Graphic and Functional Inks

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Abstract: Graphic inks are formulated to deliver colorful images for publication, packaging and product printing. Various printing processes deliver different ink film thickness and feature size. Inks are formulated for specific printing process. Depending on the ink final destination, higher or lower quality ingredients are used for their formulation. Main components of inks are pigments, binders, solvents and co-solvents, and additives. In recent years, besides graphic inks, inks for printed functionality are emerging. In such inks, functional filler replaces the pigment. Functional inks for printed electronics are formulated as conductive, semi-conductive and insulating. Attention is given to formulation of conductive inks based on carbon chemistry, and their characterization in terms of their rheology, selected physical properties and functionality.

Key-Words: Ink, formulation, ink components, rheology, surface tension, printed electronics, conductive ink, graphite

1 Introduction

Graphic inks are around us, sometimes being unappreciated or unnoticed. In fact, they are everywhere, if you read newspaper, journal, book, catalog or the ad in the mail. So-called publication sector is declining, but we still print enormous amount of pages via our digital home office printers, which is also publication. Basically, publication sector is switching focus from using printers with master image carrier such as lithography, rotogravure, and flexography to the printing without master image carrier, thus going digital. Inks for publication printing are cheaper than those used in packaging, and product sectors. They are made to produce color, thus they are mostly yellow, magenta, cyan, and black, but mostly in digital sector we may see so called extended gamut colors, thus contain also orange, green and violet, but it may be much more colors, sometimes shades of the same color. Digital printers may have twelve different color stations, just to increase color gamut.

Huge packaging printing sector is steadily growing, and it is predicted to grow in the future, too. Packaging printing is around us when we enter grocery store and look at cereal boxes, beverage boxes, or bottle labels. It is used to print all kinds of boxes for shipping goods. Inks are made as graphic for visual sensation, but also as functional, mainly with security features to protect goods from fraud, but also to deliver additional information, such as information about package storage temperature or freshness. Packaging may use so called spot colors, formulated especially for particular product, such as Coca-Cola red. Printing presses may then have seven to eight up to several more print stations. Packages may include printed RFID tags, or printed sensors employing conductive, semiconductive and dielectric inks. Printed sensors are included for all possible purposes, such as temperature, moisture sensor or gas sensor, to mention a few, and they employ functional inks as well. Package printing is mostly employing processes with master image carrier including lithography, rotogravure, flexography, and screen printing. In this sector, one may find digitally printed pieces, mainly labels for pharmaceuticals, or bottle labels of all kinds. More often we may notice that printed piece is manufactured using several printing processes thus also different inks to improve visual sensation or functionality. Example may be label with shining gravure printed “silver” ink features, which is chemically aluminum flake decorative ink, along with ink jet printed variable data message. This is example of future trends of hybrid printing, utilizing hybrid inks and presses with litho, gravure, flexo, screen and digital units on one printing press, employing units most suited for particular job. More and more evident on packages of the future will be information and sensational components along with security features and functionality printing all in one printed piece. Inks for packaging printing (cereal box may be an example), use higher quality resins and components, in order to withstand extended handling period without experiencing rubbing off or other damage [1].

Another sector of graphic printing is product printing, which we may notice on wall paper, printed fabrics for outdoor furniture, printed flooring, printed furniture components, pool liners, or car windshields. Product printing, especially sectors, printing long runs efficiently employ gravure inks and process, delivering outstanding quality and color consistency throughout print runs reaching few millions print repeats. Product printing inks are formulated with great care to withstand long-term use, thus they need to have excellent rub and scuff resistance along with many properties tailored for particular product and its way of use. Rotogravure is main print process, enjoying printing long runs of product with infinite print pattern, such as wood grain. Screenprinting on the other hand, will be used for printing any length of run and still be profitable, employing thick ink film for windshield patterns or printed circuitry. Ink film thickness, which can be reached by different printing processes, and printable feature size is illustrated on the Figure 1.

