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Introduces…

A Quick Guide to Ink-Jet Formulation

Jim Bullock & David Calvert

19th April2016

Ink-Jet Formulation Fundamentals, 9th June 2016

www.iformulate.biz/training-and-events/ink-jet-formulation-fundamentals/

iFormulate *Skills*

Overview:

1. Why Choose Ink Jet Printing?
2. How Does It Work?
3. What's in an Ink?
4. Stabilising Inks
5. Performance and Testing
6. Summary and Learning More

This webinar is being recorded and will be made available

The audience is muted and you may ask questions using the question function in GoToWebinar

This webinar will last about 30 minutes

Your Speakers

Dr Jim Bullock
iFormulate Ltd

Dr David Calvert
iFormulate Ltd

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A Little About iFormulate

A company founded in 2012 by two experienced industry professionals…

Combining diverse experiences, knowledge and wide range of contacts:

…polymers, materials science, chemistry, imaging, dyes, pigments, emulsion polymerisation, biocides, anti-counterfeiting, environmental, formulation, consultancy, marketing, business development, strategy, regulatory, training, events, R&D, innovation

Complementary network of Associates

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Our Services

iFormulate Consult

iFormulate Strategic

iFormulate Skills

Acknowledgements

- Mark Holbrook
- Ink-Jet Formulation Fundamentals

  One-day Training Workshop: 9th June 2016, Jurys Inn Hotel, East Midlands Airport, UK.

  See: http://bit.ly/IJ-Fund and at the end of this webinar

- Brand names are provided as examples of products available and are not endorsements

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1. Why Choose Ink-Jet Printing?

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1. Why Choose Ink-Jet Printing?

- Speed
- Flexibility and convenience
- Customisation
- Quality
- Integration with digital imaging and design
- Adaptability to new technologies outside imaging and reprographics
  - Using precise X-Y positioning and droplet dosage
  - Electronics, pharma, diagnostics, additive manufacturing…

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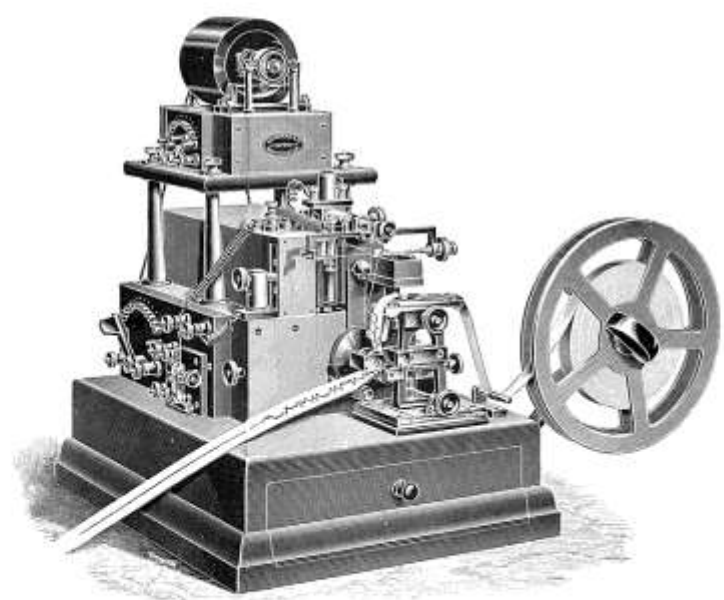
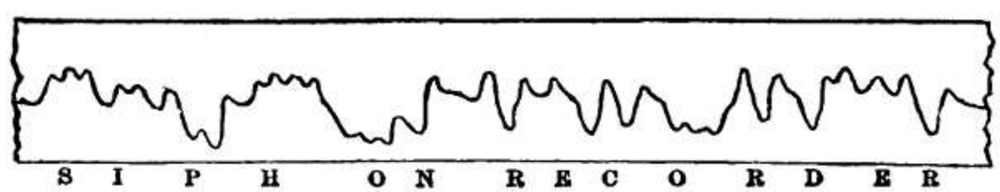
2. How Does Ink-Jet Printing Work?

