Printing Inks
Formulation & Manufacture

Spokane River Workshop October 2019

George R. Fuchs

Director of Regulatory and Technical Affairs

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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 Suppl
- Research (task forces)

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

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-NAICS: 32591-

Major Federal Regulations

- OSHA
- RCRA
- CPSA*
- CAA
- CWA
- FDCA*

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Printing Ink Industry
-NAICS: 32591-

Supply Chain

RM Supplier → Ink Mfr → Printer/Converter → Brand/CPC → Consumer

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Printing Ink Industry
-NAICS: 32591-

Chemical Manufacturing Sector

Mixing & Blending vs Reactions

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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

Harmonized Tariff System Schedule of the US

- 3215.19.9010 - News
- 3215.19.9020 - Flexo
- 3215.19.9030 - Gravure
- 3215.19.9030 - Gravure
- 3215.19.9040 - Letterpress
- 3215.19.9050 - Offset Litho
- 3215.19.9060 - Other

Sources:
IBISWorld Industry Report 2008:Ink Manufacturing in the US: 32591
NAPIM State of the Industry Report 2017
European Printing Ink Association Quarterly Report March 2018 (EuPIA)
US Bureau of Census

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Printing Ink Industry -Manufacturing-

Number of Establishments

Number of Firms: ~202

Geographic area name	NAICS.id 2012 NAICS code	NAICS Meaning of 2012 NAICS code	YEAR.id Year	ESTAB Number of establishments	EMP Paid employees	PAYQTR1 First-quarter payroll ($1,000)	PAYANN Annual payroll ($1,000)
United States	32591	Printing ink manufacturing	2016	362	10336	145488	597795
United States	325910	Printing ink manufacturing	2016	362	10336	145488	597795

Source: U.S Census Bureau

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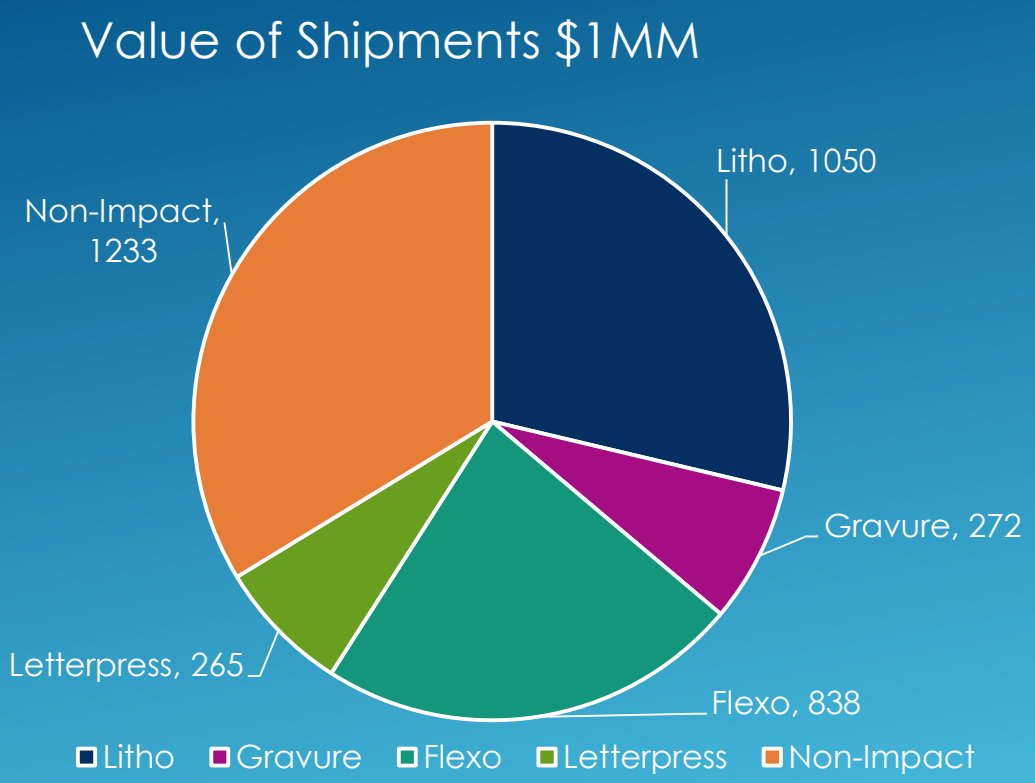
Printing Ink Industry
-US Market Composition-