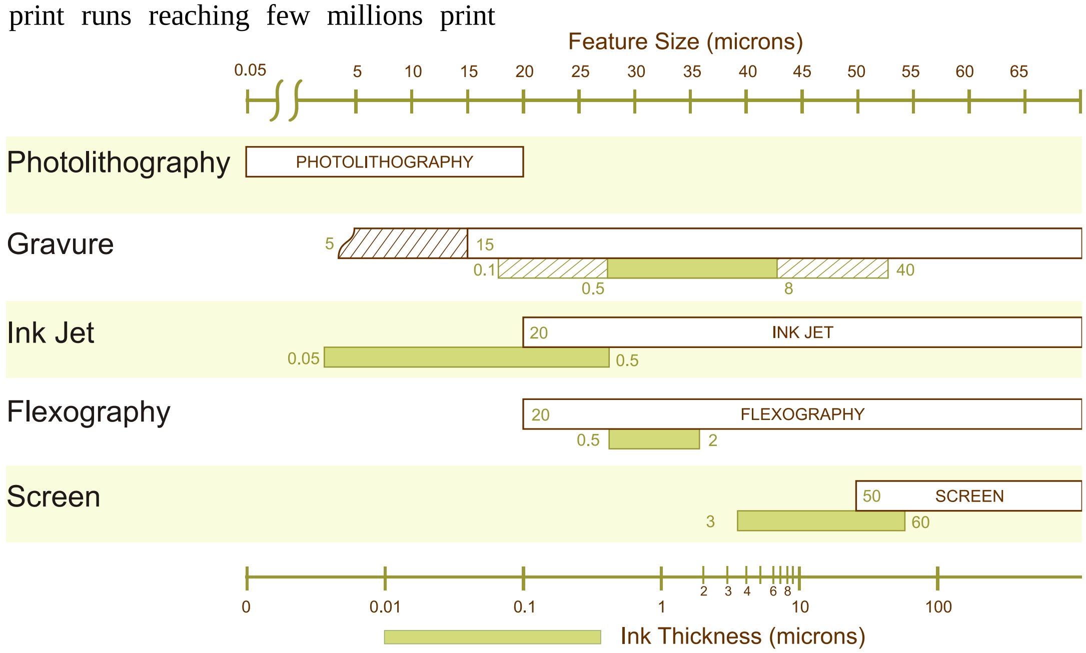

Figure 1: Ink film thickness and printable feature size

Ink film thickness also depends on the viscosity and solids content of the ink, being deposited. Among all printing processes, rotogravure is the only one, which is able to deposit variable ink film thickness on one halftone image, depending on halftone dot value. Thus, it can print from 1 micron (highlight tone) to six microns (solid print) ink film thickness all on one image. Packaging and product printing may employ higher solids inks to start with, which results in thicker print layers. Printed electronic jobs are using inks with high loads of functional particles, such as silver or copper, resulting in much thicker ink films (11micron and more) than graphic jobs. Traditional inks were targeted for graphic purposes to provide pleasing images, or to deliver certain message. Another very special category is 3D printing inks. 3D printing is mostly used for any kind of fast prototyping, or printing for medical applications, such as bones, bone or tissue replacement (Fig.2). 3D printers were successfully used for skull and jaw replacement, and other bone replacements [2]. Usually, hot melt inks employing thermoplastic polymers are involved in formulation of 3D printing inks. New biocompatible polymers for biomedical applications such as PVA (Polyvinyl Alcohol), PLA (Polylactic Acid) were introduced for bone replacement 3D printing [2]. Recently, various kinds of UV curable inks were employed in 3D printers.

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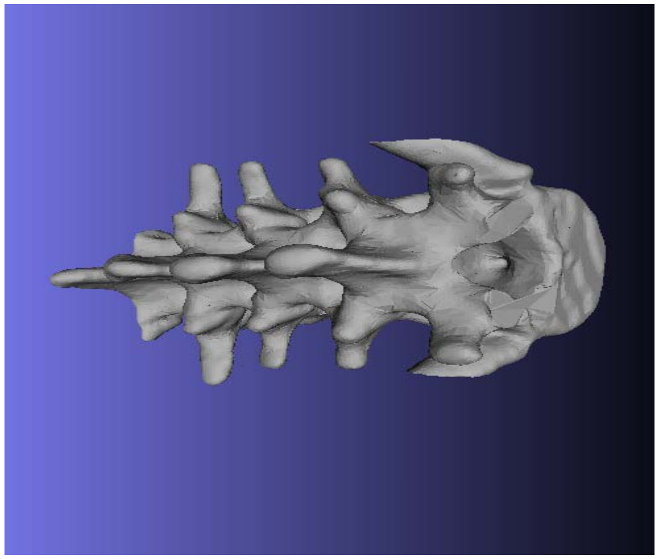

