Recent Advances in Inkjet Ink Technologies

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Summary

For those who have been involved in inkjet since those early pioneering and frankly, "unreliable" days, much has been achieved and inkjet has become a robust technology and a proven commercial success. Much of this success is due to advances in ink technology and yet the most exciting prospect is, probably the best is yet to come. There will be continued innovation and it is predicted the key driver for success which will open up many new opportunities, is ink.

The difficulty in the design of inkjet inks, essentially arises from the importance of developing an ink in synergy with a particular printhead. It is necessary to combine chemistry and physics to produce a fluid that behaves in a very precise way, reproducibly and where the principle of operation relies on the performance of the ink to run under extreme conditions as the norm.

Very simple in concept, highly complex in practice! There is no easy lesson in ink design and this paper will concentrate on the following;

Physical, chemical and stability properties of ink design for continuous multi deflection and binary inkjet, industrial piezo drop on demand and office piezo and thermal inkjet printheads.

Key aspects of ink chemistry to illustrate the range of performances now achievable for a variety of commercial inkjet printing applications.

Ink technologies will be identified and the most important recent patents will be examined to predict important trends in the future.

Introduction

Commercially inkjet printing is a relatively young industry, less than twenty years old although as a science it dates back to over one hundred and fifty years to Lord Rayleigh. The growth of inkjet printing has been truly remarkable and so far, it probably only represents the start of one of the most important changes in the printing industry we are likely to witness; an industry which has seen little significant technological advance for almost two hundred years. It is the newest of all printing processes and its diversity and versatility will ensure growth will continue at a fast pace, creating a revolutionary change over the next decade.

Today, the presence of inkjet in our daily lives is clear for all to see. From "Best Before" dates on packages in the Supermarket, through to document printing in the home and office, receipt of personalised mail and postal codes on envelopes that arrive through the letter box and even a red code found on eggs which greet us at the breakfast table at the start of each day.

The explosion in applications has occurred during the last six or seven years and the presence of polymer and colour chemistry has become increasingly more important. In the case of colour the use of dye or pigment is now one of the most widely debated topics in the industry and we have now seen the introduction of process colour inkjet printing. Similarly, for most emerging applications, polymer chemistry has become a central feature of ink development and more and more effort, is likely to be devoted to tailoring polymers for inkjet in the near future. As the application set increases, it is inevitable ink design will become more complex and more demanding. In addition, the conventional thinking of applying a particular known printhead technology traditionally used in a market for another application in a similar market, is now changing and the choice of printhead is now being driven by the application requirement. This in turn, means the inkjet chemist must now be able to design an ink for use in different printheads for a wide range of applications. The resultant outcome is an exciting prospect for the inkjet chemist.

Ink Design

There is a range of commercially important inkjet techniques, namely, continuous multi deflection and binary continuous inkjet (CIJ), drop on demand (DOD) piezo, thermal (TIJ) and valvejet. In considering ink design, it is important to emphasise whilst there are some general common chemistry and physics rules that apply across all techniques, ink design for each printhead technique is very different. No one technique, with the exception of simple valve operated systems, presents more or less difficulty than the other to produce a good reliable design.

In Table 1, an attempt is made to describe the key aspects of ink design for the various inkjet techniques. Aspects of valvejet ink design is included in Table 1 for completeness but will generally be excluded from discussion because within the set of printing applications and apart from using it as a special fluid delivery system, it is relatively un interesting from an ink development viewpoint.

Overall, the most common feature across all important inkjet techniques, is the need to design an ink with complete and total reliability. Describing reliability of ink design is difficult in terms of the usual physical properties such as viscosity and surface tension. There are many intrinsic physical and chemical properties contributing to ink design and during an ink development all of these properties need to be examined and re-examined. In the final analysis there are two essential properties which completely describe reliability and these are; consistency of flow through the nozzle and the exit contact angle of the ink leaving the nozzle. Consistency of flow, is not only the homogeneity of the fluid, it is more importantly, achieving stable rheological behaviour. Any perturbation of the flow within the nozzle region is amplified in an erratic instability of the jet during flight. Similarly, controlling the meniscus and therefore the exit contact angle largely influences jet directionality and consistency of jet break up.

If these two parameters are comprehensively controlled then reliability is assured. Conversely, if these two parameters are not well understood then reliability can not be guaranteed without subjecting an ink to many months or years of laboratory scrutiny.

Table 1. Key Aspects of Ink Design.