Source: U.S Census Bureau 2016 Annual Survey Manufactures

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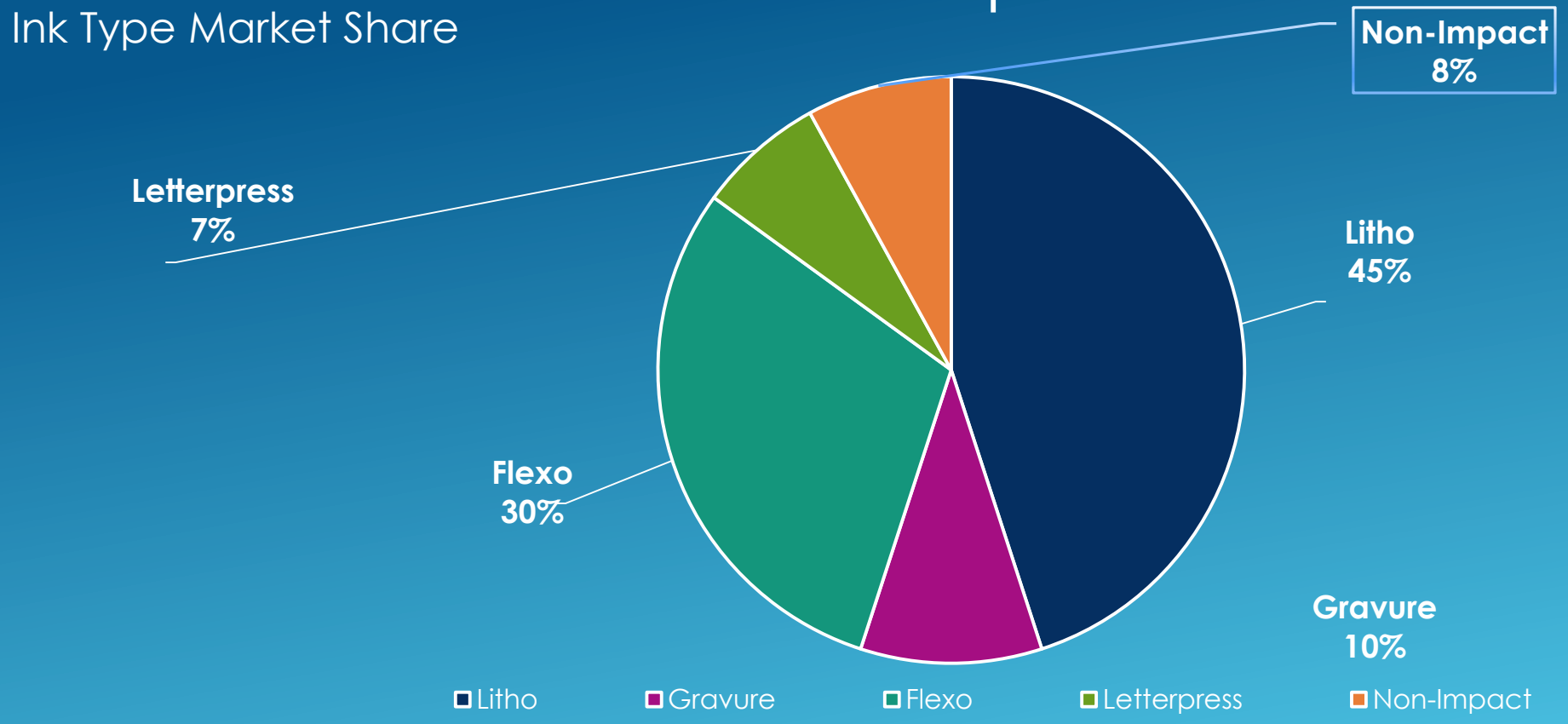
Printing Ink Industry
-US Market Composition-



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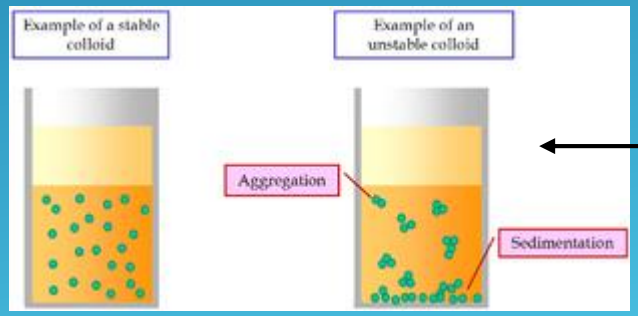
Printing Ink Industry

Inks vs Dyes

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.

Ideal →



← Not Ideal

Blame the ink!

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Printing Ink Industry

Terminology
Process vs Spot Color

CMYK

Spot

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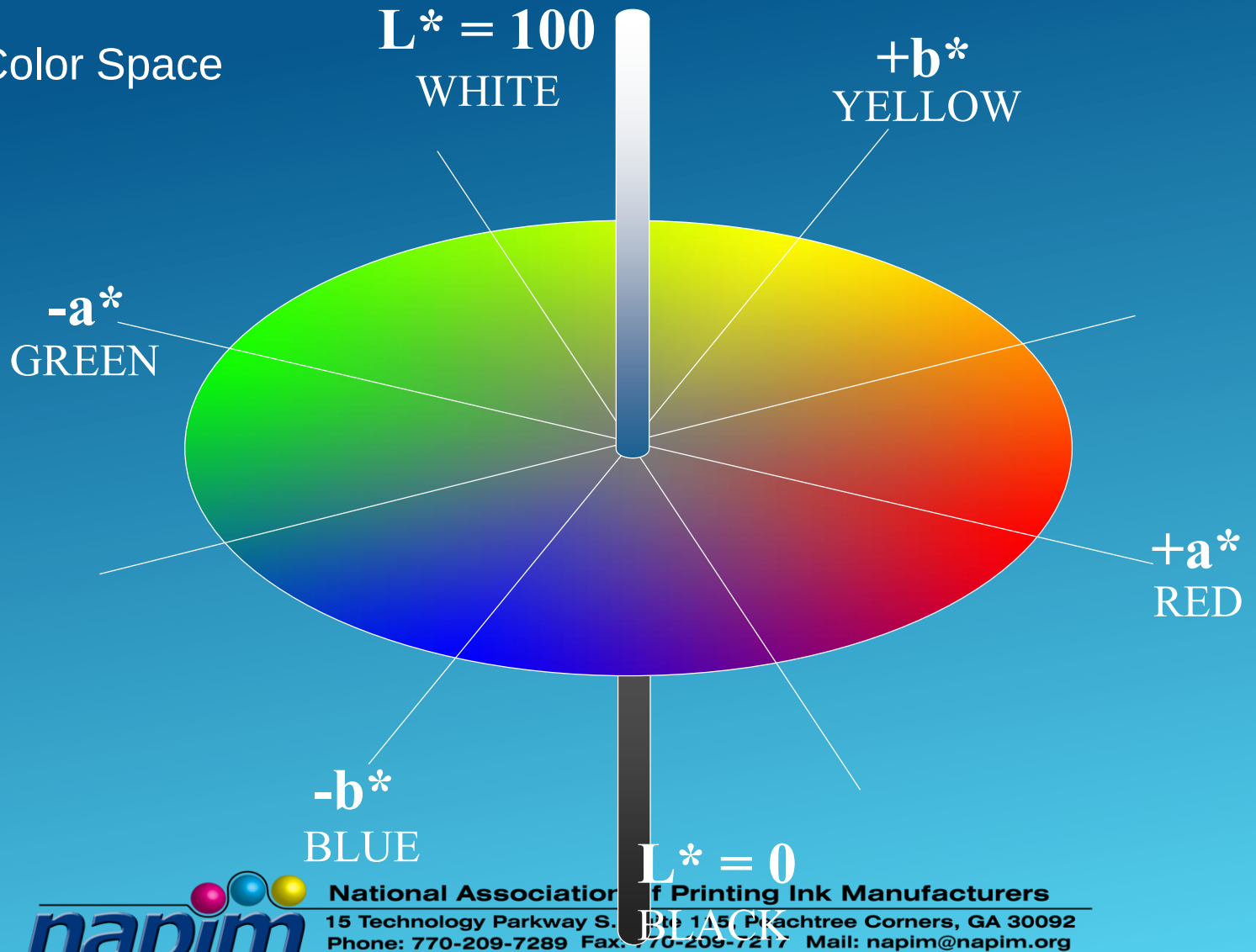
Printing Ink Industry