Figure 2: 3D printed model of vertebrae bone [2]

Current advancement of technology calls for functional inks, which need to perform certain tasks, such as conduct or block electric current. Functional inks need to be compatible with certain other inks to create targeted functionality. Usually, very strong solvents are used because they work well with functional particles or resins, and/or polymers of the ink, and after printing, they may become hydrophobic and not accepting next functional layer. All kinds of pretreatments are then used to modify the surface energy of previous down functional layer to accept next functional layer. Additionally, these inks may be conductive, dielectric, semi conductive, or may have other targeted functionalities, such as thermal conductivity, or luminescence. Such inks do inks often require forming flat uniform layers, which has to do with proper surface tension of particular ink. While graphic inks carry pigments for visual sensation, functional inks may contain metal particles, such as silver, copper or zinc. Functionality of these inks is improved with decreased particle size of metal particle, which may be in ranges of tens of nanometers.

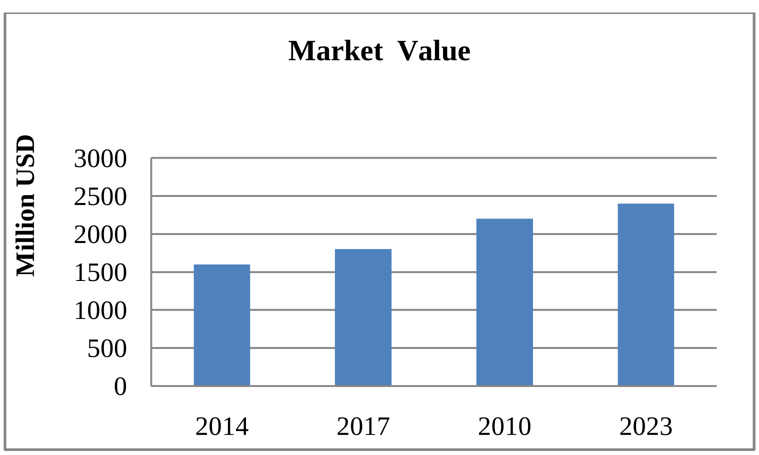

Figure 3: Ten years forecast for the conductive ink and paste market [3]

Printed Electronics (PE) is gaining wide spread popularity since it deals with the manufacturing of electronic components using conventional printing processes. Manufacturing electronics by printing is thought to be more challenging than graphic printing applications since it requires electrons to flow through the printed ink film. Several challenges that PE faces today is developing suitable electrical components do not require very high conductivity, and thus expensive material such as silver, gold or copper are replaced by cheaper materials like graphite, or conductive carbon, and make good enough resistive circuits. Silver is most widely used conductive material because of its high electrical conductivity, but carbon and copper can also be used for applications where cost is a concern. The conductivity of any ink formulation is affected also by the printing process, drying method, and substrate. In 2012, market for printed and thin electronics reached $44.25 billion [3]. Due to growth of printed electronics market, conductive inks market for printed electronics (PE) is expanding as well, predicted to grow from $1.8 billion in 2014 to constitute $ 2.26 billion market in 2023 (Fig. 3). According to IDTechEx [3] it is forecasted that $735 million market will represent silver and copper inks only.

