Ink Jet Formulation- The Art of Color Chemistry

Presented by Michael A. Andreottola
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World Expo 2005, August 24-26, 2005, Las Vegas
History & Qualifications of American Ink Jet Corporation

- Privately Held Company founded in 1984 by Michael Andreottola, President & CEO
- Over 30 years experience focused only on ink jet inks
Background

- Leading manufacturer of compatible inks
- 1st to address fine art inks
- 1st to offer fade resistant dye based inks
- Produce inks for several wide format OEM printer manufactures
Accomplishments

1985 Developed High Color Gamut Ink for Applicon Ink Jet Printers
1988 First Company to Produce SWOP Inks for Ink Jet Printers
1990 Introduced “NASH” Inks for Fine Art Market
1991 Developed First Waterproof Ink/Paper System for U.S. Army
1992 Developed First Graphic Arts Ink for Use in Encad Ink Jet Printers
1995 First Company to Introduce Ink Refill Kits, Compatible Cartridges & Papers to Staples
1996 Achieved ISO 2001 Certification
1999 Developed Jasmine Inks for Encad Printers
2000 Toll Manufacturing; Developed “Pinnacle Gold” Lightfast Ink for Iris Printers
**History of Ink Jet Printing**

<table>
<thead>
<tr>
<th>Year</th>
<th>Inventor/Invention</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1867</td>
<td>Lord Kelvin</td>
<td>First practical experiments</td>
</tr>
<tr>
<td>1878</td>
<td>Lord Rayleigh</td>
<td>Basic physics of drop formation</td>
</tr>
<tr>
<td>1929</td>
<td>Hansell</td>
<td>Electrostatic deflection to write</td>
</tr>
<tr>
<td>1938</td>
<td>Genschmer</td>
<td>Pulsed pressure drop ejector</td>
</tr>
<tr>
<td>1951</td>
<td>Elmquist</td>
<td>First application - recorder</td>
</tr>
<tr>
<td>1968</td>
<td>AB Dick</td>
<td>Videojet 9600 coding printer</td>
</tr>
<tr>
<td>1968</td>
<td>Sweet/Cumming</td>
<td>Binary jet array</td>
</tr>
<tr>
<td>1968</td>
<td>Hertz</td>
<td>Continuous Jet (Hertz)</td>
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<tr>
<td>1977</td>
<td>Endo</td>
<td>Bubble Jet</td>
</tr>
<tr>
<td>1984</td>
<td>Hewlett-Packard</td>
<td>Thinkjet</td>
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<tr>
<td>1984</td>
<td>Seiko Epson</td>
<td>Piezo ink jet</td>
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<tr>
<td>1986</td>
<td>Dataproducts</td>
<td>SI-480 solid ink jet printer</td>
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<tr>
<td>1992</td>
<td>Kodak</td>
<td>Thermal ink jet</td>
</tr>
<tr>
<td>1992</td>
<td>HP</td>
<td>DeskJet 500C</td>
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<tr>
<td>1994</td>
<td>Canon</td>
<td>Bubble Jet 200</td>
</tr>
<tr>
<td>1994</td>
<td>Lexmark, Xerox</td>
<td>Thermal ink jet</td>
</tr>
<tr>
<td>1995</td>
<td>Tektronix</td>
<td>Phaser 340 phase change transfer</td>
</tr>
</tbody>
</table>
Facilities

- Research and Development carried on in Billerica, Massachusetts – USA
- Manufacturing in Billerica, Massachusetts – USA
- Zhuhai, China (2nd QTR 2005)
Ink Manufacturing

ISO 9001:2000 Certified
ISO 9001:2000 Certified
Calibrated Color Chemistry

- C3 Calibrated Color Chemistry™
  - Culmination of AIJ’s standards, techniques, and procedures for manufacturing emerging & traditional ink jet inks.

- Synergy rather than Trade-offs
  - C3 optimizes color, stability and economic characteristics to the requirements of the application.

- Science enabling Art
  - C3 fosters synergy by advancing color science, physics & chemistry principles.