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



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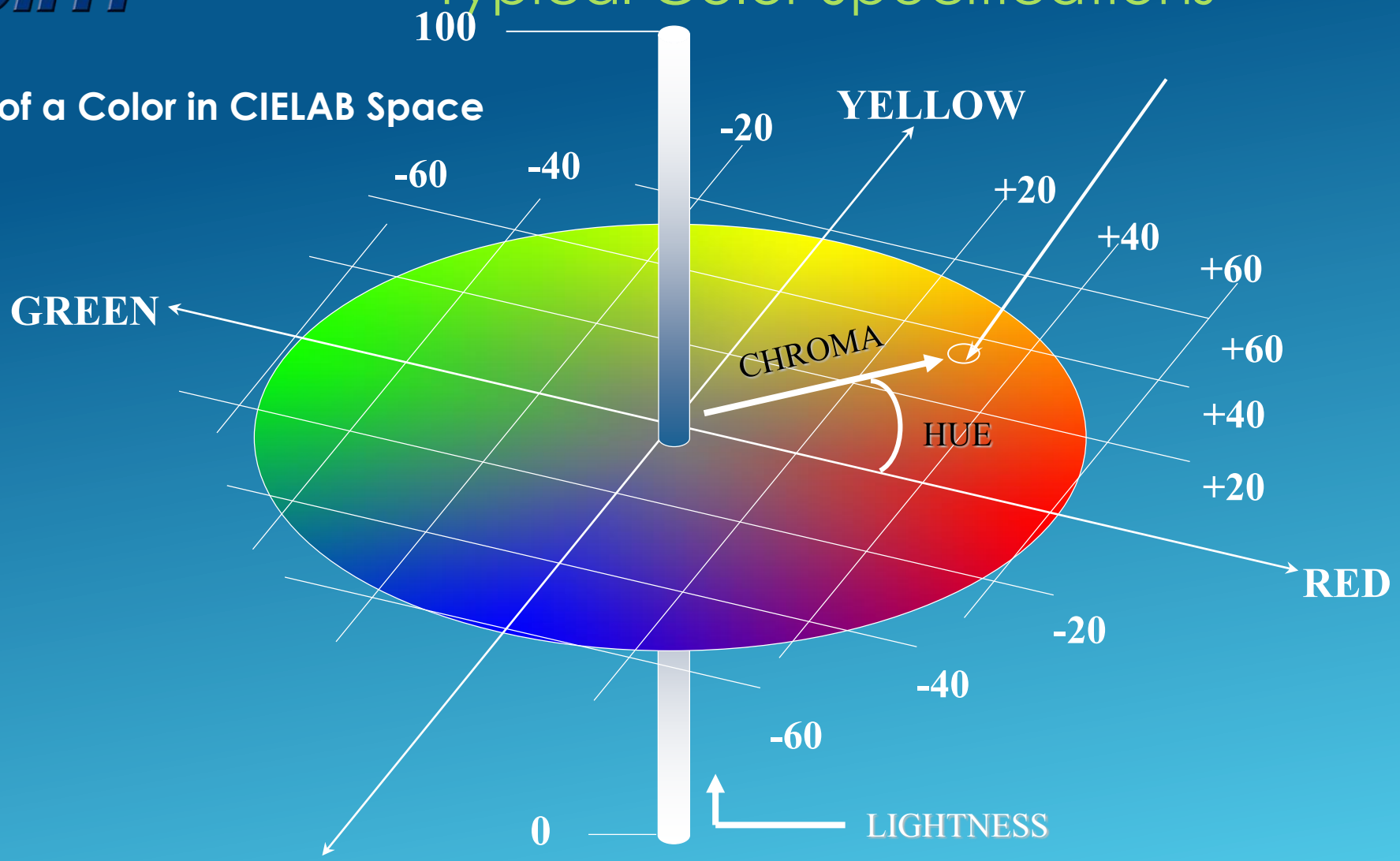
Typical Color Specifications