Ink Property	CIJ Binary	CIJ Multi Deflection	DOD Piezo	DOD TIJ	DOD Valvejet
Complexity	High	High	High	Med	Low
Flexibility	Med	High	High	Low	Med
Functionality	Med	High	High	Low	Med
Purity	High	Med	Med	High	Low
Reliability	High	High	High	High	Med

Differences in design can be highlighted in considering the different rheological behaviours in two contrasting printheads. In the case of continuous inkjet printing, an ink is subjected to very high shear rates, typically $1x10^{6}$ s^{-1}, but during flow through the nozzle, the flow is in dynamic equilibrium. In contrast, for an open nozzle piezo drop on demand system, although the shear rate is much lower, the ink is not in rheological equilibrium, as it is accelerated from rest to full speed in a short period of time. Controlling droplet formation and in particular, the break up and the corresponding tail or ligament is highly dependent on the rheology of the ink as it flows through the venturi. Simple information of the viscosity of the fluid, measured using conventional laboratory viscometers, do not yield much useful information on the mechanism of jet formation which is also different in both cases.

Examples of typical drop on demand and continuous jet formation and break up characteristics are shown in Figures 1a and 1b respectively. Images of jet break up and nozzle exit of a jet were ‘frozen in flight’ using a LED strobe synchronised to the droplet generator and captured digitally directly through a computer.

The properties of an ink which contribute to these two fundamental parameters are presented in Table 2. The properties in Table 2 highlight the physical parameters contributing to bulk features of a jet and those which often through small chemical undefinable changes can influence the reliability of the jet. The design of the nozzle, included in Table 2, is critical of all inkjet design.

Fig. 1a) DOD Droplet and Ligament

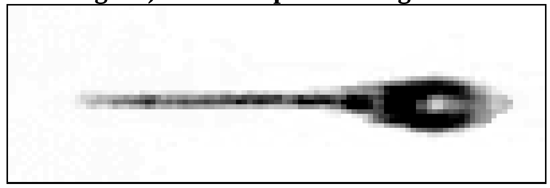


Fig. 1b) CIJ Modulation and Nozzle Exit

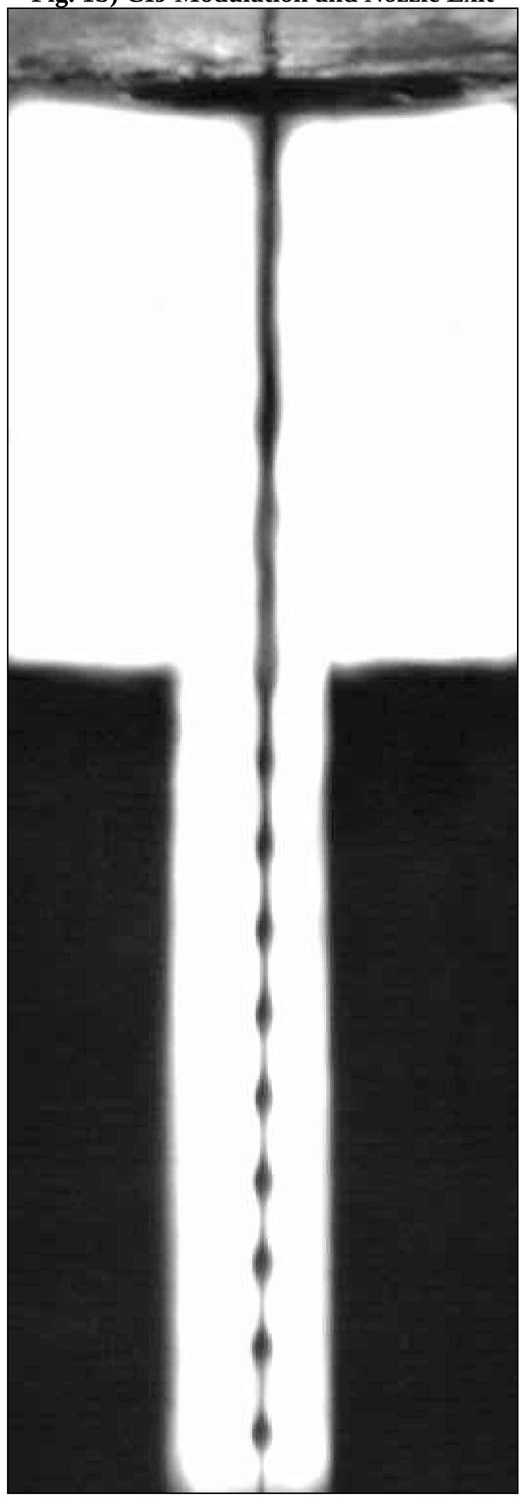


Table 2. Physical & chemical properties of ink design.		
Fundamental Properties	Bulk Properties (Jet Formation)	Secondary Properties (Reliability)
Consistency of flow	Viscosity	Compatibility
Exit contact angle	Surface Tension	Nozzle design
	Filtration	Chemical ageing
	Particle size	Polymer / dye interaction
		Chemical structure
		Viscoelasticity
		Molecular weight
		Interfacial energy