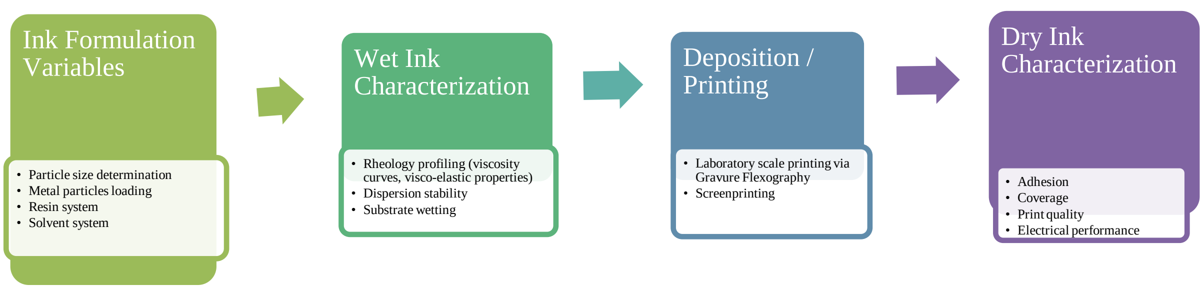

Figure 4: Conductive ink development workflow

2 Ink Components

Inks may be formulated with main components, such as pigments to add color, resins or polymers to disperse the pigment, and carry the ink to the substrate and anchor it there. Usually, resins or polymers have to be dissolved in the solvent. Depending on the type of the solvent, inks may be solvent based or water based. Solvents may or may not be present in the ink formulation, which depends on the nature of the resin or polymer used [4]. Family of hot melt inks employing thermoplastic polymers, such as currently used in 3D printing do not require solvents for formulating the ink. These polymers have the ability to become fluid under heating in the moment of printing, and solidify when they hit the substrate to be printed. Obviously, changing temperature is required to melt or solidify the polymer in the ink. Another example of ink, which does not contain the solvent, is the UV curable ink. The monomer, having low viscosity and is able to dissolve the oligomer, acts as a solvent in the moment of ink deposition. Thus, UV curable ink may contain monomer and oligomer, which is composed of monomer chains, but is able to further polymerize to create the polymer, thus cured ink. Pigments, resins and /or polymers and solvents are so called main components of the ink. To enhance or modify the final ink properties, additives may be added to the ink formulation. There are some additives, which may be found in many different types of inks, such as waxes. They modify slip, thus coefficient of friction of the ink. On the other hand, depending the nature of the ink, specific additives may be used. Example may be defoamer, which will be used only in water based ink formulations, thus its use is very specific,

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while metal dryer will be added only into offset litho inks aid drying by oxidation polymerization mechanism. Many surfactants are employed as dispersion aid additives in the process of pigment dispersion manufacture. Surfactants and wetting agents are added into ink formulations in order to alter surface tension of inks. Common formulation rule is that additives are put in the ink formulations in amounts not exceeding 5%. Functional inks may benefit from addition of certain additives, such as dispersants, while dispersing and printing. At the time when the coalescence of functional components is expected, dispersant may harm functionality, especially ink conductivity. There are numerous applications of inks, and each needs special consideration at the time of formulation, which leads to successful printing and end use properties of ink. The current state-of-the–art technologies for conductive inks are silver-flake based, nanometal particle based, conductive polymer based, and carbon-based inks. The high prices of virgin metals are constantly increasing, driving high the prices of conductive inks. The silver-flake based inks often contain high loading of silver flakes, and high specific gravity, and exhibit reduced stability upon storage. The nanometal particle based inks are becoming popular due to advancement in nanometal particle production and lower sintering temperatures required after printing. The key point in formulating nanometal based inks is to prevent agglomeration by adding stabilizers to form stable inks. The cost of the nanometal based inks is still high. The conductive polymer based inks have limitations due to lower conductivity, typically three orders lower than metal filled conductive inks. Also, it is more difficult to formulate conductive polymers into inks because of their limited solubility, stability, and processability. The concentration of conductive polymer is often low, typically from 1 to 6%, leading longer drying time and relatively thin films.

The conductive ink development approach is illustrated in the Figure 4. Inks are formulated to accommodate printing process requirements and restrictions. A typical ink formulation contains, i) functional metal particles ii) binder, iii) solvent, or mixture of solvents and co-solvents, and iv) additives. Conductive inks can be formulated by blending either nanoparticles or precursors of metal particles that are highly conductive, such as silver, gold, copper, zinc, and carbon [5,6,7]. The precursors usually reduce to the original metal compound by reaction with a reducing agent. Silver is most widely used conductive material because of its high electrical conductivity, but carbon and copper can also be used for applications where cost is a concern. The conductivity of any ink formulation basically depends on the printing process, drying method, and substrate. Different particle size and loading of metals are utilized in ink formulations. Based on the solvent system, appropriate resin is selected. For toluene, resin based chemistry combined with cellulose derivatives can be used. For acetates and alcohol systems, nitrocellulose, polyurethane and polyamide resins can be employed. For water based inks, acrylic resins (solution and emulsion) are the most common. Variables used in ink formulation are the most important factors for printability as well as electrical performance of printed conductive layers.