Mapping of a Color in CIELAB Space



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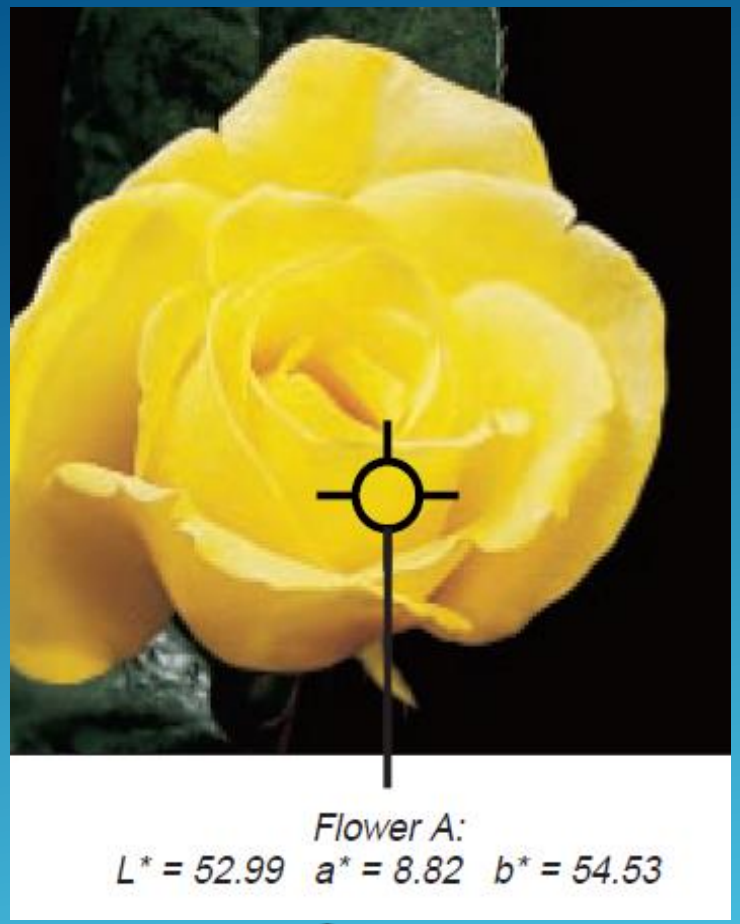
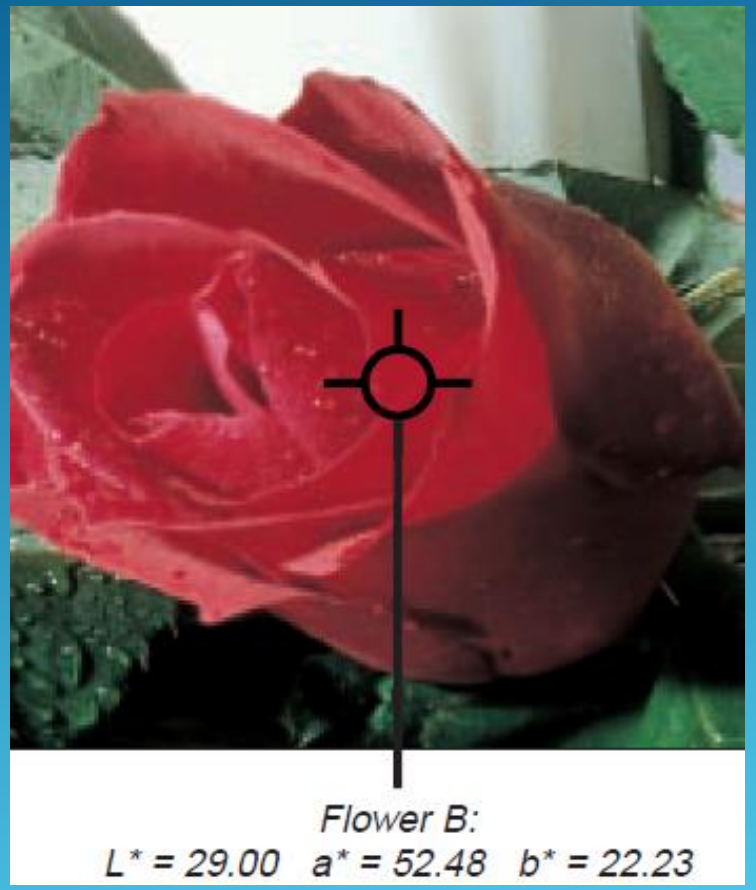
CIELAB Coordinates



Flower A:
L = 52.99 a* = 8.82 b* = 54.53*



Flower B:
L = 29.00 a* = 52.48 b* = 22.23*

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Printing Ink Industry

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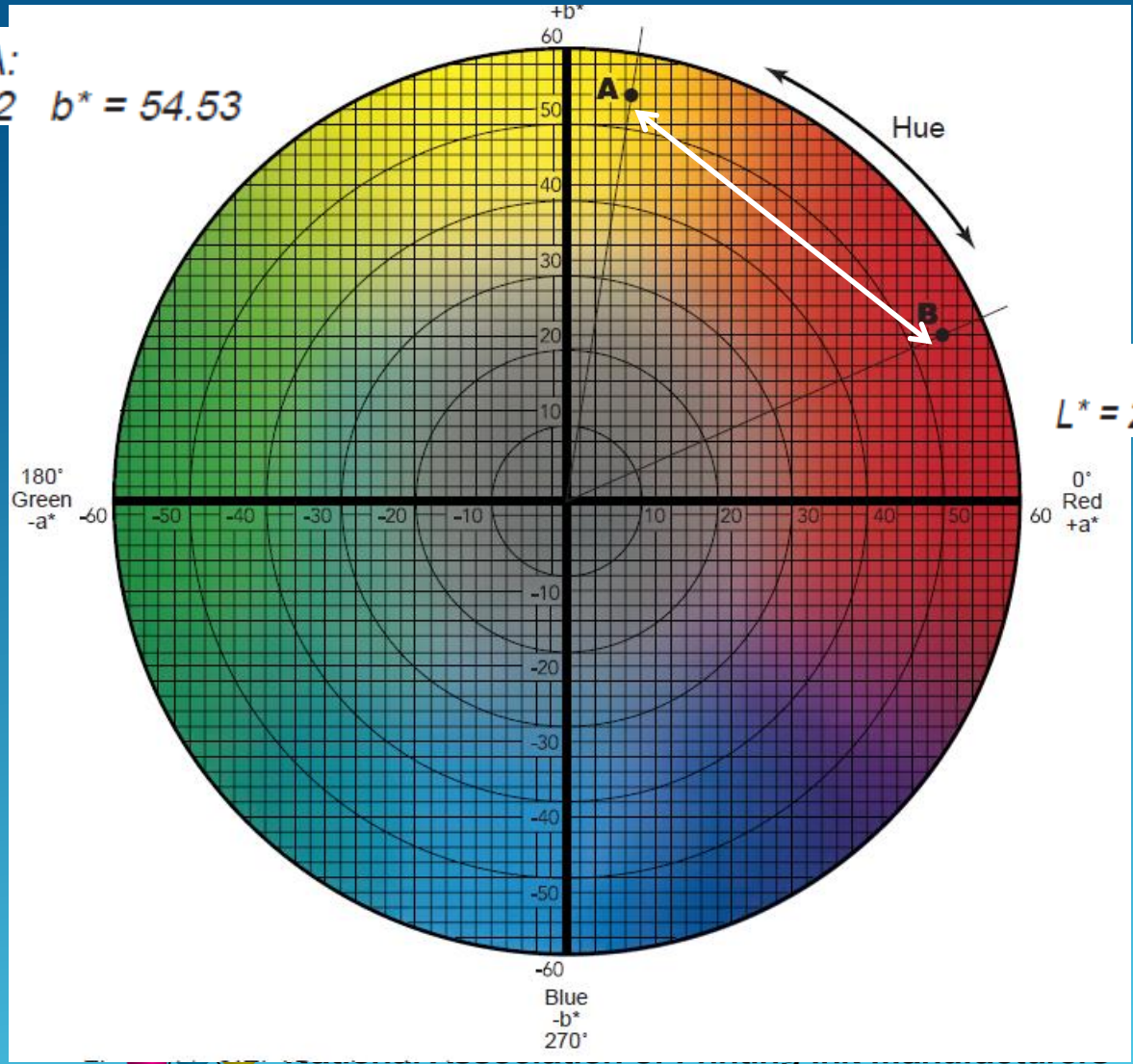

Flower B:
L* = 29.00 a* = 52.48 b* = 22.23

Line connecting the two colors maps the distance between the them.