Other aspects of ink design listed in Table 1 further enhance the differences between printheads. In the case of thermal inkjet, the design is relatively straightforward but very exacting and not flexible. Due to the low impulse energy it is also very difficult to build in additional features or application functionality into the ink and the use of polymers is very restrictive. Similarly, the demand on the chemistry is high and generally only bespoke materials of high quality can be used to achieve high reliability.

Drop on demand piezo driven systems can also have complex ink designs and generally this complexity is increasing as the recognition that much more capable inks become available. In turn this means apart from the office piezo systems, more applications are realisable as more functionality is imparted into the inks. At the same time the restrictions on the choice of materials available is less than thermal inkjet but still high.

In the case of continuous inkjet, both multi deflection and binary ink design is often highly complex and in general binary inkjet is less forgiving of an ink and requires much higher purity of materials to ensure reliability and avoid cross talk between jets.

Ink Performance

Reliability of an ink is the biggest challenge an ink developer faces. Those that incorporate reliability into the innovative part of design will achieve much and many significant advances will be made in developing inkjet ink technologies. To illustrate how this can be used to achieve success, consider a very important example of incorporating pigments into a continuous inkjet ink. There is debate, much based on hearsay rather than scientific evaluation, about the reliable use of pigments in inkjet inks.

Consider, some simple water based inkjet inks based on the formulations described in Table 3. Here a comparison of two pigments and a dye is made. The physical properties of each ink are described in Table 4.

Table 3. Continuous Inket Formulations				
Ingredient	Supplier	Form.1	Form.2	Form.3
Polyvinyl pyrrolidinone PVP K15	ISP	11.0%	11.0%	8.0%
Pigment 1 CAB-O-JET	Cabot	8.0%	-	-
Pigment 2 (Hostafine TS)	Hoechst	-	7.2%	-
Dye (Levacell SP)	Bayer	-	-	7.2%
Deionised water	Fisons	79.6%	80.4%	83.4%
Diethylene glycol	BDH	1.0%	1.0%	1.0%
Acetylenic diol Surfynol 104E	Air Products	0.2%	0.2%	0.2%
Acetylenic diol Surfynol 104E	Air Products	0.2%	0.2%	0.2%

Table 4. Physical Properties					
Property	units	CIJ spec.	Form.1	Form.2	Form.3
Viscosity	cP	4 - 5	4.48	4.36	4.40
Conductivity	mS/cm	> 500	2210	1970	853
Filtration time	sec	< 35	25	26	31
pH		< 11	6.19	5.82	8.91
Surface Tension	dynes/cm			35.0	31.8

Note: The filtration time is an internal method of assessing the ability of an ink to filter through a one micron filter and a value of less than 30 seconds is considered suitable for continuous inkjet printing.

Examining Table 4, suggests all three formulations may be suitable for continuous inkjet printing. Evaluating each ink in a printer and studying the jet break up behaviour, which is presented in Figures 2a, 2b and 2c, revealed that Formulation 1 provided an ideal jet break up image and subsequently to proved to be extremely reliable in an extended printer run. Whereas Formulation 2, based on an alternative commercially available pigment showed erratic behaviour and subsequently proved to be unreliable. Similarly the dye based formulation, Formulation 3, showed yet a different jet behaviour which proved, upon subsequent printer testing to show a build up of ink on the charge plates, probably due to the satellite behaviour shown in the jet break up image. It is important to note the behaviours of the systems which showed varying degrees of failure can be compensated by further development but this relatively simple experiment illustrates that a robust design can be characterised quickly. It is therefore, more important to select raw materials carefully, choosing a material based on suitability for the application rather than simply accepting or dismissing a class of materials based on a past experience.