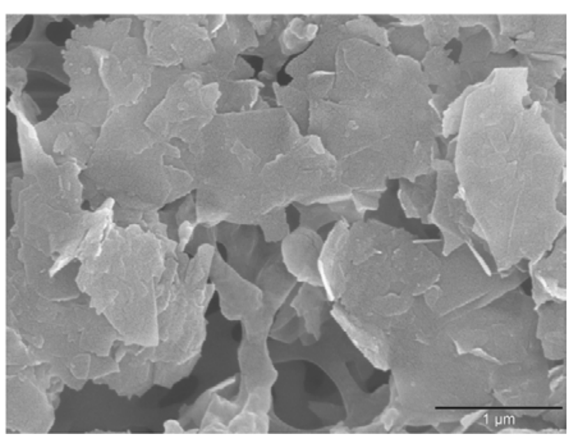

Figure 5: Graphene platelets [6]

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3 Ink Properties

The formulated functional inks are characterized in terms of their rheological, drying and wetting properties and these are correlated to dry ink end use properties. Very important properties for formulated inks are their surface tension and wetting behavior. A SensaDyne Tensiometer may be used to measure dynamic surface tension of functional inks [8]. Static surface tension of functional inks can be measured using the Dynamic Contact Angle analyzer FTA 200 (by First Ten Angstroms) using a pendant drop shape method [9]. These methods have been successfully used to study and predict printability of printing inks for both graphic inks [10], and for functional inks for printed electronics applications [8]. Electrical Resistivity measurements may be performed using a 4-point probe, where an electrical current is caused to flow through the material using two probes at opposite ends of the printed traces and a voltage is measured at the desired length along the test trace.

3.1 Rheological Behavior of Inks

The rheological properties of the inks may be measured with a TA AR 2000 dynamic stress rheometer equipped with 20 mm parallel plate geometry. Parallel plates are usually used for high viscosity, high solids materials containing large particles. This is because unlike the cone and plate geometry, parallel plates do not require a defined gap to be set. Since large particles can damage the surface of the cone and plate geometry parallel plates are better suited for such inks, especially when assessing screen printing inks. In order to eliminate any shear history within the samples, all samples should be pre-shared at 1000 sec^{-1} for 30 seconds, and equilibrated at rest for 1 minute prior to running each test. The temperatures of the inks are maintained at 25 º C throughout all experiments. Previously, a set of rheological tests for metal filled conductive inks has been developed that can be used to correlate and predict the ink printability on the press [10]. Both rotational (to determine flow properties) and oscillatory tests (to determine viscoelastic properties) are useful for characterization of formulated inks.

3.2 Step-Change Test with Controlled Stress

In Figure 6, the rheology of the formulated graphite/carbon ink is compared to a commercial silver and carbon ink. All the inks decrease in viscosity with shear, but the recovery of each of the inks vary significantly. The silver ink recovers very quickly, compared to other two inks, where as the recovery for the graphite ink is moderate. The carbon ink recovered the least. The step change test is shear and time dependent; as shear is applied to the ink, the ink decreases in viscosity. Upon removing the shear, the ink regains its viscosity, but the recovery of the ink depends upon the elastic property of the ink. A high recovery rate has been reported to reduce the potential for print defects [11]. Among all the tested inks, the silver ink recovered the quickest and reached a significantly higher viscosity. This behavior is favorable for fine line printing because the quick recovery would prevent slumping (spreading). The carbon ink recovered to a much lower viscosity, which would make it suitable for the printing of solids where coverage is needed. The graphite/carbon blend's intermediate viscosity makes it suitable for fine line, as well as solids printing.

The flow properties of inks under shear are shown in the Figure 7. Most of the inks are shear thinning, which apply also for graphite/carbon and silver inks, too. The initial viscosity of the carbon ink is lower than that of silver and silver and carbon/graphite inks, but less shear thinning. The viscosities of all of the inks level off at shear rate of ~50 sec^{-1}. From that shear rate the viscosities of all inks are approximately the same.