The distance between two colors estimates the visual color difference

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Printing Ink Industry

Color Measurement

X-Rite i1Pro 2

X-Rite eXact Scan

Konica Mi[illegible]FD-7

Techkon Spectrodens

Datacolor Spectravision

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Printing Ink Industry

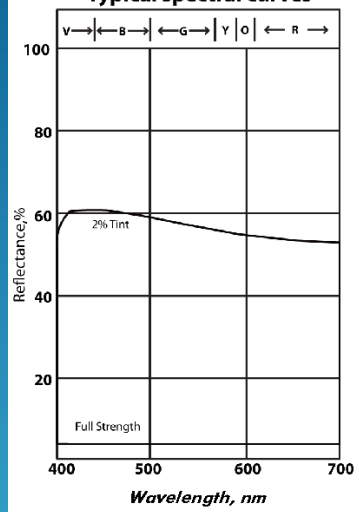
Other Parameters and Characteristics

Its not just the color!

Commercial product data

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

Typical spectral curves



Physical data

Specific gravity	1.60 - 2.00	$H_2O=1$
Solid Bulk Density	13.3 - 16.6	lb/US gal
Melting point		0^C
Particle shape		
Particle size, mesh	0.06 - 2.0	micro-meters
325 mesh retention		%>44u
Surface area	5.2	m^2/g
pH	3.2 - 5.0	10% slurry
Hiding Power	Semiopaque	
Oil Absorption	40 - 80	wt/100 wt

Fastness data

Acid	hydrochloric acid 5%	N'	Oxygen-ated solvents	Ethyl alcohol	A'
	lactic acid 3%			Ethyl acetate	
	acetic acid 2%			Diethylene glycol	
Alkali	NaOH 2%	S		Methyl ethyl ketone	A
	Na2CO3 5%			Lacquer sol-vent, DCMA	
Water	20° C	N'	Other DOP	20° C	N'
	100 ° C			175 ° C	
	Process sterilization			Oils, fats, greases	N'
HC's	Mineral spirits	N'		Parrafin wax 80°C	
	Xylenes	N'		Soap sandwich	

Color permanency*

Indoor [fadeometer]	Change at 72-80 h	N	(full)	(tint)	Max tol.	120	hrs(full)	20-30	hrs(tint)
Outdoor 0 Florida 45 S	Change at 12 months		(full)	(tint)	Max tol.		mos(full)		mos(tint)
Baking (tin plate)	Change at 150°C	N	(15')	(30')	Max tol.	180	°C(10')	160	°C(30')

*Key to fastness/permanency ratings: N-no bleed/discoloration; S- slight; A-appreciable, 'ratings vary by source. Key to permanency failures: F-fades; D-darkens; L-loses gloss; B - turns bluer; G - turns grayer or greener; Y - turns yellower; Z -bronzes.

Other data

High hiding is attributed to strong absorption and low scattering power. Pigment is electricaly non-conducting and does not tend to form agglomerates.

Application data

Major usage	Paints, printng inks and baked enamels requireing deep matte black or velvety appearance. Cotton printing and dyeing.	Major weakness	Bleeds in oxygenated solvents. Poor tint lightfastness. Low tinting strength compared to carbon black.

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Printing Ink Industry
-Markets-

Commercial
Newspapers, Magazine, Books, Reports, etc.

Packaging
Food and Non-food

Substrates
Paper/Paperboard/Film/Metal

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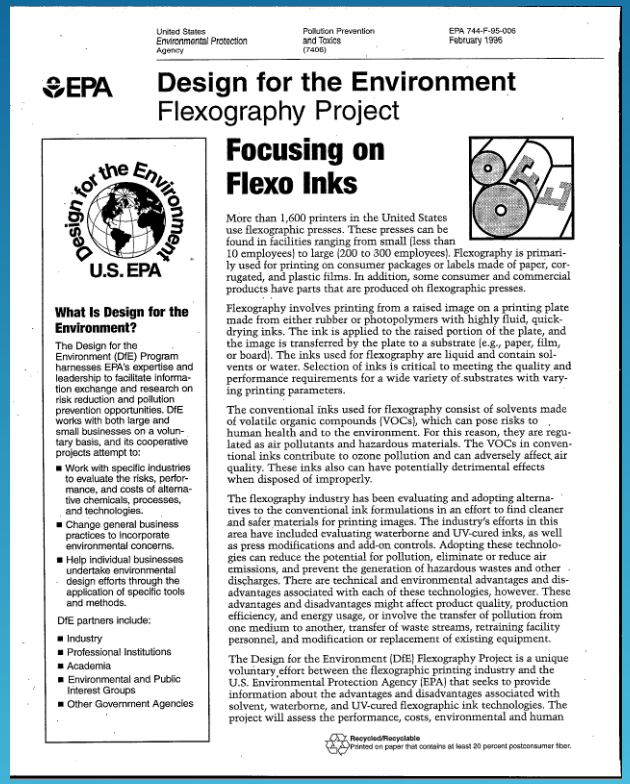
Printing Ink Industry
-EPA Design for the Environment-

Flexographic Printing

Control Technology Substitute Assessment

Health/Safety Evaluation of Ink Components



United States Environmental Protection Agency | Pollution Prevention and Toxics (7406) | EPA 744-F-95-006 February 1996

EPA

Design for the Environment
Flexography Project

Design for the Environment U.S. EPA

What Is Design for the Environment?