Ink-Jet: History

1749: **Abbé Nollet** demonstrated the effect of static electricity on a stream of drops

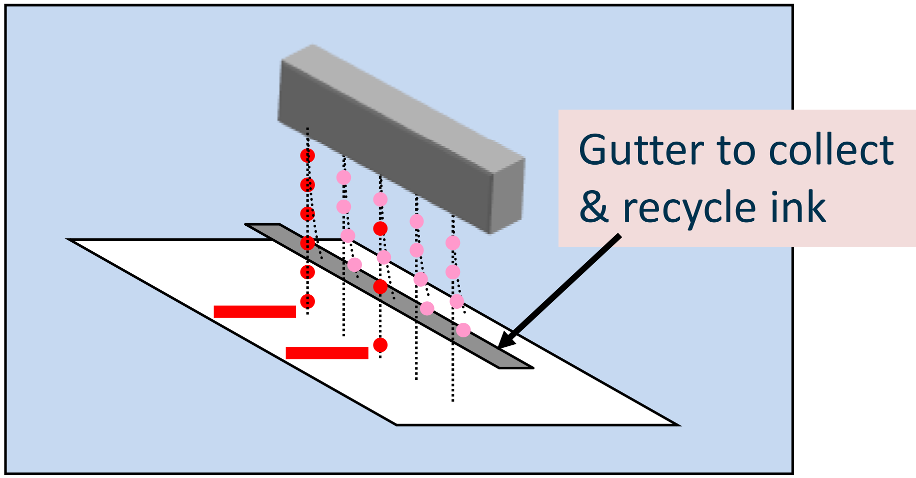
1858: The Siphon recorder (**William Thomson**) was the first practical continuous inkjet device.
Used for recording telegraph messages





Basic Ink-Jet Technologies

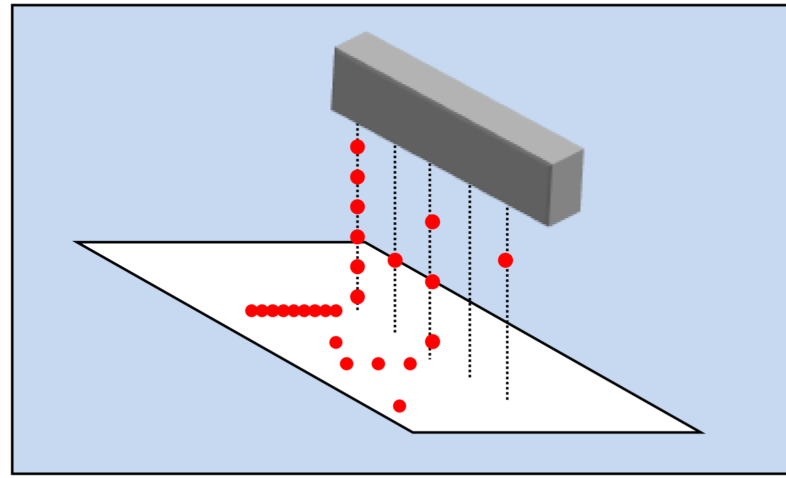
Continuous



Continuous streams of drops generated and deflected onto or off the substrate

Binary **Multi-level** **Hertz**

Drop-on-Demand



Drops generated only when required

Piezo **Thermal**

Images: Mark Holbrook
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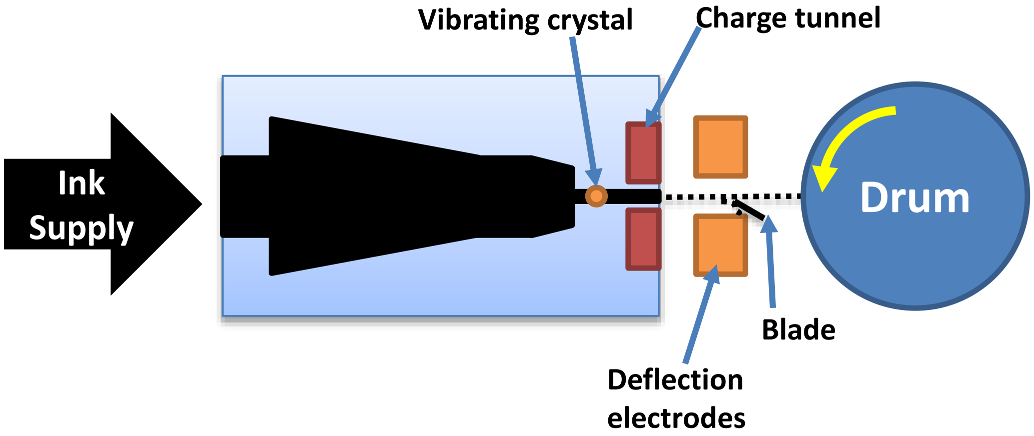
Continuous Ink-Jet