Fig. 2a) Formulation 1

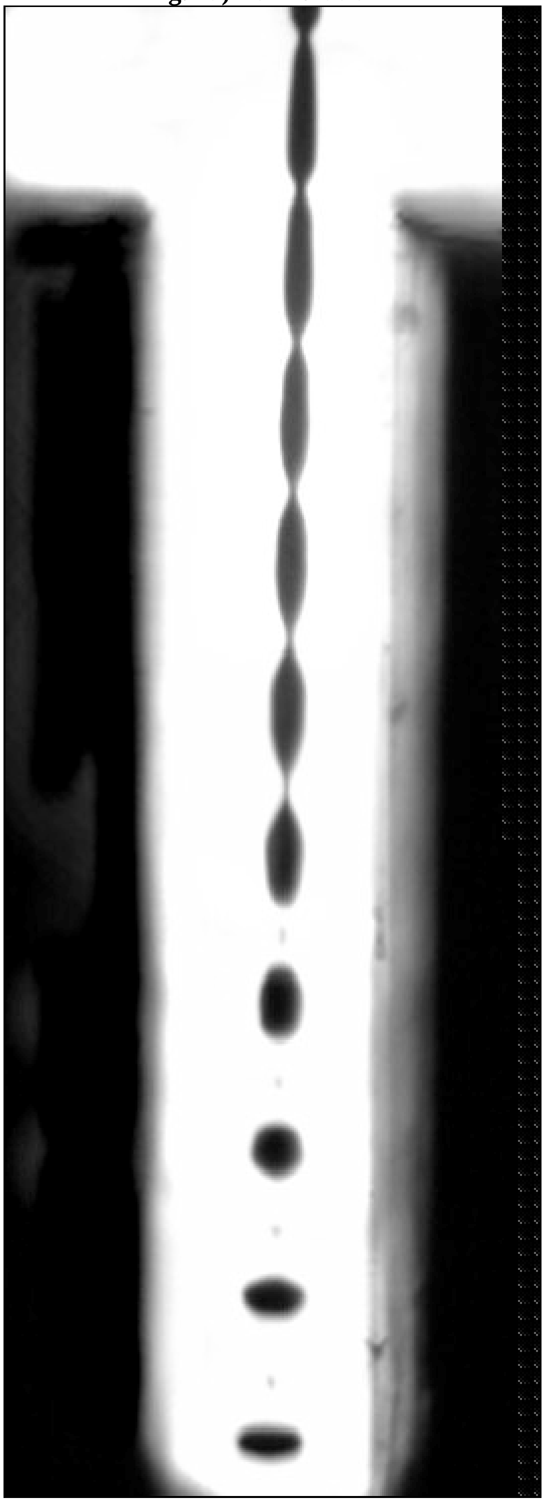


Fig. 2b) Formulation 2

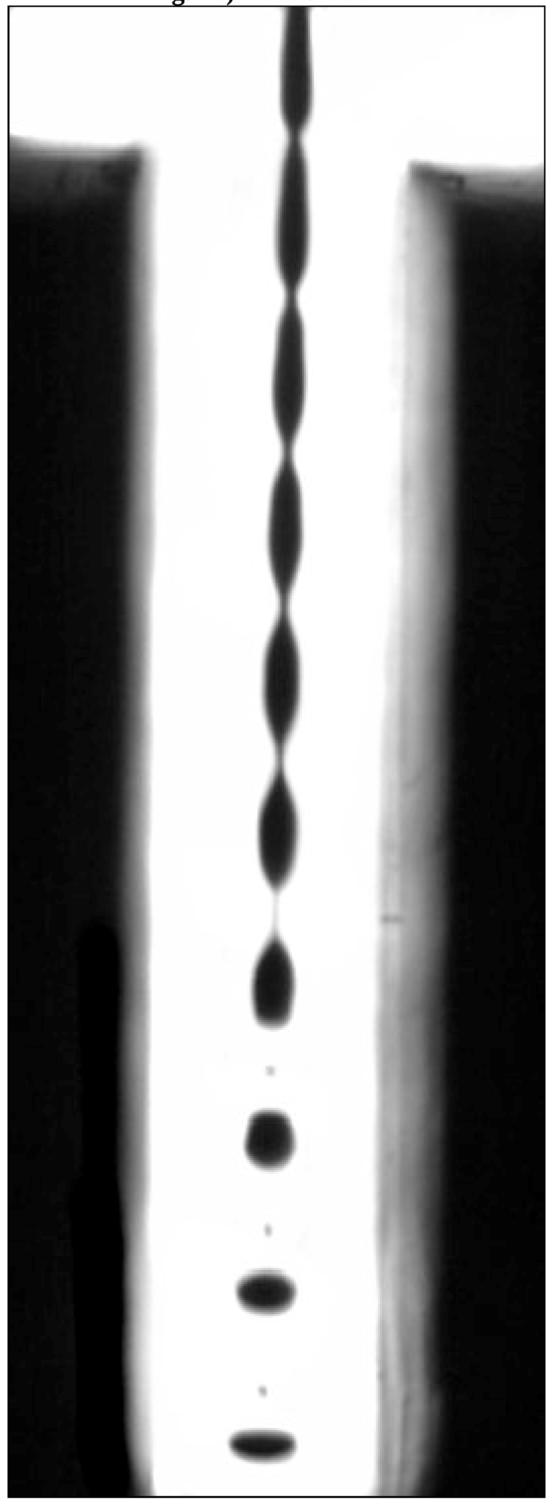
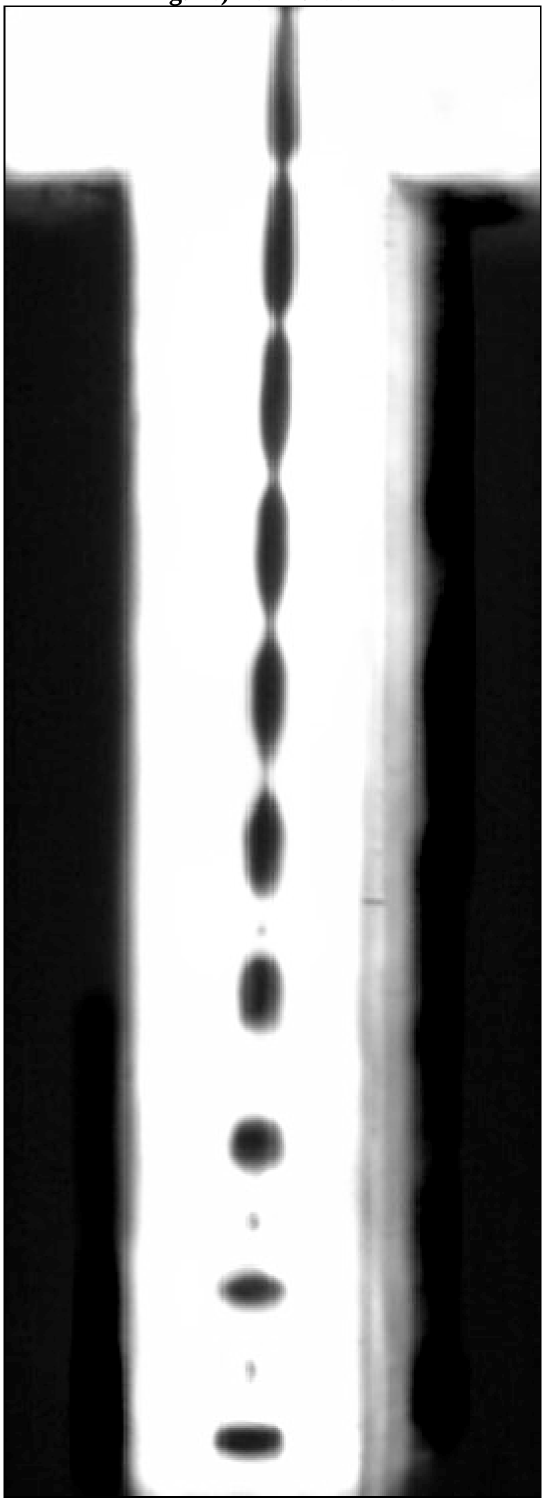


Fig. 2c) Formulation 3



In other words there are exceptionally good pigments suitable for inkjet compared with the best dyes and equally there are poor dyes to match the poor performing pigments found in some formulations.

Suitability of pigments for inkjet is reinforced by considering the performance of Formulation 1 after the ink has been subjected to an accelerated ageing trial, stored for 1 month at 60C. This is a tough storage condition and usually reveals problems with a design if there are any shortcomings. The jet break up image of the aged ink is presented in Figure 3 and shows even after 1 month at 60C, the formulation is stable and highly reliable and this was demonstrated through successfully running the ink in a printer for an extended period.

Jet break up characterisation is a powerful technique in understanding ink design and when supported by traditional physical property data it can be used with a high degree of confidence to predict the reliability of an ink and also to diagnose the cause, mode of failure and understand the corrective chemistry necessary to develop a robust product.