The Design for the Environment (DfE) Program harnesses EPA's expertise and leadership to facilitate information exchange and research on risk reduction and pollution prevention opportunities. DfE works with both large and small businesses on a voluntary basis, and its cooperative projects attempt to:

- Work with specific industries to evaluate the risks, performance, and costs of alternative chemicals, processes, and technologies.
- Change general business practices to incorporate environmental concerns.
- Help individual businesses undertake environmental design efforts through the application of specific tools and methods.

DfE partners include:

- Industry
- Professional Institutions
- Academia
- Environmental and Public Interest Groups
- Other Government Agencies

Focusing on Flexo Inks

More than 1,600 printers in the United States use flexographic presses. These presses can be found in facilities ranging from small (less than 10 employees) to large (200 to 300 employees). Flexography is primarily used for printing on consumer packages or labels made of paper, corrugated, and plastic films. In addition, some consumer and commercial products have parts that are produced on flexographic presses.

Flexography involves printing from a raised image on a printing plate made from either rubber or photopolymers with highly fluid, quick-drying inks. The ink is applied to the raised portion of the plate, and the image is transferred by the plate to a substrate (e.g., paper, film, or board). The inks used for flexography are liquid and contain solvents or water. Selection of inks is critical to meeting the quality and performance requirements for a wide variety of substrates with varying printing parameters.

The conventional inks used for flexography consist of solvents made of volatile organic compounds (VOCs), which can pose risks to human health and to the environment. For this reason, they are regulated as air pollutants and hazardous materials. The VOCs in conventional inks contribute to ozone pollution and can adversely affect air quality. These inks also can have potentially detrimental effects when disposed of improperly.

The flexography industry has been evaluating and adopting alternatives to the conventional ink formulations in an effort to find cleaner and safer materials for printing images. The industry's efforts in this area have included evaluating waterborne and UV-cured inks, as well as press modifications and add-on controls. Adopting these technologies can reduce the potential for pollution, eliminate or reduce air emissions, and prevent the generation of hazardous wastes and other discharges. There are technical and environmental advantages and disadvantages associated with each of these technologies, however. These advantages and disadvantages might affect product quality, production efficiency, and energy usage, or involve the transfer of pollution from one medium to another, transfer of waste streams, retraining facility personnel, and modification or replacement of existing equipment.

The Design for the Environment (DfE) Flexography Project is a unique voluntary effort between the flexographic printing industry and the U.S. Environmental Protection Agency (EPA) that seeks to provide information about the advantages and disadvantages associated with solvent, waterborne, and UV-cured flexographic ink technologies. The project will assess the performance, costs, environmental and human

Recycled/Recyclable
Printed on paper that contains at least 20 percent postconsumer fiber.

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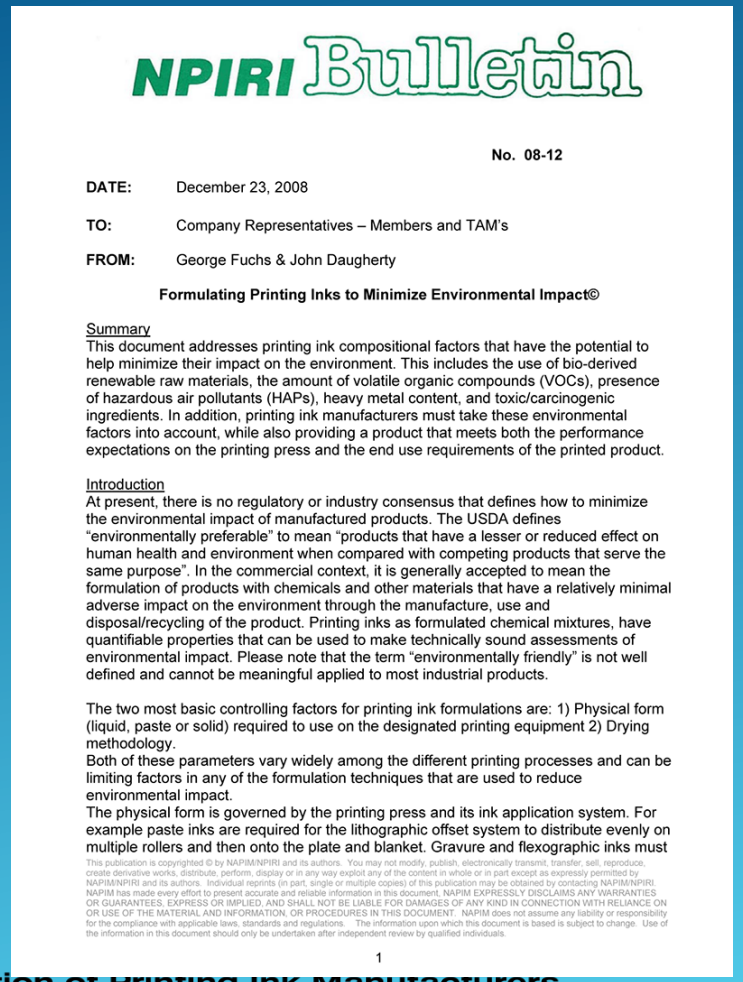
Printing Ink Industry
-Printing Inks and Sustainability-

Elimination of heavy metal pigments
Development of waterbased inks
Development of energy curable inks
Increased usage of biorenewable content
Elimination of CMR's



NPIRI Bulletin

No. 08-12

DATE: December 23, 2008

TO: Company Representatives – Members and TAM's

FROM: George Fuchs & John Daugherty

Formulating Printing Inks to Minimize Environmental Impact©

Summary

This document addresses printing ink compositional factors that have the potential to help minimize their impact on the environment. This includes the use of bio-derived renewable raw materials, the amount of volatile organic compounds (VOCs), presence of hazardous air pollutants (HAPs), heavy metal content, and toxic/carcinogenic ingredients. In addition, printing ink manufacturers must take these environmental factors into account, while also providing a product that meets both the performance expectations on the printing press and the end use requirements of the printed product.

