Report March 2018 (EuPIA)
- US Bureau of Census

Harmonized Tariff System Schedule of the US

- 3215.19.9010 - News
- 3215.19.9020 - Flexo
- 3215.19.9030 - Gravure
- 3215.19.9040 - Letterpress
- 3215.19.9050 - Offset Litho
- 3215.19.9060 - Other
# Printing Ink Industry - Manufacturing -

## Number of Establishments

Number of Firms: ~202

<table>
<thead>
<tr>
<th>Geographic area name</th>
<th>NAICS.id</th>
<th>Meaning of 2012 NAICS code</th>
<th>YEAR.id</th>
<th>ESTAB</th>
<th>EMP</th>
<th>PAYQTR1</th>
<th>PAYANN</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>32591</td>
<td>Printing ink manufacturing</td>
<td>2016</td>
<td>362</td>
<td>10336</td>
<td>145488</td>
<td>597795</td>
</tr>
<tr>
<td>United States</td>
<td>325910</td>
<td>Printing ink manufacturing</td>
<td>2016</td>
<td>362</td>
<td>10336</td>
<td>145488</td>
<td>597795</td>
</tr>
</tbody>
</table>

Source: U.S Census Bureau
Printing Ink Industry
-US Market Composition-

Value of Shipments $1MM

- Litho, 1050
- Gravure, 272
- Flexo, 838
- Letterpress, 265
- Non-Impact, 1233

Source: U.S. Census Bureau 2016 Annual Survey Manufactures
Printing Ink Industry
- US Market Composition -

Ink Type Market Share

- Litho 45%
- Gravure 10%
- Flexo 30%
- Letterpress 7%
- Non-Impact 8%
Dyes dissolve completely in the vehicle system and are more stable than pigments at the very high temperatures reached by ink-jet printers. Dyes recently developed for ink-jet systems perform better than those adapted from traditional printing. There have also been new developments in pigments for this application to overcome some of the typical problems encountered early on in the development cycle, particularly with respect to dispersion, shelf stability, and settling.
Printing Ink Industry

Terminology
Process vs Spot Color

CMYK

Spot
CIE 1976 L*, a*, b* Color Space

- L* = 100 WHITE
- +b* YELLOW
- -a* GREEN
- -b* BLUE
- L* = 0 BLACK

Printing Ink Industry
Typical Color Specifications

Mapping of a Color in CIELAB Space

- HUE
- CHROMA
- LIGHTNESS

- BLUE
- RED
- GREEN
- YELLOW

LIGHTNESS
-60
0
100

HUE
-60
-40
-20
+20
+40
+60

CHROMA
-20
-40
-60
+40
+60

Typing Ink Industry
Printing Ink Industry

CIELAB Coordinates

Flower A:
$L^* = 52.99 \quad a^* = 8.82 \quad b^* = 54.63$

Flower B:
$L^* = 29.00 \quad a^* = 52.48 \quad b^* = 22.23$
The distance between two colors estimates the visual color difference.

Line connecting the two colors maps the distance between them.
Printing Ink Industry
Color Measurement

X-Rite i1Pro 2
X-Rite eXact Scan
Konica Minolta FD-7
Techkon Spectrodens
Datacolor Spectravision
Printing Ink Industry

Other Parameters and Characteristics

It's not just the color!

Commercial product data

Entries represent data compiled for dry powders without reduction or other surface treatment. Data are intended solely as a general guide. See manufacturers' literature for properties of specific products.

Physical data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.60 - 2.00</td>
</tr>
<tr>
<td>Solid Bulk Density</td>
<td>12.3 - 16.6</td>
</tr>
<tr>
<td>Melting point</td>
<td>5°C</td>
</tr>
<tr>
<td>Particle charge</td>
<td>25.6 - 9.6</td>
</tr>
<tr>
<td>232 mesh retention</td>
<td>% &gt; 64%</td>
</tr>
<tr>
<td>Surface area</td>
<td>0.2 m²/g</td>
</tr>
<tr>
<td>pH</td>
<td>3.2 - 5.6</td>
</tr>
<tr>
<td>Viscosity</td>
<td>10% slurry</td>
</tr>
<tr>
<td>Solvent</td>
<td>40 - 80 wt/100 wat</td>
</tr>
</tbody>
</table>

Color permanency

<table>
<thead>
<tr>
<th>Color permanency</th>
<th>Indoor</th>
<th>Outdoor</th>
<th>Other data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanence Index</td>
<td>200%</td>
<td>175%</td>
<td>High hiding is attributed to strong absorption and low scattering power. Pigment is electrically non-conducting and does not tend to form agglomerates.</td>
</tr>
<tr>
<td>Light fastness</td>
<td>120</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Dye fastness</td>
<td>Y</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>Alcohol fastness</td>
<td>U</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Toluene fastness</td>
<td>U</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Petrol fastness</td>
<td>Y</td>
<td>Y</td>
<td></td>
</tr>
</tbody>
</table>

