Graphite Inks and their Applications

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Abstract

In this experimental work, conductive water based inks were prepared from multiple graphite grades. All graphites that were chosen for this experimental work have a platelet morphology and varied surface area. Similarity between grades was the particle diameter. Diameter of selected platelets was 5 and 15 microns. Inks H5, H15, M5 and M15 were prepared using the same formula. The binder for the inks was commercially available acrylic based resin. Each grade resulted in ink with different viscosity. Inks were printed on polyethylene terephthalate (PET). Printed samples were dried in a laboratory oven at 70 °C for 10 minutes. The effect of surface area and diameter on conductivity was observed. Sheet resistance of inks was measured via 4-point probe method. Lastly, inks with conductivity larger than 60 Ohms/sq were tested for microwave susceptor application.

Introduction

Graphite pigments can have various morphologies; therefore graphite-based inks have numerous properties and can be classified into four categories, a) conductive, b) semiconductive, c) dielectric, and d) resistive inks. The application areas for these functional inks have been expanding rapidly in the recent years, including touch screens, printed circuit boards, display panels, RFID (Radio Frequency Identification) tags, and sensors. Inks that have resistivity in the range of 60/ohms/sq/mil and lower can be used for formulating thermally conductive inks used for printing of thermally conductive patterns, to use for packages heated in microwave ovens. An SEM of graphite platelets is shown in Figure 1.

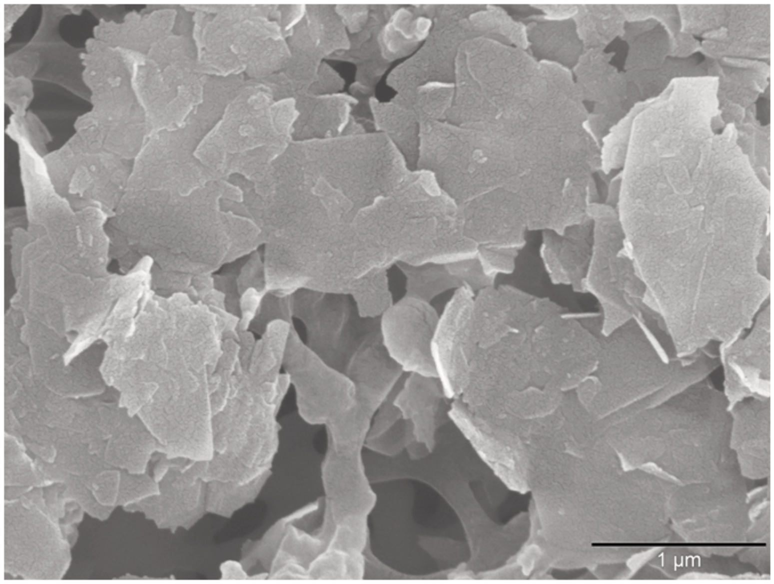

Figure 1.: *SEM of XGnP® Graphite Platelets*

The trend is to improve and increase the conductivity property of the inks. One way of doing this is to overprint the original layer with subsequent layers of the same ink. This approach is however time demanding and consumes more of the conductive material (Perelaer et al., 2010). The additive technique might be effectively viable for inkjet printing rather than conventional printing techniques (Perelaer et al., 2008). Another approach is to use the metal –based inks ranging from copper, expensive gold, nickel and most widely used, still costly silver. The choice of suitable metal is typically related to bulk resistivity, cost of the material as well as the handling and compatibility with the resin system. Once metal-based ink is printed, it requires a sintering step in order to acquire conductive paths (Perelaer et al., 2010).

Besides formulating the most conductive ink out of provided materials, the additional objective of this experimental work was to find the application for the less conductive inks. Thus, graphite particles that produced inks with sheet resistance of 60 Ohms/sq and more, were formulated into thermal conductive inks and printed on PET and coated paper. The shape of the trace was modified to achieve optimum microwave absorbency- meaning the trace that produces just enough heat (e.g. for heating the food), but not too much to burn the substrate, is desirable. Thus, the goal of this work was to formulate graphite ink and print the trace that will distribute microwave energy across the print in such a way that the substrate is not charred, but heated.