- Ink is pumped through small nozzle breaks into droplets
- "Plateau-Rayleigh Instability" – liquids tend to minimise their surface area (dripping tap effect) .
- Droplet deflection is achieved by electrically charging these droplets.
- Unused drops are collected and recycled



- Hertz technology (Iris, Stork) has highest image quality
- 10pl droplets
- High frequency > 1MHz

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Continuous Ink-Jet

Advantages

- High speed printing – due to high drop ejection frequency
    - E.g. Videojet 1650 UHS CIJ Printer claims >500m/min line speed (marking)
- Wide solvent choice: Aqueous, volatile organics
- High drop velocity means long “throw” distances – head can be further from substrate

Disadvantages

- Low resolution images (apart from Hertz technology)
- High maintenance requirements
- Fluids must be electrically chargeable

Typical Uses

- Most usage is for industrial and commercial printing
- Industrial marking – sell by dates, lot numbers and packaging (food, drinks), eggs.
- Textile printing (Hertz)

Other Technologies for Continuous

- Binary (Scitex, Videojet), Multilevel (Domino)

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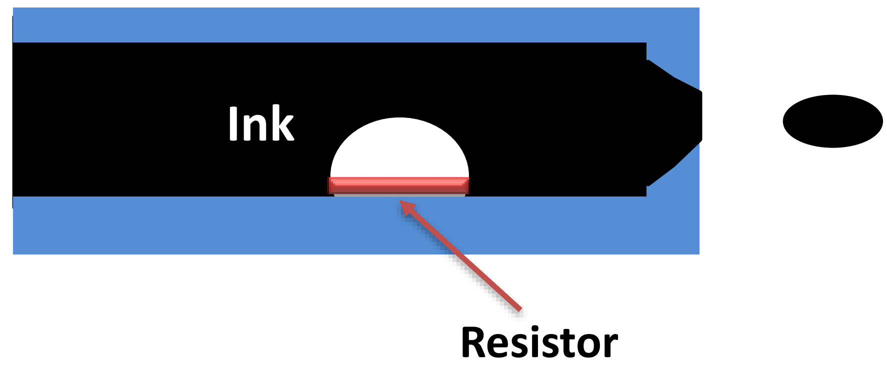
Drop-on-Demand Ink-Jet

Thermal DoD (Canon, HP, Lexmark)

Resistor heats the ink producing a bubble which ejects a droplet

Most commonly used for desktop (**Small Office Home Office: SOHO**) and office printers, but also in wide format graphics.

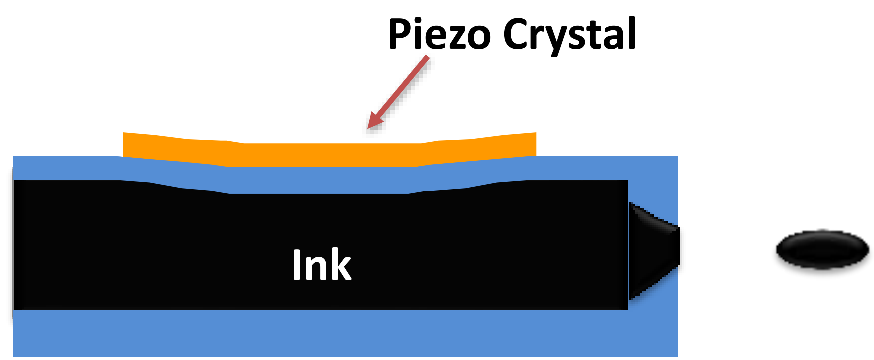


Piezo DoD (Epson)

Piezo crystal lead zirconium titanate (PZT) deforms under application of electric field

Piezo effect introduced by 'poling' the crystal in a strong electric field

Used in desktop (SOHO), business and industrial/commercial applications.