Application data

<table>
<thead>
<tr>
<th>Major useages</th>
<th>Points, printing inks and baked enamels requiring deep matte black or velvety appearance. Cotton printing and dying.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major weaknesses</td>
<td>Bleeds in oxygenated solvents. Poor tint lightness. Low tinting strength compared to carbon black.</td>
</tr>
</tbody>
</table>

National Association of Printing Ink Manufacturers
15 Technology Parkway S. Suite 115, Peachtree Corners, GA 30092
Phone: 770-209-7289 Fax: 770-209-7217 Mail: napim@napim.org
Printing Ink Industry
-Markets-

Commercial
Newspapers, Magazine, Books, Reports, etc.

Packaging
Food and Non-food

Substrates
Paper/Paperboard/Film/Metal
Flexographic Printing

Control Technology Substitute Assessment
Health/Safety Evaluation of Ink Components

National Association of Printing Ink Manufacturers
15 Technology Parkway S. Suite 115, Peachtree Corners, GA 30092
Phone: 770-209-7289 Fax: 770-209-7217 Mail: napim@napim.org
Elimination of heavy metal pigments
Development of water-based inks
Development of energy-curable inks
Increased usage of biorenewable content
Elimination of CMR's
Printing Ink Industry
-Printing Inks and Heavy Metals-

What is a heavy metal?

CONEG
RCRA TCLP

Cadmium (Cd),
Chromium (Cr\(^{+6}\)),
Lead (Pb),
Mercury (Hg)

Arsenic (As),
Barium (Ba),
Cadmium (Cd),
Chromium (Cr),
Lead (Pb),
Mercury (Hg),
Selenium (Se),
Silver (Ag)
Printing Ink Industry

Typical Printing Substrates

**Film**

- LDPE
- HDPE
- LLDPE
- PET
- Metalized Polypropylene
- Nylon
- PVC
- PLA (Polylactid/Polyactic Acid) sugar/corn-based

*excluding metals and glass

**Folding Carton (FBB)**

FBB construction (corrugated** and cardboard):
1 – Coating (kaolin, clay-based)
2 – Bleached chemical pulp
3 – Mechanical pulp
4 – Unbleached/Bleached chemical pulp

**alternatively**

PE, PP, PO –based - O₂/H₂O barrier
**primarily secondary/tertiary packaging**
Litho Heatset Ink (sheetfed)

Drying sequence
Penetration
Phase separation
Oxidation/polymerization*

* Catalytic driers (manganese/cobalt based organic compounds) sometimes used to accelerate oxidation/polymerization. There are other driers used (zirconium, serium, etc.)

Note: Litho coldset/web not used in folding carton applications
## Printing Ink Industry
### Example Formulations
#### Lithographic Ink

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% Phthalocyanine Blue water paste (C.I. Pigment Blue 15)</td>
<td>18.0</td>
</tr>
<tr>
<td>Extender (White pigment TiO2)</td>
<td>5.0</td>
</tr>
<tr>
<td>Varnish (oleoresinous/alkyd)</td>
<td>50.0</td>
</tr>
<tr>
<td>Soya oil</td>
<td>25.0</td>
</tr>
<tr>
<td>Additives</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### Quickset Varnish
- Phenolic resin: 30%
- Hydrocarbon resin 5%
- HiViscosity Linseed alkyd: 24.5%
- 280°-320° Aromatic-free distillate: 40%
- Aluminum-based gallant: 0.5%

### Additives
- Silica
- Talc
- Clay
- Dispersants
- Waxes
- Driers
- Stabilizers
## Printing Ink Industry
-Example Formulations-

### Waterbased Flexographic Ink

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% Phthalocyanine Blue water paste (C.I. Pigment Blue 15)</td>
<td>24.7</td>
</tr>
<tr>
<td>Acrylic emulsion</td>
<td>50.0</td>
</tr>
<tr>
<td>Water</td>
<td>20.0</td>
</tr>
<tr>
<td>Polyethylene wax compound</td>
<td>3.0</td>
</tr>
<tr>
<td>Monoethyleamine</td>
<td>2.0</td>
</tr>
<tr>
<td>Organic defoamer (polysiloxanes and hydrophobic solids in polyglycol)</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Printing Ink Industry
-Example Formulations-