Microwave food packaging with a printed on susceptor could be the potential market for the conductive inks with lower electrical properties than those suitable for printed electronics. One possible application of such inks would be the printed on microwave susceptor for food where electro conductive ability will be transformed into a thermal one (Zeng et al., 2000). Typically, food prepared in a microwave oven is hot inside, while warm outside (Hamblin; 2000). This is the opposite of conventional oven cooking. The principle of a microwave susceptor is the conversion of the microwave energy into infrared heat energy. The potentially successful susceptor has to brown and crisp the food such as popcorn, pizza, fish and sandwiches.

Carbon black and graphite are suitable materials for microwave susceptor application as they absorb microwave energy (Parks et al., 1990; Mast, 2002). The potential of carbonaceous pigments is its thermal conductivity. In addition they come in various particle sizes and thicknesses, which further provides various electrical and thermal conductivity. Graphite is frequently used as a susceptor because it provides good machinability and high resistivity, which is ideal for induction. The surface resistivity of the inks suitable for susceptor is in the range of 60 – 5000 ohms/sq (Parks et al., 1990). They can be fluid or pasty depending the printing process. Often the printed susceptor is overprinted with clear varnish that serves as a flame retardant.

The topography of the substrate plays a crucial role in the final performance of the ink. Smoothness of the substrate influences the heat generation. If the same ink is printed on rough and on smooth substrates, the smooth one will generate higher temperatures. Further, while formulating the ink one has to comply with FDA guidelines for contact with aqueous and fatty foods. The substrate specification is not only its topography but also its inertness to microwave radiation. In other words the chosen substrates have to be stable up to ~400°F. Above 400°F destruction of substrates occurs.

Paper substrates are FDA approved, but can be quickly destroyed by microwave energy. If protected by flame retardant, paper becomes suitable. Another alternative is the greaseproof paper that is laminated to bleached white paper (20-30 lbs). Lastly, PET is the substrate of choice, due to its dielectric properties, its inertness to microwave energy and FDA approval. The susceptor layer is typically printed in the thermal barrier layer and is printed as a pattern. The printed pattern can vary in thickness. The varying thickness is responsible for differences in generated heat in microwave ovens. Thicker ink films result in higher temperatures than the thinner ones. The susceptor can be printed as various shapes in different sizes. Typically, the active heating area is 10 cm2 (Cole et al., 2004). Microwaves range from 1 millimeter to as long as 1 meter (Pozar, 1990). For the best browning and crisping results the dimensions and the shapes of the susceptor should be equal of smaller then ¼ of the microwave wavelength.

An improper ink formulation or large covered area can cause overheating and often result in the substrate shrinkage or its damage (Mast, 2002). To overcome arcing, the spaces between features are designed. Overloading of the conductive material within the ink can also cause arcing or burning of the substrate. On the other hand temperature tailoring is unique to an ink and it is difficult to achieve with metallization techniques (Zeng et al., 2004). In addition to temperature control, printing of the susceptor is more economical then metallization.

Experimental

In the first part of the experimental, graphite pigments of different sizes and with varied surface area were tested for ink making suitability. The differences in morphology of the graphites can be seen in the Table 1.

Surface Area [m^2/g]	Thickness [nm]	Particle size [µm]
60-80	12	5, 15, 25
120-150	6	5, 15, 25
300-750	2	< 2

Table 1.: *XGnP® Families of Graphite Platelets*

The ink composition was formulated with regards to the differences in graphite's surface area and particle size. The ink formulation was done using commercial styrene-acrylic resin. The representation of the ink formulation is depicted in the Figure 2.