Images: Mark Holbrook
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Thermal Printhead

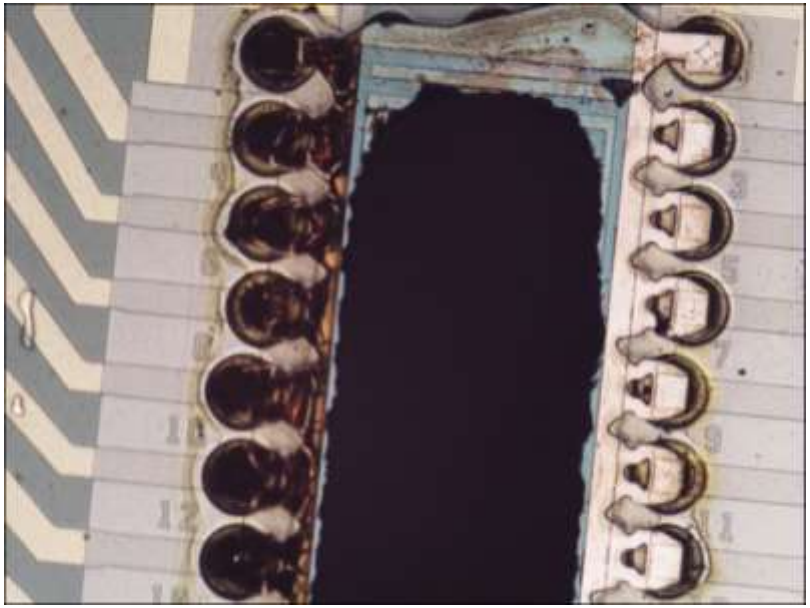

Image: Looking underneath the gold nozzle plate

Image: Mark Holbrook
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1995 SOHO (HP Deskjet):
300 nozzles operating at 8kHz
Producing a 35pl droplet
With an image resolution of 600 dpi

2006 Industrial (HP Designjet):
10,000 nozzles operating at 36kHz
Producing a 2pl droplet
With an image resolution of 1200dpi

Today: Canon FINE (Photolithography)
9600 dpi
>6,000 nozzles in a 20mm x 16mm area
1pl (1×10^{-12} litre) droplet
Drop diameter 1.24×10^{-5} m
Nozzle size: 9µm (about 75% of drop)

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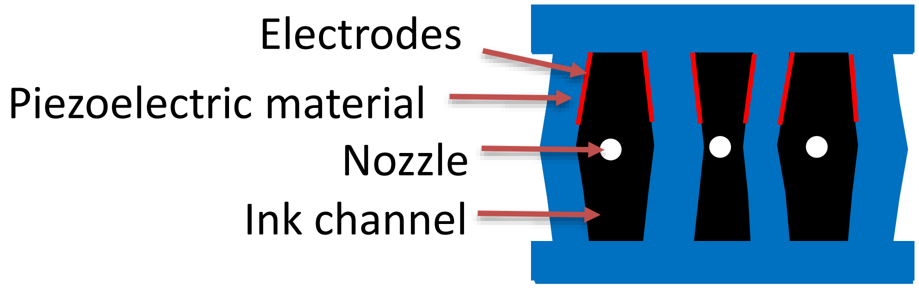
Piezo Ink-Jet

Piezo is the preferred printhead technology for DoD industrial applications despite the higher cost

Advantages over thermal:

- More robust → longer lifetimes
- More controlled droplet formation process
- Greater range of ink chemistries possible (no heating)
- Tolerates wide range of ink physical properties

Several different piezo modes including “edge shooter” (Fujifilm Dimatix Spectra), “piston” (Trident) and “shared wall” (Xaar)



Shared wall

Shear mode – electric field is perpendicular to poling direction

Images: Mark Holbrook
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3. What's in an Ink?