Introduction

At present, there is no regulatory or industry consensus that defines how to minimize the environmental impact of manufactured products. The USDA defines "environmentally preferable" to mean "products that have a lesser or reduced effect on human health and environment when compared with competing products that serve the same purpose". In the commercial context, it is generally accepted to mean the formulation of products with chemicals and other materials that have a relatively minimal adverse impact on the environment through the manufacture, use and disposal/recycling of the product. Printing inks as formulated chemical mixtures, have quantifiable properties that can be used to make technically sound assessments of environmental impact. Please note that the term "environmentally friendly" is not well defined and cannot be meaningful applied to most industrial products.

The two most basic controlling factors for printing ink formulations are: 1) Physical form (liquid, paste or solid) required to use on the designated printing equipment 2) Drying methodology.
Both of these parameters vary widely among the different printing processes and can be limiting factors in any of the formulation techniques that are used to reduce environmental impact.
The physical form is governed by the printing press and its ink application system. For example paste inks are required for the lithographic offset system to distribute evenly on multiple rollers and then onto the plate and blanket. Gravure and flexographic inks must

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Printing Ink Industry
-Printing Inks and Heavy Metals-

What is a heavy metal?

CONEG

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

RCRA TCLP

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

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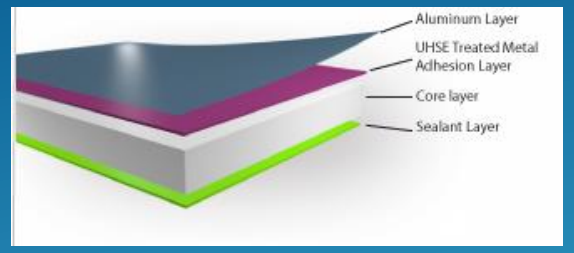
Printing Ink Industry
Typical Printing Substrates

Film

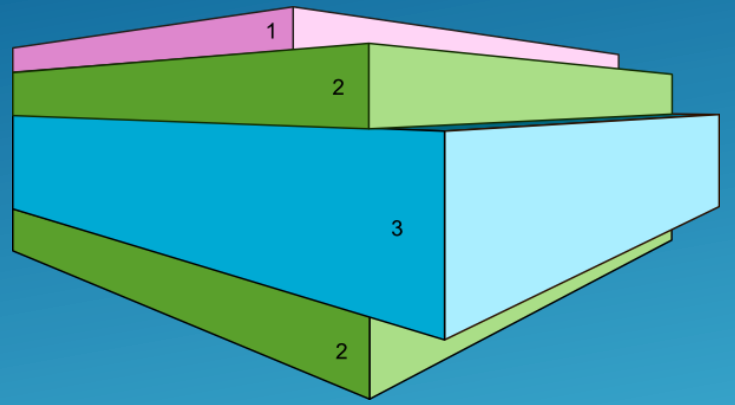
LDPE
HDPE
LLDPE
PET
Metalized
Polypropylene
Nylon
PVC
PLA (Polylactid/Polylactic Acid)
sugar/corn-based



PE, PP, PO –based - O_2/H_20 barrier

*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

**primarily secondary/tertiary packaging

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Printing Ink Industry
-Ink Systems and Substrates-

Litho Heatset Ink (sheetfed)

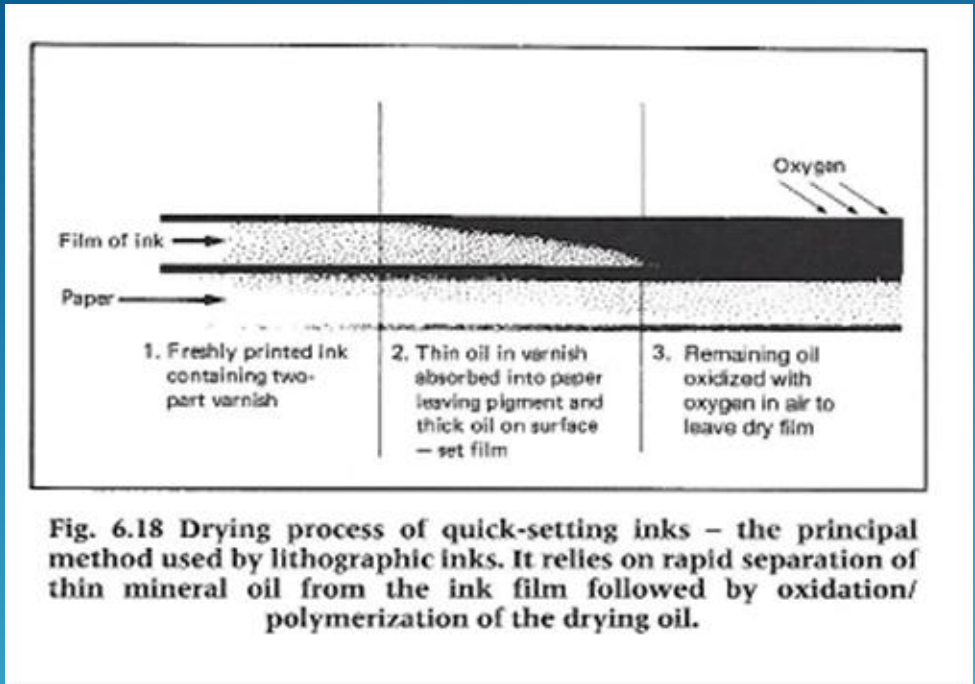

Fig. 6.18 Drying process of quick-setting inks – the principal method used by lithographic inks. It relies on rapid separation of thin mineral oil from the ink film followed by oxidation/ polymerization of the drying oil.

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 (xirconium, serium, etc.)