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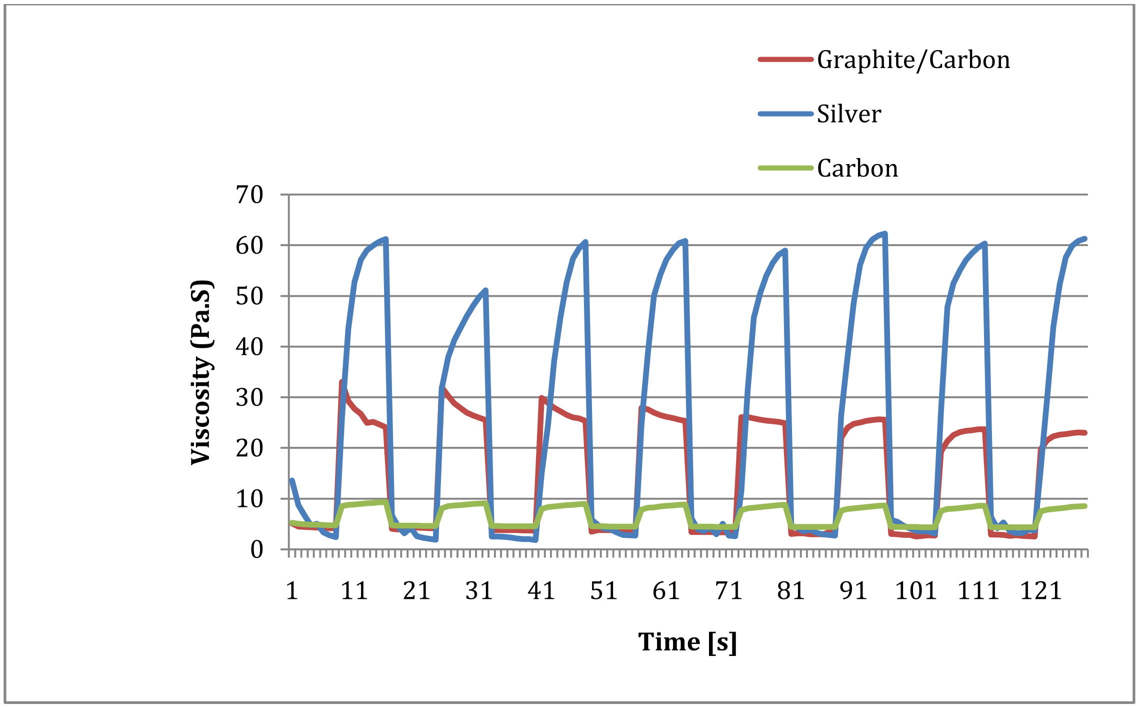

Figure 6: Step-change test for three different inks: carbon /graphite, silver and carbon