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Printhead Technology Places Demand on Inks

Examples

- Stability to repeated heating cycles (thermal)
- Stability to repeated shear cycles (piezo, thermal)
- Evaporation loss (continuous)
- Avoidance of nozzle blocking (all)
- Droplet charging (continuous)
- Reliable droplet formation (all)
  - Function of rheology, surface tension
- Materials compatibility (all)
  - E.g. direct contact with piezo material in shared wall heads

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End-Use Application Places Demand on Inks

Examples

- Consistent reproduction of colour (hue, saturation)
- Image resolution and colour depth
- Colour fastness (light, water, touch, abrasion)
- Colour bleed
- Rapid drying (industrial)
- Substrate compatibility (appearance, mechanical stability)
- Substrate affinity (paper, textile, plastic…)

And of course inks need to be stable to storage under a wide range of conditions as well as during the filling process…

What’s in an Ink Formulation?

- **Colour** (usually): Dyes or pigments
- **Dispersing agents** (for pigments): Usually a functionalised co-polymer rather than a classical surfactant
- **Wetting agents** (surfactants): Control surface tension
- **Co-solvent**: Enhance solubility of dyes
- **Humectant**: Prevent drying out or make the “crust” more mobile
  - Also act to tune the viscosity of the ink
- **Penetration enhancer** (e.g. glycol ethers)**:** Enhance end application properties
- **Binder:** Polymer to enhance affinity to substrate
- **Biocide:** Preservative for water-based inks
- **pH buffer:** Dyes or dispersing agents may be pH sensitive.
- **Solvent**: Water or organic

Dyes or Pigments in Ink-Jet?

- Dyes are **soluble** in the ink medium.
- Pigments are **insoluble** and are dispersed in the ink medium

Property	**Dyes**	**Pigments**
Ease of formulation	Soluble – easy to formulate	Insoluble – harder to formulate
Colour shade	Bright. Tuneable shades	Bright. Restricted shades
Colour strength	Lower	Higher
Clogging nozzles	Low risk	Higher risk
Rub fastness (dry)	Good	Poorer
Gloss	Good	Poorer
Water fastness	Poor	Good
Light fastness	Poor	Good
Penetration and spread	Poor	Good
Image quality	Poorer	Better
Chemical degradation	Higher risk	Lower risk
Storage stability	Better	Poorer

Example Dyes in Ink-Jet

Yellow:

e.g. Acid Yellow 23 (tartrazine), Direct Yellow 86 (disazo), Direct Yellow 132 (disazo)

Magenta:

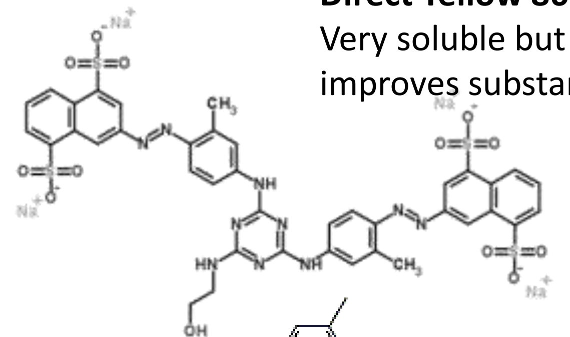
e.g. Acid Red 52 (rhodamine B), Acid Red 249 (azo), Reactive Red 180 (azo)

Cyan:

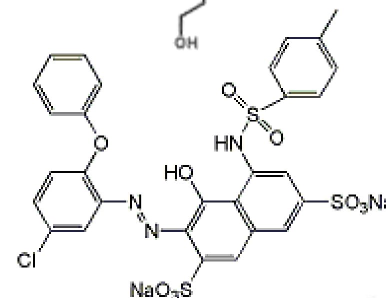
e.g. Acid Blue 9, Direct Blue 199 (phthalocyanine)

Black

e.g. Food Black 2 (disazo), Direct Black 168 (disazo), Direct Black 19 (tetrakissazo)

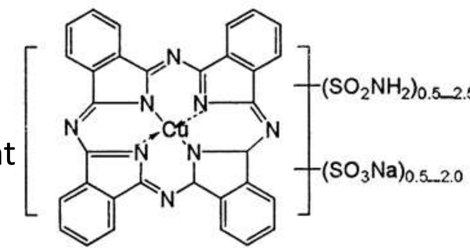


Direct Yellow 86
Very soluble but large size improves substantivity

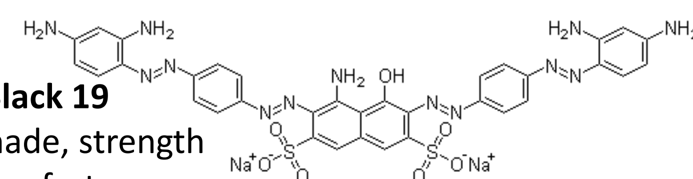


Acid Red 249
Less bright than Red 52 but with better light fastness

Direct Blue 199
Cheap, soluble and bright with high light fastness. *"Fade to blue".*