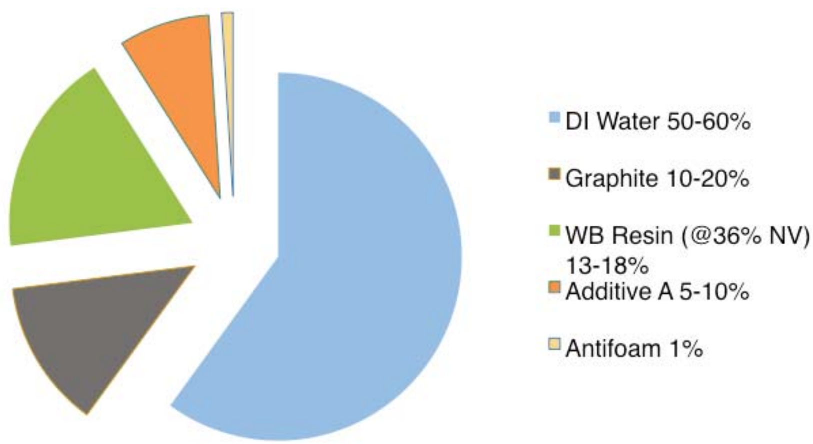

Figure 2.: *Composition of water-based graphitic ink*

Further, rheology of inks was monitored via a Brookfield viscometer Model DV III. Inks were diluted to 50cps and were printed using wire wound rod #6 and via laboratory gravure RK press with 100% solid 145 lpi plate. Inks were printed on PET substrate and were oven dried at 70°C for 10 minutes. In addition, the aim was to detect electrical properties of printed inks, which was done using a Kethley 2000 multimeter and 4-probe technique. Based on the electrical properties, inks were divided into two groups as it can be seen in the Figure 3. Ultimately, the experimental work was focused on the formulations that resulted in "poorer" electrical values (values higher than 60Ohms/sq/mil). This criterion was established by customers and their requirements for graphite based inks.

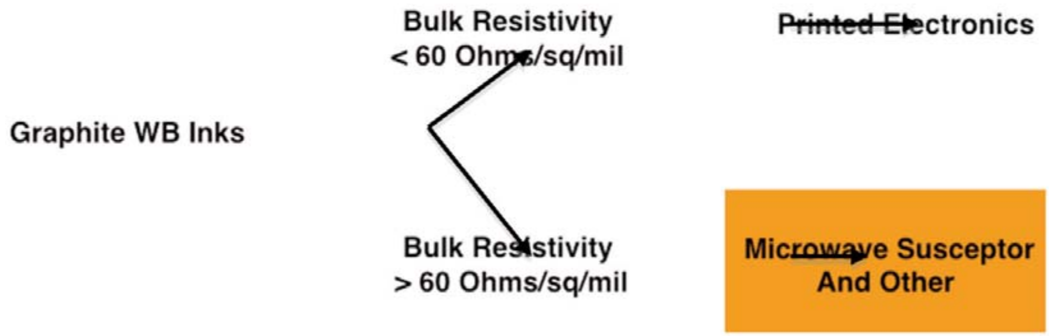

Figure 3.: *Inks Applications based on Electrical Properties*

Ultimately, the objective of the second part of the experimental work was to find applications for inks that do not meet criteria of printed electronics. The search for such applications leads towards food packaging, specifically the printed microwave susceptor. The substrate used for application of the lower conductivity graphite based ink was solid bleached sulfate board approved for food contact as well as PET. Both substrates were chosen with aim to be printed via flexo or gravure. The microwave susceptor patterns were printed using wire wound rod #6 and via laboratory gravure RK press with 100% solid 145 lpi plate. A commercial water-based resin was chosen with help of technical support. The parameters for the resin choice were direct and indirect food contact and non-toxicity. In addition, the browning of the food occurs at 190-200°C and it chars at 225-230°C. The chosen resin was intact at 200°C (400°F). During the testing, the printed susceptor was placed in a home type, Emerson 1000-watt microwave oven. Printed samples were placed on a Pyrex pedestal. This set up was chosen to avoid the loss of heat to the rotating tray. Heating was at 100% power and heating time was set up to 30 seconds. If the susceptor generated too much heat, fire was started in 4-5 seconds. Based on the US Patent search, it was realized that microwave susceptor packaging or printed on susceptor contained either one type or mixture of various water-releasing reagents that are activated at specific temperatures, while releasing small amounts of water. The "water-blowing" agent controls overheating and assures steady increase of temperature (Bohme et al., 2011). Heat energy generated by susceptor diminishes with the distance from it. The most effective heat zone is within 3 mm proximity. Ideally, the temperature generated by susceptor should be measured via a flouroptic probe. In the laboratory set up, thermal paper was used as preliminary indicator of the temperature generated by the printed susceptor. Static sensitivity of the thermal paper indicates the temperature at which it will turn its original color to black. In addition, some of the ink samples caused the PET to shrink or destroyed the substrate completely when exposed to microwave energy.