Note: Litho coldset/web not used in folding carton applications

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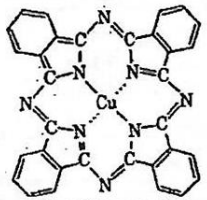
Printing Ink Industry
-Example Formulations-
Lithographic Ink

Component	%
50% Phthalocyanine Blue water paste (C.I. Pigment Blue 15)	18.0
Extender (White pigment TiO2)	5.0
Varnish (oleoresinous/alkyd)	50.0
Soya oil	25.0
Additives	2.0

Structural formula	 Blue 15
CAS Registry Number and CA Index Name	147-14-8 Copper,[29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-,(SP-4-1)-

Additives

Silica
Talc
Clay
Dispersants
Waxes
Driers
Stabilizers

Quickset Varnish

Phenolic resin: 30%
Hydrocarbon resin 5%
HiViscosity Linseed alkyd: 24.5%
280^0-320^0 Aromatic-free distillate: 40%
Aluminum-based gallant: 0.5%

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Printing Ink Industry
-Example Formulations-

Waterbased Flexographic Ink

Component	%
50% Phthalocyanine Blue water paste (C.I. Pigment Blue 15)	24.7
Acrylic emulsion	50.0
Water	20.0
Polyethylene wax compound	3.0
Monoethyleamine	2.0
Organic defoamer (polysiloxanes and hydrophobic solids in polyglycol)	0.3

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Printing Ink Industry
-Example Formulations-

Energy Curable Flexographic Ink

Component	%
50% Phthalocyanine Blue water paste (C.I. Pigment Blue 15)	15-20
Oligomer (polyester acrylate)	30-45
Monomer (trimethylol propane triacrylate, pentaerythritol triacrylate)	10-20
Photoinitiator	5-10
Wax	4-6
Additives	2-4

Photo-initiator Chemistry & Applications

PHOTOINITIATOR	PROPERTIES	APPLICATION
Benzophenone(s) / amine and BDK	□ Considerable yellowing upon UV exposure □ Absorption of UV-C and UV-B	□ Co-initiator for overprint varnishes and pigmented systems (surface cure)
□-Hydroxyketones	□ Absorption of UV-C and UV-B □ Low yellowing upon UV exposure	□ Overprint varnishes □ Co-initiator for pigmented systems (surface cure)
□-Aminoketones	□ Absorption of UV-B and UV-A □ Strong yellowing upon UV exposure	□ Highly pigmented systems (through cure)
MAPO / BAPO	□ Absorption of UV-A up to visible range	□ Highly pigmented systems □ White pigmented systems (TiO_2)

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Printing Ink – Film Thicknesses

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Table 2.1 Main characteristics of the printing processes

Print process	Ink film thickness (μ)	Typical halftone screen ruling (lines/cm)	Substrate types	Typical applications
Offset litho				
Sheet-fed	<2	47–80	Wide range of paper and board, plastic sheet and metal	All general print, business forms, technical documentation, promotional, magazines, credit cards
UV drying		60	Carton board	Packaging
Web-fed				
Heat-set	<2	52–69	Wide range of coated and uncoated paper	Magazines and similar format products
Cold-set	<2	25–40	Newsprint	Newspapers
Flexography				
Narrow web	0.75–2	60	Paper and plastic film	Labels, flexible packaging
Wide web	0.75–2	33	Newsprint	Newspapers
	0.75–2	52	Wide range of plastic film, paper, corrugated cardboard	Boxes and many other types of packaging, sacks
Gravure				
Large web	<6	60–80	Coated or uncoated paper	Magazines and similar products, mail order catalogues, woodgrain patterns
Smaller web	<6	60–80	Coated or uncoated paper, plastic films, board	Packaging (esp. flexible), cigarette cartons, postage stamps
Sheet	<6	150–200	Paper	Fine art reproductions

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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
- = 0.00007cubic 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)

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Printing Ink Industry

-Raw Material Supply Chain-

Pigments
Resins
Solvents
Additives

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Printing Ink Industry

-Manufacturing Processes/Unit Operations-

Weighing
Mixing
Milling
Filtering

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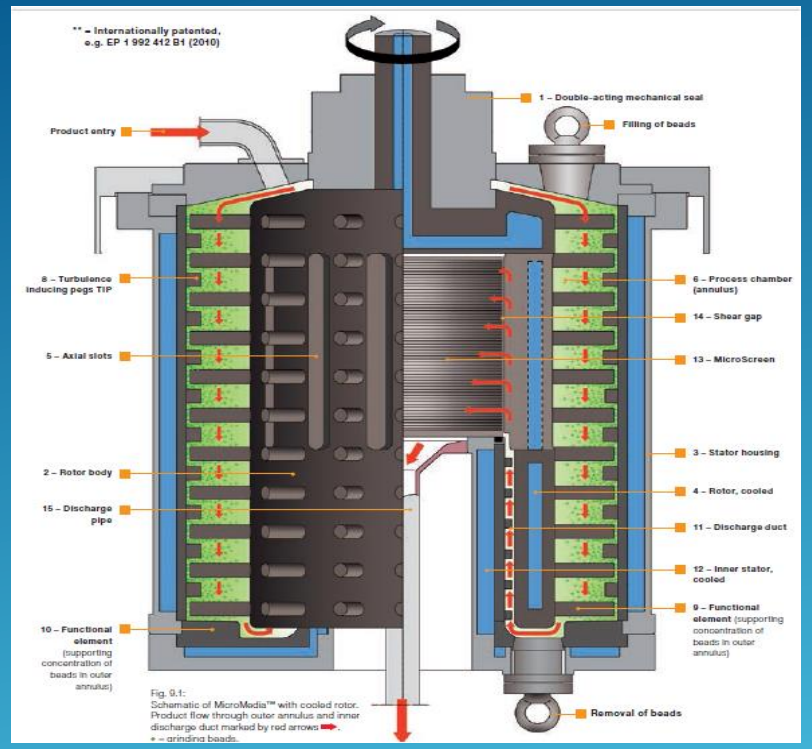
Printing Ink Industry

-Manufacturing Processes/Unit Operations-

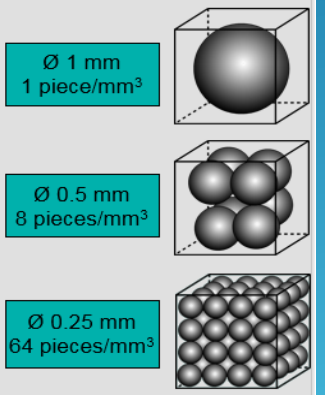


Number of Grinding Beads per Liter Grinding Chamber Volume

NETZSCH

Bead size (mm)	Number of beads (piece/l)
10	1,000
1	1,000.000
0.1	1,000.000.000
0.05	8,000.000.000

$$\text{Number} \uparrow \propto \left(\frac{d_{GM,large}}{d_{GM,small}} \right)^3$$



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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

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Thanks for Listening!

Questions?

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