- The Future of Ink Jet Printing
  - AIJ’s C3 approach to ink jet manufacturing is dedicated to realizing the findings of color science to build and deliver the best imaging and output technology available.
Dual Aspects of Ink Development

**CHEMICAL SCIENCE**
- Must be designed for compatibility with hardware
- Must be suitable to application
- Must be a reliable solution/suspension

**COLOR SCIENCE**
- Must be designed for compatibility with software
- Must be suitable to application
- Must maintain consistent density and accuracy

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WHERE
- Fine Art Printing
- Fine Art Reproduction
- Photographic Reproduction

WHY
- Advances in...
  - Ink Jet Droplet Sizes
  - Printhead Technology
  - Photo and Fine Art Ink Jet Media
  - Ink Jet Printer Cost Down
Applications: Driving the New Ink Technology

- FINE ART PRINTING
  - Types of Paper Used
    - Somerset
    - Arches
  - Ink Requirements
    - Highly Chromatic
    - Highly Saturated
    - Lightfast

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Applications: Driving The New Ink Technology

- TEXTILE
  - Cloth
    - Pre and Post Treatments to acquire Permanence
  - Ink Requirements
    - Specific Dye Class to react with Cloth
    - Inks must be Highly Saturated
What do customers want from their ink?

- Consistency
- Repeatability
- Color Match
- Print Image Quality
Ink Formulation Requirements

**INK**
- Good Stability
- Low Viscosity
- High Surface Tension
- Conductivity
- Long Shelf Life
- Non-Flammable
- Non-Toxic
- No Biological Growth
- Dye Solubility

**MATERIAL COMPATIBILITY**
- Non-Corrosive
- Plastics Compatible
- Adhesives Compatible
- No Particulate Formation

**DROP EJECTION**
- Uniform Drop Size
- High Drop Velocity
- High Drop Frequency
- No Orifice Wetting
- Non-Crusting
- Non-Clogging

**PRINT**
- High Optical Density
- Color Quality
- Fading Resistance
- Lightfastness
- Waterfastness
- Solvent Resistance
- Smear Resistance
- Off-Setting
- Crack Resistance
- Media Sensitivity
- Spreading
- Feathering
- Dry Time

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Ink Formulation Trade-Offs

TRADITIONALLY:
Optimizing ink composition for one requirement happens at the expense of another requirement.
Design of Ink Jet Inks

- Physical Properties
  - Viscosity
  - Surface Tension
  - Conductivity
- Purity
  - Filtration Properties of Dyes & Pigments
- End User Properties
- Print Quality of Samples
It’s All in the Ink

Viscosity
pH
Surface Tension
Conductivity
Filterability
Particle Size
Color
**Viscosity**

**DEFINITION:**
How easily an ink will flow. A property of a fluid that characterizes its perceived “thickness” or resistance to pouring. Viscosity along with surface tension determines drop size.

- If too high – ink may not flow through print head, starvation may also occur.
- If too low – ink will leak through print head

**UNITS OF MEASUREMENT:** Centipoise (cP)
Viscometer

EQUIPMENT:
Viscometer at a cost of $1,000 to $7,000 US. Requires a constant temperature bath at a cost of $2,000 to $10,000. Must check daily and calibrate at least annually.

TEST PROCESS:
Ink must be run at a constant temperature, volume and speed to ensure accurate & consistent measurements.
**DEFINITION:**

The acidity or alkalinity of the finished ink. Colorants also can determine the pH of ink as each dye has its own stable pH range.

- If too acidic – cogation/damage to print head electronics and other metal components.
- If too alkaline – cogation/damage to print head.

**UNITs OF MEASURMENT:**

A scale of 0 to 14. A pH of less than 7 is acidic; a pH of greater than 7 is alkaline. A pH of 7 is neutral.
What is pH?
The term pH derives from a combination of p for the word power and H for the symbol of the element Hydrogen.
Surface Tension

DEFINITION:
A measure of energy necessary to increase the surface area of a liquid. This along with viscosity determines drop size and determines how much a drop of ink will penetrate and spread on the paper.

- If too high – ink droplets will be too small and the droplets may not spread enough resulting in white space or underbanding; image will appear too light.
- If too low – ink droplets may spread too much causing excessive bleed, wicking and overbanding. Also, the drops may become too large reducing image resolution.

UNITS OF MEASUREMENT: Dynes per centimeter
Conductivity

**DEFINITION:**

This is a crucial measurement in determining the purity of an ink. Since dyes usually contain a quantity of salts i.e. NaC1 and Na₂₂₂₂₂₄₄₄₄S, significant amounts of these salts can precipitate from the ink and cause clogging of the jets.

**UNITS OF MEASUREMENT:** milli Siemens(mS)
Conductivity Probe

EQUIPMENT:
Conductivity probe at a cost of $200 to $2,000.