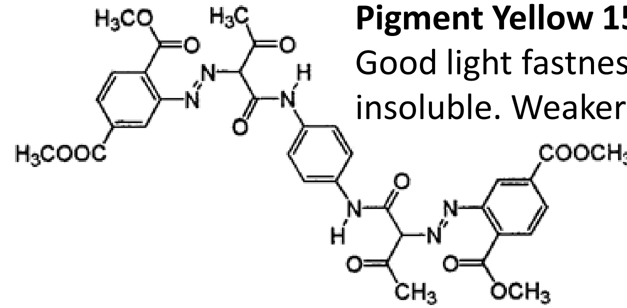
Direct Black 19
Good shade, strength and water fastness



Example Pigments in Ink-Jet

Yellow:

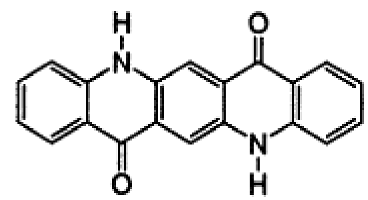
e.g. Pigment Yellow 74 (azo), Pigment Yellow 155 (disazo)



Pigment Yellow 155
Good light fastness and insoluble. Weaker than PY74

Magenta:

e.g. Pigment Red 122, Pigment Red 202, Pigment Violet 19 (all quinacridones)

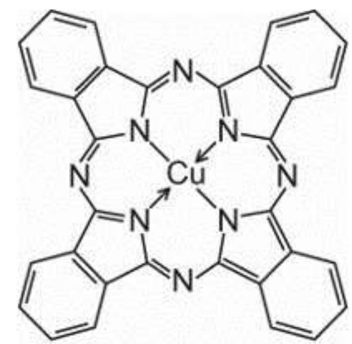


Pigment Violet 19
Red shade magenta, blend with e,g. PR 122

Cyan:

e.g. Pigment Blue 15 (copper phthalocyanine)

Pigment Blue 15
Good shade, v.good light fastness, low solubility, easy to disperse and stabilise



Black

Pigment Black 7 (carbon black)

Carbon black
Numerous variety of grades and suppliers
Purity is important

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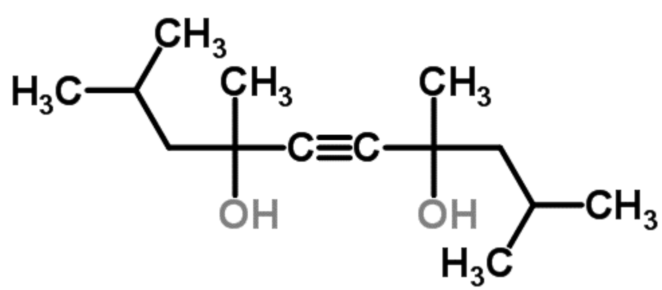
Some Other Components and Properties

Surfactants

- Control surface tension (ST) of the ink - usually 32-36 mN/m (dynes/cm)
  - If ST is too high the droplets won't disengage
  - If ST is too low the droplets may drip and nozzle plate wetting may occur
- Must act at a range of shear rates from <1 sec^{-1} in flowing ink to 10^6 sec^{-1} as the ink passes through the nozzle
  - **Dynamic** surface tension is critical here → fast acting surfactants
- Low foaming surfactants also required
- Frequently used: Acetylenic diols (e.g. Surfynol® types - Air Products)



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Some Other Components and Properties

Viscosity Adjustment

- Control viscosity of the ink - usually 1-3 cps for SOHO printers or around 10cps (at 30°C) for industrial piezo printheads
  - If viscosity is too high, the nozzles will refill too slowly
  - If viscosity is too low, the droplets may break up
- Sometimes the other ink components will give a viscosity in the right range
- For higher viscosity inks it may be necessary to adjust the polymeric components of the formulation or use a higher mol. wt. PEG