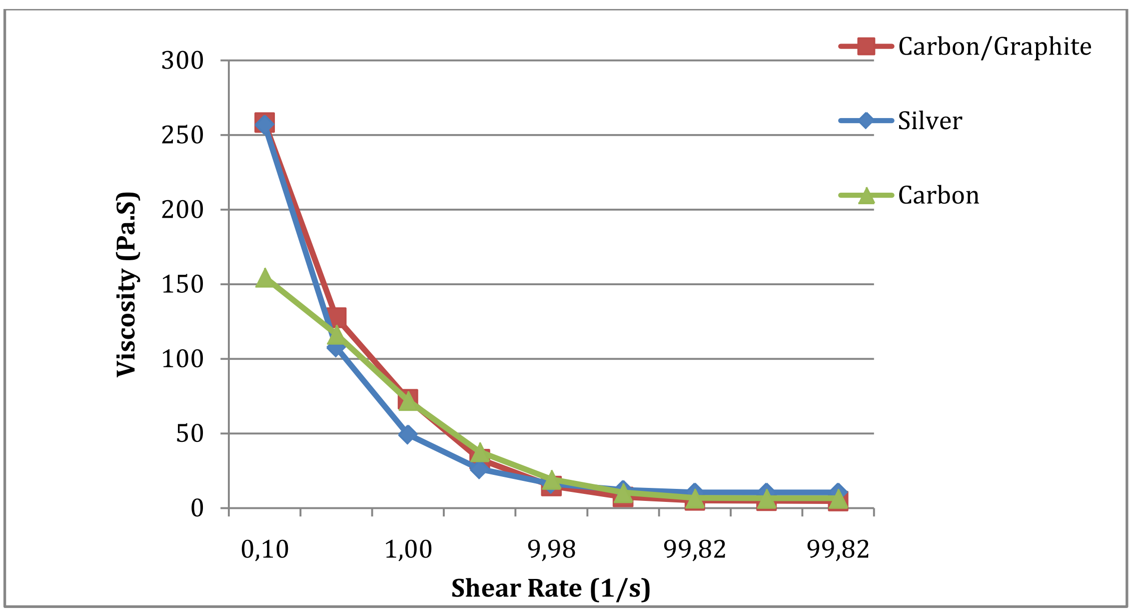

Figure 7: Steady state test for carbon/graphite, silver and carbon inks [13]

3.3 Ink End Use Properties

Printing ink roughness is important property for graphic as well as functional inks. Smoother ink film makes print shinier, or more glossy, which may be desirable. Functional inks roughness can affect the way, how the next functional ink will lay and adhere. Usually, the requirement is to print as even ink film as possible. Often, especially when printing ink jet functional inks, so called coffee ring effect occurs, which creates elevated edges leading to uneven conductivity across the ink layer. The average roughness for the graphite/carbon printed ink film

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measured by white light interferometry was ~1.11 µm, while that for the commercial silver ink it was ~1.29 µm. Example of the white light interferometry measurements for both the inks is shown in the Figure 8. Comparing different topographical plots of different graphite/carbon samples showed that the ink films were rougher at the edges as compared to the center. The higher roughness values at the edges indicate that the leveling properties of the ink need to be improved. The smoothness of the ink film can be improved by increasing the recovery of the ink via blending in another resin or polymer, which is a good film former and elastic in nature. The commercial silver ink printed with no trouble, but the recovery of the ink was too fast to allow for good leveling. A fast recovery is good for printing fine lines, but the poorer for leveling. Degree of polymerization and glass transition temperature are good predictor of leveling, which may be used with advantage in formulation of graphic inks. Functional inks usually prefer polymers with shorter degree of polymerization, because shorter chain polymer does not represent barrier to electron transfer.

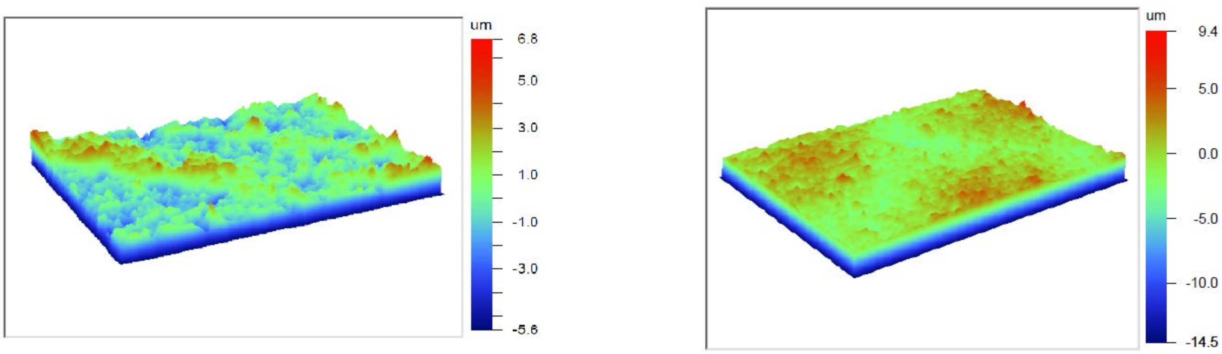

Figure 8: White light interferometry (WYKO) images of ink film topography for carbon/graphite ink (L) and nanosilver ink (R) [13].

4 Conclusion

Inks are formulated for publication, packaging and product sector. Depending on their final destination and expected performance, they are formulated with various quality resins, fillers, and additives. Depending on the printing process, inks are formulated with specific viscosity requirements and printed at various ink film thickness. Recently, world of inks was enriched with functional inks for printed electronics. Family of printed electronics inks has its own specific formulation requirements, often calling for minimum amount of resin or polymer and additives. Precious metals such as gold or silver in conductive inks may be replaced with graphite or conductive carbon fillers for inks with medium to low conductivity, sufficient for many printed electronics applications. It is preferable to formulate conductive inks with binders or resins with lower degree of polymerization for easier electron transport.

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