Energy Curable Flexographic Ink

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% Phthalocyanine Blue water paste (C.I. Pigment Blue 15)</td>
<td>15-20</td>
</tr>
<tr>
<td>Oligomer (polyester acrylate)</td>
<td>30-45</td>
</tr>
<tr>
<td>Monomer (trimethylol propane triacrylate, pentaerythritol triacrylate)</td>
<td>10-20</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>5-10</td>
</tr>
<tr>
<td>Wax</td>
<td>4-6</td>
</tr>
<tr>
<td>Additives</td>
<td>2-4</td>
</tr>
</tbody>
</table>

**Photo-initiator Chemistry & Applications**

<table>
<thead>
<tr>
<th>PHOTOINITIATOR</th>
<th>PROPERTIES</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone(s)</td>
<td>Considerable yellowing upon UV exposure</td>
<td>Co-initiator for overprint varnishes and pigmented systems (surface cure)</td>
</tr>
<tr>
<td>Hydroxyketones</td>
<td>Absorption of UV-C and UV-B</td>
<td>Overprint varnishes Co-initiator for pigmented systems (surface cure)</td>
</tr>
<tr>
<td>Aminoketones</td>
<td>Low yellowing upon UV exposure</td>
<td>Highly pigmented systems (through cure)</td>
</tr>
<tr>
<td>MAPO / BAPO</td>
<td>Absorption of UV-A up to visible range</td>
<td>Highly pigmented systems (TiO₂)</td>
</tr>
</tbody>
</table>
# Printing Ink – Film Thicknesses

## Table 2.1 Main characteristics of the printing processes

<table>
<thead>
<tr>
<th>Print process</th>
<th>Ink film thickness (μ)</th>
<th>Typical halftone screen ruling (lines/cm)</th>
<th>Substrate types</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Office Ink: Sheet-fed</td>
<td>&lt;2</td>
<td>47–80</td>
<td>Wide range of paper and board, plastic sheet and metal</td>
<td>All general prints, business forms, technical documentation, promotional, magazines, credit cards</td>
</tr>
<tr>
<td>UV drying</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Web-fed</td>
<td></td>
<td>60</td>
<td>Carton board</td>
<td></td>
</tr>
<tr>
<td>Heat-set</td>
<td>&lt;2</td>
<td>52–69</td>
<td>Wide range of coated and uncoated paper</td>
<td>Magazines and similar format products</td>
</tr>
<tr>
<td>Cold-set</td>
<td>&lt;2</td>
<td>25–40</td>
<td>Newsprint</td>
<td>Newspapers</td>
</tr>
<tr>
<td>Flexography</td>
<td>Narrow web</td>
<td>0.75–2</td>
<td>60</td>
<td>Paper and plastic film</td>
</tr>
<tr>
<td></td>
<td>Wide web</td>
<td>0.75–2</td>
<td>33</td>
<td>Newsprint</td>
</tr>
<tr>
<td>&amp; 0.75–2</td>
<td>52</td>
<td>Wide range of plastic film, paper, corrugated cardboard</td>
<td>Boxes and many other types of packaging, sacks</td>
<td></td>
</tr>
<tr>
<td>Gravure</td>
<td>Large web</td>
<td>&lt;6</td>
<td>60–80</td>
<td>Coated or uncoated paper</td>
</tr>
<tr>
<td></td>
<td>Smaller web</td>
<td>&lt;6</td>
<td>60–80</td>
<td>Coated or uncoated paper, plastic films, board</td>
</tr>
<tr>
<td>Sheet</td>
<td>&lt;6</td>
<td>150–200</td>
<td>Paper</td>
<td></td>
</tr>
</tbody>
</table>
Weight of Ink per Square Inch of Substrate Calculation

- Offset/flexo dried ink thickness = 2 microns
- 2 microns = 0.00008 inches (from the Printing Ink Manual p. 77)
- Volume (in cubic inches of 1 square inch) at height of 0.00007874015748031496
  - (1*1*0.00008) – assumes 100% coverage
  - = 0.00007 cubic inches or 0.001290 ml

Assuming 1 g/ml ink density  (the density should be adjusted with the removal of any VOC’s or other volatiles - interested in the final weight percent – after the ink has dried)

0.001290 ml = 0.001290 g or 1.29 mg ink/square inch

Technical experience: 1.45 mg ink/square inch (conservative estimate)
Printing Ink Industry

-Raw Material Supply Chain-

Pigments
Resins
Solvents
Additives
Printing Ink Industry

- Manufacturing Processes/Unit Operations -

Weighing
Mixing
Milling
Filtering
Printing Ink Industry
-Manufacturing Processes/Unit Operations-
Formulating Inks Without Phthalocyanine and Diarylide Pigments

Impacts & Challenges
Changes in Performance and Compatibility
Decreases the color gamut – range of available colors
Revision of Global Color Standards:
  - GRACol
  - FOGRA
  - ISO
  - ICC Profiles
  - Others
Thanks for Listening!

Questions?