Molecular Rebar® for Advanced Performance Silver Inks

Market Opportunity

Silver conducting inks represent about 20% of the global $2+ billion conducting ink market and growing in excess of 7% AGR. Existing large markets (~60%) include silver flake screen printed inks for solar panels, printed circuits and circuit boards. Rapidly growing markets are in wearable electronics and applications requiring flexible circuitry and miniaturization using digital ink printing methods. Performance needs for improved silver inks are improved durability (flex fatigue resistance), improved printing speed, resolution, quality and lower temperature curing. **Molecular Rebar®, MR, (individual clean carbon nanotubes with tailored surfaces) is uniquely advantaged to provide all these needed improvements** in the variety of silver inks by providing molecular scale interconnection of silver particles via its tailored functionality and by providing improved mechanical and heat absorption in the matrix. The particles of silver can range from nanoscale spheres to wires and flake. Thinner traces are now possible with MR resulting in **significant cost reductions in ink usage by the end-user**. MR further increases the printing speed when using flash photolysis because of MR's high energy absorptivity and mechanical property improvement resulting in **significant cost reductions by the end user in fixed cost per unit**.

The MR is provided as various concentrates for ease of formulations and use by silver ink manufacturers or end-users, thus allowing retention of proprietary formulation knowledge. For customers already working with this new material, there have been no problems with formulations once the MR surface chemistry requirements of the formulations are understood and the MR is adjusted accordingly.

Approaches and Performance Needs in the Conducting Ink Markets

Two main approaches for printing conducting structures such as solar panels, or circuit boards are:
1) Analog printing, involving the use of linear/rotary machines that can realize multiple copies of the same pattern at high speed (serigraphy, gravure, offset, flexography), generally utilizing micro-structured inks (silver flakes 1-5 micron in diameter); and 2) Digital printing, or drop-on-command, where raster machines print single copies of a pattern that could be changed by simply working at the software level (inkjet printing, 3-D printing), involving nanostructured inks. Today, complex inkjet printing systems are being engineered that can deposit alternating layers of silver nanoparticle and insulating inks, thereby creating multi-layer PCBs with narrow tracks compatible with most SMDs. A target market is rapid prototyping, or low volume manufacture of boards with four layers or higher. This approach seeks to reduce prototyping turnaround time for multi-layer circuits while keeping all the circuit IP in house. As miniaturization continues and markets such as RFID tags and smart clothing grow, the drive is towards thinner traces on flexible substrates. This means the digital printing market is growing rapidly.

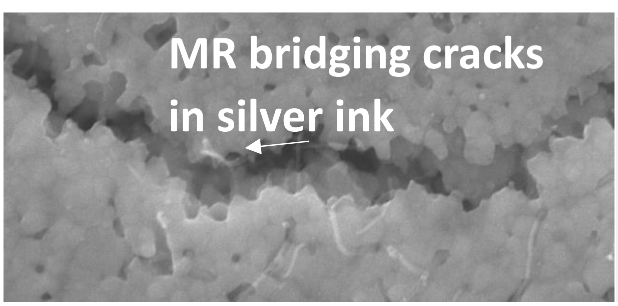
In both types of ink, control of rheology and surface tension are required. Digital printed inks are usually much lower viscosity than the analogue inks and require high degrees of particle dispersion to prevent print head blockage. Low levels of binders and wetting agents are often used. The performance needs of conducting inks can be summarized as; improved durability (flex fatigue resistance), improved printing speed, improved resolution, improved quality, and lower temperature curing (sintering to achieve a desired conductivity).

Digital Printing Silver inks can be in a hydrocarbon, an aqueous alcoholic or fully water base. They are generally obtained from reduction of silver nitrate or acetate during drying by chemicals such as ethanol, or facilitated by UV light. The aqueous alcoholic base silver nano-inks are preferred for faster printing with better wetting on flexible polymeric substrates compared to the fully water-based inks. The aqueous based inks are considered more environmentally acceptable than the hydrocarbon-based inks. Use of nanoscale silver particles with diameters in the range 10-50 nanometers, allows for low temperatures of fusion around 80-140 °C. Silver particles in the micron diameter range require 200-220 °C. The low temperature is much preferred as it allows for a wider range of substrates to be employed without damage or deformation.

New developments with silver wires for ITO replacement in touch screens and flexible circuitry can benefit strongly from addition of Molecular Rebar to maintain continuity and uniformity of conductance in repeated flexure.