Ink Technologies

Advances in inkjet ink technology over recent years have been significant. If you simply examine the patent literature, there is every evidence to suggest that over the next few years, new ink development activity will be even more prolific. There is an apparent trend to patent ink technologies and the respective ink formulations, as there becomes a clear need to be innovative with the chemistry to produce practical solutions for many emerging applications.

Here, a few key examples from the Patent literature are presented, to reveal some of the most notable ink technologies and developments, as well as highlighting the diversity and innovation that is currently underway.

Continuing the dye versus pigment debate, a Seiko Epson Corporation, reveals a patent EP 0745651A1 which attempts to create high quality water fast, water based inks through dispersing water insoluble dyes in a water based ink to yield stable 25 nm particles of narrow size distribution without the need for dispersants or milling. In contrast, Canon (USP 5,618,338) attempt to solve this very important problem by using a two component system, where by a liquid composition containing a cationic substance and a finely ground cellulose is printed just before the ink, containing an anionic dye or pigment. The two components interact to produce a water fast ink. Similarly, Scitex Digital Printing apply a similar principle for commercial binary systems. A quasi uniform surface coating is produced as individual droplets remain discrete on the surface without coalescing. It is interesting to note that this approach has been applied to a non printing application to produce well controlled doses for pharmaceutical patches. Indeed, it is possible to go one step further and use this technique to produce very precisely controlled particles; may be a binary continuous inkjet printer can be used to produce pigment particles for inkjet ink formulations. Overall, there is much activity in this area of ink technology and there is great interest across many printhead techniques and markets.

Taking the problem of water further, Videojet (USP 5,596027) has demonstrated an innovative approach to solve a notoriously difficult application, to use a continuous multi deflection inkjet printer to print through a condensate onto returnable glass bottle which rapidly becomes water resistant, yet is water washable when the bottle is recycled. This has been achieved through the application of polymer science and utilising polymers of contrasting acidic and basic properties to achieve a very high performance.

In contrast, Canon (EP 0745479A1) attempt to put a new lease of life into thermal inkjet and widen its flexibility and application base for industrial applications. A valve is employed to direct more forward energy into an ink droplet. This is perhaps, the most important limitation in the design and applicability of thermal inkjet. The technique creates drops with larger throw distance and allows high viscosity inks to be used. It can also use two incompatible liquids, one optimised for the surface properties required and the other designed purely to create drop ejection properties.

Environmental trends within the commercial inkjet industry is important and this is witnessed by a series of strategic patents (eg USP 5316575) from Videojet who attempt to create a strong position in the development of low volatile content (VOC) waterbased inks across continuous and drop on demand printing technologies. It is an example of much activity and illustrates a wide range of water soluble polymers.

UV curable inkjet development is receiving much attention especially by those players looking to exploit wide format durable inkjet applications. An example of the development of UV curable inkjet inks is presented in a patent by the Scitex Corporation (USP 5,623,001). Who use water based UV curable technology to print onto porous materials and overcome strike through.

Hot melt ink technology has received little attention by the inkjet chemist and consequently, the current performance of hot melts inks is very poor. It is envisaged that many of the limitations of hot melt inks can be overcome with some innovative chemistry and performances similar to liquid inkjet inks are likely to be available within a few years.

Finally, what may be one of the most important ink and printhead developments which is likely to witness significant advance in the next few years is the use of industrial piezo driven open nozzle drop on demand printheads to a wide and diverse applications; especially an ability to print onto a wide range of surfaces, including non porous films with very fast drying times. Coupled with an ability to print over wide areas with high resolution, positions this form of inkjet printing as one of the strongest contenders for much of the new applications. An example from the patent literature is Markpoint (PCT WO 94/03546) which describes the use of fast drying inks without blocking open nozzles. The approach has been, to blend volatile and non volatile solvents and dissolve the solid ink ingredients into the volatile solvent. As the volatile solvent evaporates at the nozzle, a non volatile film forms with the solid ingredients migrating back down the channel into the volatile portion. This is an example of much activity in this area and Trident has recently launched a fast drying ink with an ability to print onto a range of non porous and porous surfaces and maintain high operational reliability in the printhead.

Conclusions

Ink development is not a hit and miss process and innovation can be achieved through a mixture of good scientific practice and a careful pragmatic approach. By careful understanding the properties of jet formation, it is possible to design inks with confidence for reliable operation. Increasingly, innovative chemistry will be applied to inkjet to provide many solutions in the future and this will be achieved by carefully selecting new materials. This can be done as illustrated in the case of pigments with significant results.

Fig. 3 Aged Formulation 1