Results and Discussion

Aqueous graphite inks were prepared using conventional water-based resins. Resins with varied molecular weight were used. All of the inks demonstrated shear thinning properties. Grades with larger surface area resulted in inks with higher viscosity than the inks based on pigments with lower surface area, while particle size of compared grades was the same. The comparison of viscosities of grades with different surface areas but the same particle sizes is presented in the Figures 4 and 5 below.

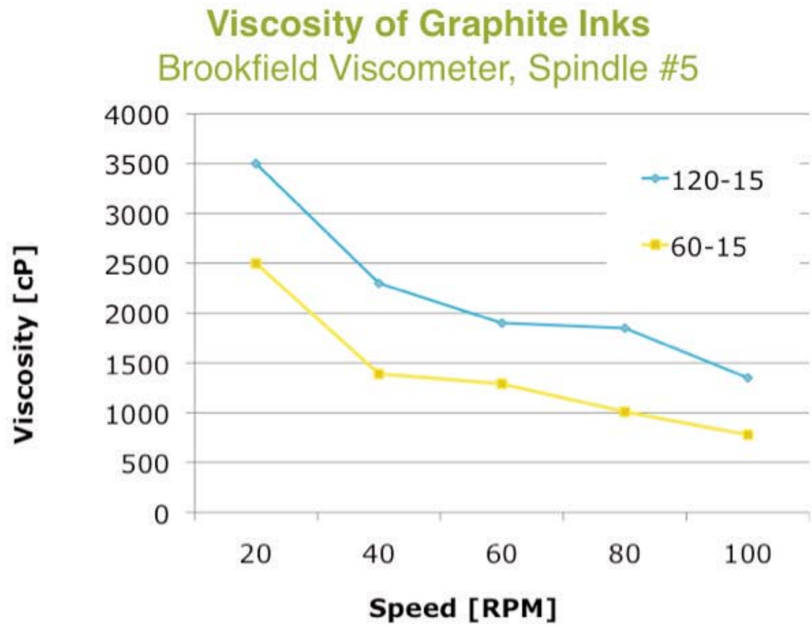

Figure 4. *Viscosity of 15-micron graphite platelets with 120m^2/g and 60 m^2/g surface area.*

It is evident that the higher surface area of the platelets contributes to the increase in viscosity. In addition, if two sizes of the platelets with same surface area were compared, it was apparent that smaller particle size platelets will result in ink with lower viscosity.

During the early stages of this study it was realized that the uniform ink thickness is crucial while printing the microwave susceptor. The unevenness of the ink thickness resulted in fire due to the areas with graphite plate accumulation. Therefore, the uniform ink metering was essential and therefore printing was done only via the RK proofer. A similar situation arose if two same ink formulations were prepared, each using the same particle size but different particle thicknesses. It was found that grades with 12 nm thicknesses would overheat or burn faster than grades that were 6 nm thick. Further, the microwave susceptor pattern is crucial for consistent heating and prevention of arcing or burning of the substrate. The solid areas would burn or shrink within seconds. Due to this fact, the printing of the substrate was followed by either hole punching or creating various patterns of susceptors. As an example, the print with 100% solid areas and areas with 20% and 10% tone was prepared. This approach assured slower speed in heating and prevented substrate from burning. In addition to this design, the 100% solid areas were combined with 0% covered areas or areas that were cut out. These efforts were done to better understand the principle of the microwave susceptor and learn the ways to control the temperature build up. The pattern constructions are presented on Figures 6-9.