Demonstrated Features of MR in Silver Nano-inks

In addition to the preferred aspect ratio of about 60 for Molecular Rebar®, the surfaces of MR are specially tailored for dispersion in the silver ink or paste and for their bonding with the silver particles during sintering. The aspect ratio of about 60 provides an optimum balance of mechanical strength and flowability in the silver inks. MR can be dispersed in silver nano-inks over a wide concentration range, usually effective for improved durability at 0.1 to 0.2% wt. One can go as high as 10% wt. or more relative to the dry silver content, dependent on the property requirements needed of the conducting print. Above about 1% wt. MR in the fluid imparts higher viscosity at low shear rates but rapidly shear thins at higher shear rates. As the silver inks are drying MR further provides additional viscosity control for morphology control and improved integrity of ink edges.



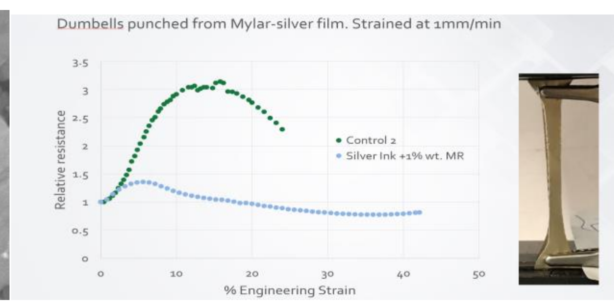


Figure 1a. Electron micrograph of MR and silver

Figure 1b. Relative resistance vs. Tensile strain.

An example of the high strength of the silver film after sintering is given in Figures 1 a and b. using 1% wt. of MR relative to solids content for illustrative purposes. Using a Mylar film substrate without surface treatment, the silver film was broken, and an electron micrograph image taken (Figure 1a). The MR is clearly seen to bind the silver particles together and bridge the crack. As a scale for the micrograph 1a, the tubes are about 13nm in diameter. Note also the excellent dispersion of the MR. A more quantitative measure of the durability improvement of the silver film with MR is seen in Figure 1b. Here the silver coated Mylar film is pulled in tension while the resistance measured. As the film is pulled there is a competition in the effects of tensile pulling which separates silver particles (increases resistance) and a decrease in the width of the specimen which pushes silver particles together (decreases resistance). **The well-dispersed and interactive surface of the MR clearly connects silver particles resulting in retention of conductivity to much higher strain.** Lifetimes of silver traces with MR under a flexural-fatigue condition in dynamic applications are expected to be greatly extended.

When using sintering aids such as flash photolysis, or infra-red, the addition of MR can significantly reduce the energy requirements or increase the film throughput speed by 30% and more. The lower energy of sintering translates to the ability to print more confidently on temperature sensitive substrates like polypropylene or fabrics.

The MR can be easily added to the silver ink formulation during or after the final formulation. Usually 0.1 to 1% wt. MR is all that's needed for superior durability and printing performance based on the results from customers.

How is MR supplied?

For ink jet printing, Molecular Rebar® is supplied as a shelf stable, very mobile fluid masterbatch at 3% wt. MR in water for ease of handling by the customer. The MR concentrate allows the ink formulator to maintain their own proprietary knowhow and further improve their product performance. Two masterbatch products are available, for wholly water based and aqueous-alcohol based inks. Evaluation samples in small to large bottles, or larger containers are available on request. MR for solvent-based silver inks are also available on specific request. In some cases proprietary silver particle dispersion additives can effect stability of MR dispersions. For more information on potential interactions of your additives with Molecular Rebar please call our technical representative.

For screen printing a 13% wt. masterbatch is provided in butyl carbitol.

Company Summary

Molecular Rebar Design, LLC (MRD), based in Austin, Texas, was established in 2010 to develop and commercialize a breakthrough form of modified multi-wall carbon nanotubes called MOLECULAR REBAR® (MR). These are the world's first carbon nanotubes that are fully disentangled, cleaned and specifically functionalized for significantly enhanced performance in a myriad of high-value materials such as silver inks. The tubes are 10,000X times thinner than a human hair, being about 13 nanometers in diameter and 900 nanometers in length. MR is currently integrated into multiple advanced performance applications, such as lead-acid batteries, lithium-ion batteries, coatings, composites, drug delivery, elastomers and more. MRD has state-of-the-art laboratory capabilities to ensure consistent improvements in market applications and formulations, as well as a commercial plant, ISO 9001:2015 certified, of capacity 50 tons, going shortly to 100 tons annually. There have been 71 patents granted around the globe to MRD.

Contact Detail

For further information please contact.

Emily Cole, PhD. Product Director

Tel. 512 537 0100 Office

Tel. 512-423-9430 Cell

Email: ecole@molecularrebar.com

General Office: 512-394-0922