TEST PROCESS:
Ink should be measured within a predefined temperature range for consistency and accuracy of readings. The conductivity probe and/or cell constant of the probe is key, as different probes accurately measure conductivity only within specific conductivity ranges. The probe being used must match well to the sample.
Filterability

DEFINITION:
Determines if the ink been filtered properly. Ability to filter the ink through a sub micron filter in a specified amount of time.
If an ink is not filtered properly then clogging of the print head can occur.
If too high—may indicate bad components or biog

UNITS OF MEASUREMENT: A scale of 0-20
Filterability Test (SDI)

**EQUIPMENT:**
Lab flask, filter assembly and vacuum pump at a cost of $100-$900.

**TEST PROCESS:**
In this test, one measures the time ratio it takes for a specific volume of ink to pass through a filter paper of a predefined pore size.
Color

DEFINITION:

Color – accuracy of dye concentration

- If too high – bleed, precipitate, image will be too dense resulting in loss of detail.
- If too low – image will be too light resulting in loss of detail

UNITS OF MEASUREMENT:

Absorbance, % Transmission and Cie L*a*b*
How to Measure Color

1. Measurement versus a standard:
   CIELAB- Commission International de l’Eclariage
   - L=lightness
   - a=red to green
   - b=yellows to blues

   The three dimensional color standard by which we measure inkjet colors using Gretag equipment.

2. Visual, subjective judgment
COLOR MEASUREMENT

EQUIPMENT:
Spectrophotometer $9,000 to $50,000. The prices vary based on the instrument and the options on the instrument.

TEST PROCESS:
You are measuring the absorbance or percent transmission of an ink at a specific wavelength. The ink is diluted to a known volume (ie 1000 µL of ink in a 500 ml volumetric flask).
Primary Particle Size

DEFINITION:
Parameter used to quantify the size or mean value of a pigment particle in the ink after final filtration. This value is given in microns.

UNITS OF MEASURMENT:
Microns (µ) (One millionth of a meter)
Particle Size Analyzer

Particle size distribution
Particle Size Analyzer

**EQUIPMENT:**
Particle Size Analyzer at a cost of $20,000 to $60,000.

**TEST PROCESS:**
Ink is loaded into a sample chamber, where, for example, a laser is beamed through the sample and the amount of light scattering is related to the size of the particles in the ink. With these instruments, the average particle size and the particle size distribution can be measured.
## Component Chart

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactants</td>
<td>Ethoxylated alcohols, Ethoxylated Amines, Diphenyl sulfonate derivatives</td>
</tr>
<tr>
<td>Humectants</td>
<td>Glycols</td>
</tr>
<tr>
<td>pH Buffers</td>
<td>KCl &amp; HCl, Borax &amp; HCl, Borax &amp; NaOH, KCl &amp; NaOH</td>
</tr>
<tr>
<td>Colorants</td>
<td>AB9, DK168, RR31, DY132</td>
</tr>
<tr>
<td>Water</td>
<td>Reverse osmosis, De-ionized</td>
</tr>
</tbody>
</table>
Surfactants

Surfactants are used to help the ink coat the media properly and to reduce drop size (to increase image resolution).

- Multiple surfactants are sometimes needed
- Too much or the wrong surfactant can cause poor dry time.
Humectants/Viscosity Modifiers

Humectants are used to improve the drying properties of the ink and helps maintain the components solubility.

- If too much humectant is used there could be longer dry times. Adding humectants increases viscosity.

- If not enough humectant is used the inks could dry on the nozzle surface.
pH Buffers

pH buffers can become necessary if the pH of an ink is not stable.

- There can often times be a change of pH due to interactions between components

- Reactive dyes will hydrolyze over time dropping the pH.
## Colorants

- Dyes and/or Pigments are used to provide color to the inks

### Dye
- Not Usually Waterfast
- Brighter Colors
- Less UV Stability
- Larger Color Gamut
- Lower Optical Density
- Use with many medias

### Pigment
- Usually Waterfast
- More Dull Colors
- UV Stable
- Smaller Color Gamut
- Higher Optical Density
- More Media Specific
Complexities of Ink Formulas

- **PAST**
  - $\text{H}_2\text{O}$  85-90
  - Glycerine  10-15
  - Biocide   <1%
  - Dye      2-8%
### Inks: Past, Present & Future

#### PRESENT

- Printheads More Sophisticated
- Smaller Orifice
- Smaller Drop Size
- Dyes are Cleaner (salts, heavy metals, etc. removed)
- Ultra-Filtration and Ion Exchange used
- New Methods of Manufacturing being used
- More versatile applications for ink jet are being introduced which translates into more ink R&D
- Disciplines of Bio-chemistry, Chemical Engineering, Organic Synthesis, Polymer Chemistry, Colloid Science, & Color Science now being utilized
Complexities of Ink Formulas