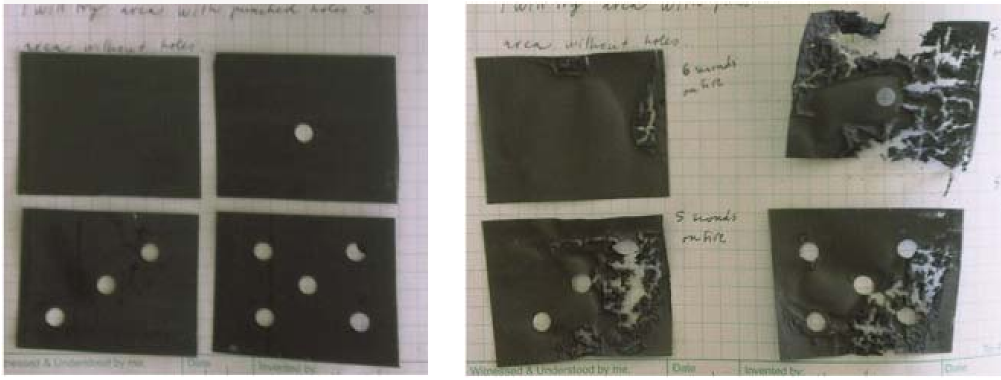

Figure 6. *Early stages of printed susceptor pattern, before (left) and after (right) microwave cycle.*

It was found, that the resin choice had a huge impact on the speed of the heating. It was realized that resin with lower molecular weight overheated significantly faster than resin with high molecular weight. Therefore some adjustments were done in ink formulation and susceptor was no longer resulting in fire, but with extended time in microwave oven was resulting in shrinking. The results of the shrinking can be visualized in Figure 7.

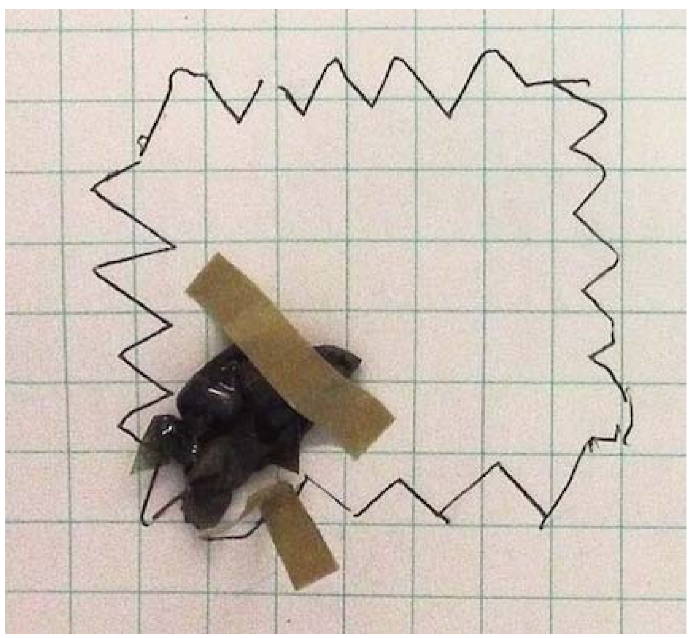

Figure 7. *Susceptor ink resulted in shrinking of PET.*
Outline represents original design and size of the susceptor.

Another approach that resulted in slower heating was the ink formulation with lowered amount of pigment. In that case, multiple layers were needed to result in rapid overheating of the substrate.

It was evident that the graphite pigment can generate needed heat, the curiosity during this project was focused on the topic of slower raising of temperature. It was noted that overprint varnish can be used to tailor the speed of heating of the susceptor.

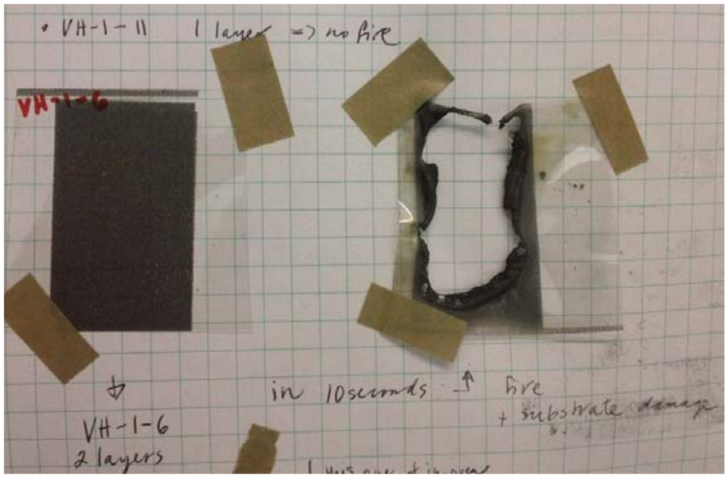

Figure 8. *Susceptor constructed out of 2 layers on the left.*
Same susceptor after 10 seconds in microwave oven.