Humectants

- Prevent water loss and inhibit formation of a hard crust
- Bind to water using a hydrogen bonding network
- Glycols, glycerol, urea (for textile inks)

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Generic Ink-Jet Formulation

Component	%	Purpose
Dye or Pigment	2 - 6	Colour
Diethylene Glycol	5 - 15	Water miscible solvent
Glycerol	0 - 10	Humectant
2-Pyrollidone	0 - 10	Humectant / Dye solubility
Surfynol® 465	0.5 - 2	Surfactant
Proxel® GXL	0.2	Biocide
Buffer	0.5 - 2	pH control
Water	to 100	

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Example Ink-Jet Formulation

(Canon US Application US 2012/268532 A1)

Pigment	4.0%
Resin	0.8%
Glycerol	9.0%
Diethylene Glycol	3.0%
Acetylenol E100	0.39%
Water	Balance

Ink surface tension = 36mN/m

- A simple but typical formulation
- The resin (polymeric dispersing agent) is to improve dispersibility and ejection stability in thermal ink jet.
- The example resin is quite typical: Low mol wt. styrene/ butyl acrylate / (meth)acrylic acid copolymer

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4. Stabilising Inks

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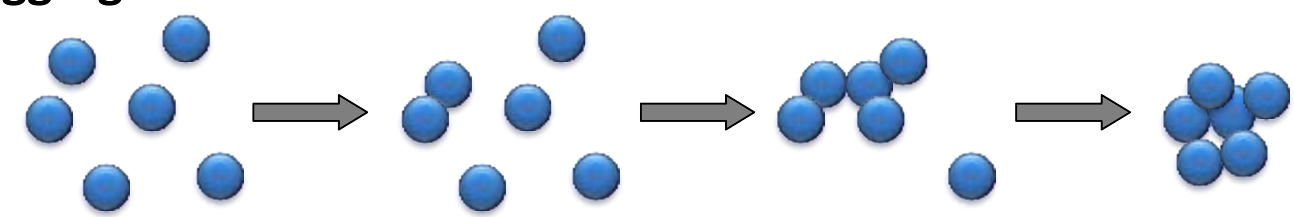
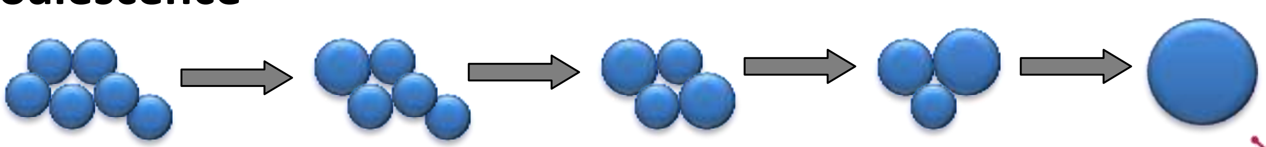
Colloids and Collisions: A Little Science

- Many ink-jet inks contain (colloidal) particles well under 1μm in diameter
  - Pigment particles, polymers and occasionally emulsion droplets
- Colloidal particles collide with each other due to Brownian motion, convection, gravity
- This can result in **coagulation** of the particles and **destabilisation** of the colloid.

Aggregation



Coalescence



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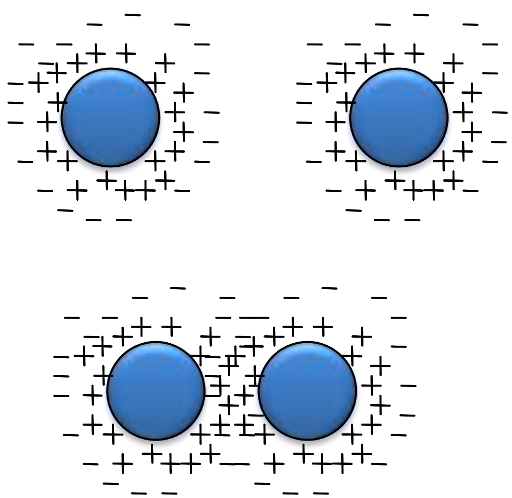
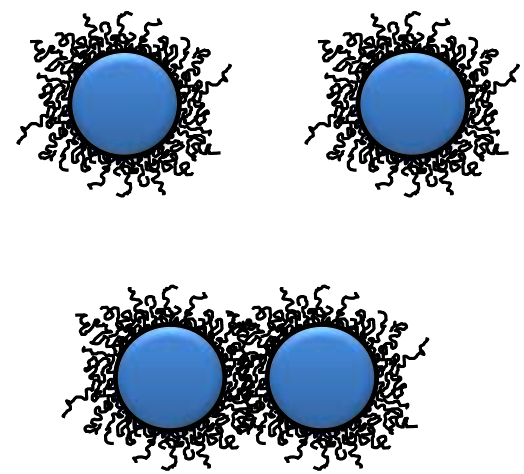
Two Ways of Stabilising Dispersions of Particles