- PRESENT - FINE ARTS / GRAPHIC ARTS
  - H₂O
  - Humectants
  - Solvent 1
  - Solvent 2
  - Surfactant
  - Dyes
  - Biocides
  - Buffer
  - Ultrafiltration
  - Ultrasonics
Formulations

❖ TEXTILE INKS
  ❖ Dye or Pigment
  ❖ Biocide
  ❖ Glycols
  ❖ Glycol Ether
  ❖ Alcohol
  ❖ Surfactants
  ❖ Resins
  ❖ Electrolyte
  ❖ Manufacturing Process
  ❖ Filtration
Formulations

- UV CURABLE INKS
  - Dye or Pigment
  - Solublizer
  - Biocide
  - Resins
  - Glycol
  - Glycol Ether
  - UV Initiator
  - Manufacturing Procedure
  - Filtration
Design of Ink Jet Inks

- Droplet Generation & Jet Stability
  - Polymer Solution Thermodynamics
  - Rheology & Jet Restoring Energy
- Reliability
  - Chemical & Ageing Stability on a Molecular Level
  - Formulation Sensitivities
- Functionality
  - Build in Application Features
Good Print Quality Starts with Good, Uniform Drops of Ink

- Are the ink drops uniform in shape—round?
- Is the distance between ink drops similar?
- Are the drops of ink in a consistent pattern?
- Does the ink wick into the paper (or paper fibers)?
- Does there appear to be extra drops of ink?
Calculation of Drop Velocity
Examples of Good & Poor Drop Formation Due to Varying Dynamic Surface Tension

AIJ-Poor

Competitor-Poor

AIJ-Good

OEM-Good
Dot Quality

Multipurpose Copy Paper

Poor Dot Quality

Good Dot Quality

This image is of a period after an 8 point font and is comprised of several drops of ink.
Dot Gain

- Dot Gain is the degree of spreading of a given dot
  - Controlled = smaller dots = better print quality
  - Not Controlled = larger dots = poor print quality
Measuring Dot & Text Quality

Image Analyzer

ISO 9001:2000 Certified

American Ink Jet Corporation
Color Gamut (plain paper)

Epson Printer on Plain Paper
a* b* projection, D65 2deg obs

OEM ink

Not much difference on plain paper

3rd party ink

ISO 9001:2000 Certified

imageXpert inc.
Color Gamut (plain paper)

Superimposition shows small differences

OEM ink
3rd party ink

ISO 9001:2000 Certified
Color Gamut (Photo Paper)

OEM ink

3rd party ink

Much more difference on photo paper

ISO 9001:2000 Certified
Color Gamut (Photo Paper)

Superimposition shows significant differences

Epson Printer on Photo Paper
a* b* projection, D65 2deg obs

OEM ink
3rd party ink

imageXpert inc.
Color Charts

3D Gamut

2D Color Plots
CIELAB Gamut Volume

- Chroma
- Hue
- Lightness

AIJ Pinnacle Gold Watercolor
How to Measure Color

Spectrophotometer

- measures dye concentration for ink development in matching colors.

Color Profile System
Defining Fade

- No industry standard for measuring ink jet print life at this time
  - Currently using textile and photographic testing models
  - ANSI Std. IT9.3 in process; defines metric for testing but not endpoints nor extrapolation of print life
- Commonly measured as loss of optical density
  - Common endpoint 30% loss of weakest primary
- Two key factors overlooked
  - Resulting color changes (∆E)
  - Fade rates for individual colors (vs. average)
Catalytic Fading

- When inks are more stable individually than in combination, accelerating their own fading.

- Excited dyes can produce singlet oxygen leading to oxidative fading as well as transfer their absorbed energy to another dye at a lower energy level resulting in more radiative exposure & fading.
Reductive Fading of Azo Dyes

- Dye reduced to its corresponding amines by abstracting a hydrogen atom from a hydrogen donor.

- Many ink vehicle and media components are hydrogen donors and can function as photocatalysts.
  - Alcohols, amines, ketones, carboxylic acids, ethers & esters.