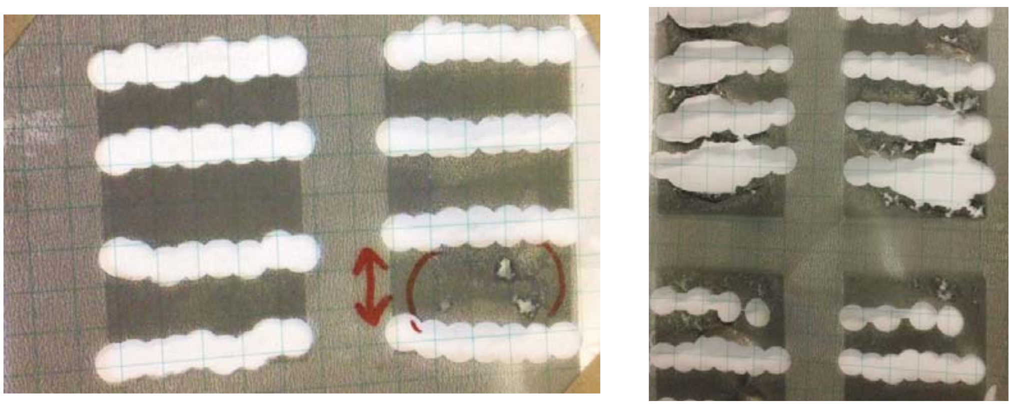

Figure 9. *Pattern construction and spacing is crucial to avoid arcing and burning of substrate.*

Overprint varnish based on resin with lower molecular weight was sufficient for arcing prevention, but allowed the susceptor to heat and remain hot. The overprint varnish based on high molecular weight resin prevented the heat generation to the point that the susceptor was heating but the speed of heating was not sufficient.

Due to limited resources, it was found that thermal paper can be used as early indicator of the generated heat Figure 10. The static sensitivity curves of thermal paper allowed the selection of the grade that would turn black at 150°C. This technique served only in early stages of the project; later the sensitivity of this kind of the paper was not

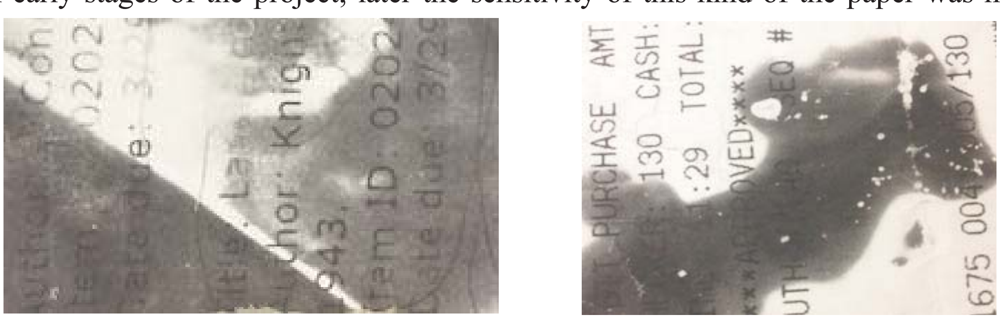

Figure 10. *Use of thermally sensitive paper for early evaluation of susceptor's performance.*

enough for temperature indication. Ideally the temperature measurement of this kind of print should be done via a fluoroptic probe, which was outside the means of our budget. In addition, the melting temperature of the PET substrate are in the 250-260°C range. During our experiment, it was proven that the graphite ink could result in melting or burning of the substrates, which unprinted is inert to microwave energy.

Conclusion

The goal of this experimental project was to find the application for inks or pigments that would not satisfy the printed electronic market. It was concluded that graphite based conductive inks made in the laboratory have capacity to serve as inks for printed on microwave susceptors. Tested graphite grades came in various thicknesses, which resulted in varying degrees of heating. It was found that the molecular weight of the resin has direct impact on the speed of heating of the microwave susceptor. The benefit of the printed on susceptor is the ability to lay down ink with various pigment morphologies and various pigment concentrations, which at the end result in various temperatures. It was proven, that custom-made ink formulations have the ability to beneficially tweak the temperature of the microwave susceptor.

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