Electrostatic potential



Coulombic repulsion →
electrostatic stabilisation

Steric potential



Entropic hindrance →
steric stabilization

- In **non-aqueous solvents** charged surfaces are less likely and the fluid is insulating, so **steric** stabilisation will dominate

Adapted from Prof Ian Scowen, iFormulate Nanoformulation Course 2013

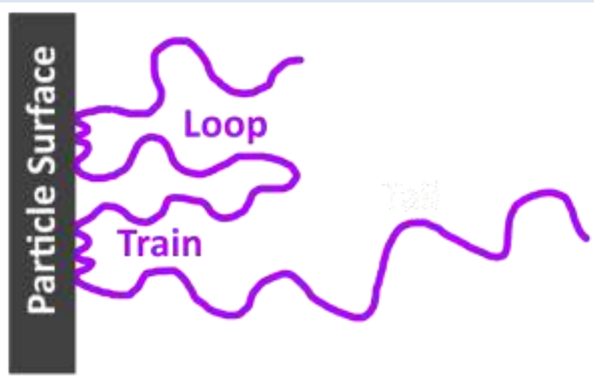
How Do I Build in Stabilisation?

Electrostatic Stabilisation

- Provide a charged pigment surface, typically by adsorbing charged species
- Usually anionic
- A zeta potential (ζ) measurement may be useful.
  - Rule of thumb: a Zeta potential of -30mV (or +30mV) is required
  - Can also observe how ζ changes with pH, to set an optimum pH

Steric Stabilisation

- Adsorption of long polymeric chains protruding from the surface
- Co-polymers with a region which also binds tightly to the pigment surface
- Polyelectrolytes may provide electrostatic and steric stabilisation in one



5. Performance and Testing

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5. Performance and Testing

- **Testing During Ink Development, e.g.:**
  - pH, viscosity, surface tension (static and dynamic), contact anle
  - Particle size (dynamic light scattering), zeta potential
  - Storage stability
- **Operability Tests, e.g.:**
  - Drop formation (stroboscopic high speed camera)
  - Operability (extended printing times, restart performance, “open time”/decap, nozzle clogging
- **Print Tests, e.g.:**
  - Colour properties, reflected optical density
  - Bleed, strikethrough, image quality, mottle
  - Fastess to water, rub, light, highlighter pen

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6. Summary and Learning More

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Summary

- Choice of dye or pigment
- Understand functions of additives
- Understand stability mechanisms
- Understand substrate and end-application
- Measure and understand performance parameters: Formulation, jetting, image quality
- Be aware of IP
- These principles are also applicable to non-imaging Ink-Jet applications

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Learning More: Ink Jet Formulation Fundamentals

One-day Training Workshop:

9th June 2016, Jurys Inn Hotel, East Midlands Airport, UK.

See: http://bit.ly/IJ-Fund

Back by popular demand in 2016, and featuring experienced ink-jet formulator and iFormulate Associate Partner Mark Holbrook, the workshop will enable you to:

– Learn about the principles of ink-jet printing

– Better understand the science that underpins stable ink formulation

– Introduction to main print-head technologies and printer architectures

– Learn about the different types of ink-jet colorants, their key properties and performance in formulations

– Understand the function and performance of the main additives used in aqueous ink-jet formulations

– Know how inks are tested and prints are evaluated

– Gain an overview of newer applications for ink-jet technology

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Any Questions?

- Participants remain muted
- Please use the GoToWebinar question boxes
- Any follow up questions or other enquiries:

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