- The reaction is accelerated when the hydrogen donor or dye is photo-excited.
Oxidative Fading of Azo Dyes

- The attack of singlet oxygen on the hydrazone tautomer of an azo dye
- The initial reaction leads to the formation of an unstable peroxide which then undergoes decomposition
- The reaction is promoted by singlet oxygen sensitizers. Some dyes are themselves sensitizers.
Black Magic vs. Molecular Modeling

- Chromophore
- Partial charges on selected atoms for substituted
- 1-phenylazo-2-naphthols
Fade Testing

Atlas Ci3000
Xenon Weather-Ometer
Standards For Ink Jet Print Output

For years there has not been standard for ink jet prints

FADING

- Wilhelm
- Kodak
- Epson
Ink & Media Relationship

- Poor spread & excess penetration
- Ideal spread & penetration
- Excess penetration & spread

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Media Independence

AIJ 1 on Canary/ Paper 1 Poor Wetting

AIJ 1 on Xerox/ Paper 2 Good Wetting

ISO 9001:2000 Certified
Media Independence

AIJ 2 on Canary/ Paper 1 Good Wetting

AIJ 2 on Xerox/ Paper 2 Good Wetting
How Important is it to Choose the Proper Surfactants & Co-Solvents?

- Pigment Black AIJ 1
  - Poor Wetting

- Pigment Black OEM
  - Acceptable Wetting

- Pigment Black AIJ 2
  - Improved Wetting

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Specific Inks vs. Universal Type Inks

Good Color Match

Original Photo Image

Poor Color Match

Universal Type Inks

ISO 9001:2000 Certified
What is Intercolor Bleed?

When printing two different color inks next to each other the objective is to have clean, distinct borders between the colors. When one color migrates into the space of the other color & the border becomes tattered & uneven.

Spreading - overall expansion of the printed area.

Feathering - wicking of ink along a narrow band or line away from the image area.
## Inter-color bleed

Here are the measurements:

### Bleed SQ 3 Run 2 Fail

<table>
<thead>
<tr>
<th>Status</th>
<th>Measurement Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>focus on Y</td>
<td>20.10679</td>
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<tr>
<td>F</td>
<td>on Y line width</td>
<td>0.28409</td>
</tr>
<tr>
<td>F</td>
<td>top on Y mean dev</td>
<td>0.00374</td>
</tr>
<tr>
<td>F</td>
<td>top on Y RMS dev</td>
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</tr>
<tr>
<td>F</td>
<td>bottom on Y mean dev</td>
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<tr>
<td>F</td>
<td>bottom on Y RMS dev</td>
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<td>F</td>
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<tr>
<td>F</td>
<td>bottom on P RMS dev</td>
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### Bleed SQ 2 Run 1 Fail

<table>
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</thead>
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<td>F</td>
<td>on Y line width</td>
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<tr>
<td>F</td>
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<td>F</td>
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<td>F</td>
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<td>F</td>
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<tr>
<td>F</td>
<td>bottom on P RMS dev</td>
<td>0.00899</td>
</tr>
</tbody>
</table>
How to Measure Image Quality

- Compare samples printed on the same paper type and brand
- Print and measure on both low cost and higher cost substrates since print quality varies widely
- Use the same driver settings
- Flush printing system between ink sets to avoid contamination...
Intercolor Bleed
Compatible ink on different media.

Multipurpose Copy Paper

Bright White Inkjet Paper

Photo glossy paper

ISO 9001:2000 Certified
Intercolor Bleed HP Colors

- **FORMULA**
  - H2O
  - Humectant –1
  - Humectant –2
  - Humectant –3
  - Surfactant –1
  - Surfactant –2
  - Dye
  - Biocide
  - Dye

- **To Solve the Problem:**
  - Replace Surfactant –2 with Penetrant
  - This allows the ink to be absorbed vertically into the paper & decrease the lateral spreading of the inks
Most Promising To Date

  - Designation: F 1944-1998
    Standard Practice for Determining the Quality of Text, Line - and Solid Fill
    Output Produced by Ink Jet Printers
  - Designation: F 1857-1901
    Standard Terminology Relating to Ink Jet Printers & Images Made There from
More information on Ink Jet Inks...

Ink Jet Technology & Product Development Strategies
By Stephen F. Pond, Ph.D. & Torrey Pines Research
Copyright 2000
ISBN# 0-9700860-0-8
Website: www.tpr.com

Handbook of Imaging Materials 2nd Edition Revised & Expanded
Co-edited by Art Diamond of Diamond Research Corp. & Dr. David S. Weiss of Heidelberg Digital LLC
Copyright 2001
ISBN# 0-8247-8903-2
Website: www.imagingnews.com