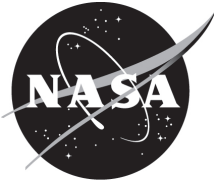


NASA/TM—2017–219690



Transparent Conductive Ink for Additive Manufacturing

X.J. Patlan

University of Illinois at Chicago, Chicago, Illinois

T.D. Rolin

Marshall Space Flight Center, Huntsville, Alabama

October 2017

The NASA STI Program...in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the lead center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.
- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and mission, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results...even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI program home page at <<http://www.sti.nasa.gov>>
- E-mail your question via the Internet to <help@sti.nasa.gov>
- Phone the NASA STI Help Desk at 757-864-9658
- Write to:
NASA STI Information Desk
Mail Stop 148
NASA Langley Research Center
Hampton, VA 23681-2199, USA

NASA/TM—20172017–219690



Transparent Conductive Ink for Additive Manufacturing

X.J. Patlan

University of Illinois at Chicago, Chicago, Illinois

T.D. Rolin

Marshall Space Flight Center, Huntsville, Alabama

National Aeronautics and
Space Administration

Marshall Space Flight Center • Huntsville, Alabama 35812

October 2017

Available from:

NASA STI Information Desk
Mail Stop 148
NASA Langley Research Center
Hampton, VA 23681-2199, USA
757-864-9658

This report is also available in electronic form at
<<http://www.sti.nasa.gov>>

TABLE OF CONTENTS

1. INTRODUCTION	1
2. PROCEDURE	4
2.1 Substrate Preparation	4
2.2 Chemical Reaction to Create Ink	4
2.3 Post-Processing of Ink	6
2.4 Preparation of 2- by 2-Inch Slide	7
3. DATA AND ANALYSIS	8
3.1 Subsequent Experiment	10
4. CONCLUSIONS	12
REFERENCES	13

LIST OF FIGURES

1.	Example of TDEL construction	1
2.	Ink containing carbon nanotubes	2
3.	IZTO ink	3
4.	Color change of experimental solutions due to concentration increase in time	4
5.	Lab setup	5
6.	2- by 2-in developmental slide image	8
7.	Developmental slide results	8
8.	Film in low magnification	9
9.	Film in high magnification	10
10.	Multimeter measurement	11

LIST OF TABLES

1.	Tube furnace set points and dwell times	6
2.	2- by 2-in developmental slide results	9
3.	Subsequent experiment lab observations	11

LIST OF ACRONYMS

EEE	electrical, electronic, and electromechanical
IZTO	indium-zinc-tin-oxide
KSC	Kennedy Space Center
MSFC	Marshall Space and Flight Center
TDEL	thick film dielectric electroluminescent
ICP	inherently conductive polymers

TECHNICAL MEMORANDUM

TRANSPARENT CONDUCTIVE INK FOR ADDITIVE MANUFACTURING

1. INTRODUCTION

NASA analyzes, tests, packages, and fabricates electrical, electronic, and electromechanical (EEE) parts. Nanotechnology is listed in NASA's Technology Roadmap as a key area to invest for further development.¹ This research project focused on using nanotechnology to improve electroluminescent lighting in terms of additive manufacturing and to increase energy efficiency. Specifically, this project's goal was to produce a conductive but transparent printable ink that can be sprayed on any surface for use as one of the electrodes in electroluminescent device design. This innovative work is known as thick film dielectric electroluminescent (TDEL) technology. TDEL devices are used for "backlighting, illumination, and identification due to their tunable color output, scalability, and efficiency" (I.K. Small, T.D. Rolin, and A.D. Shields, "3D Printed Electroluminescent Light Panels," NASA Fiscal Year 2017 Center Innovation Fund Proposal, unpublished data, 2017). These devices use a 'front-to-back' printing method, where the substrate is the transparent layer, and the dielectric and phosphor are layered on top.

This project is a first step in the process of creating a 3D printable 'back-to-front' electroluminescent device. Back-to-front 3D-printed devices are beneficial because they can be printed onto different substrates and embedded in different surfaces, and the substrate is not required to be transparent, all because the light is emitted from the top surface through the transparent conductor. Advances in this area will help further development of printing TDEL devices on an array of different surfaces. Figure 1 demonstrates the layering of the two electrodes that are aligned in a parallel plate capacitor structure (I.K. Small, T.D. Rolin, and A.D. Shields, "3D Printed Electroluminescent Light Panels," NASA Fiscal Year 2017 Center Innovation Fund Proposal, unpublished data, 2017). Voltage is applied across the device, and the subsequent electron excitation results in light emission at the top layer.

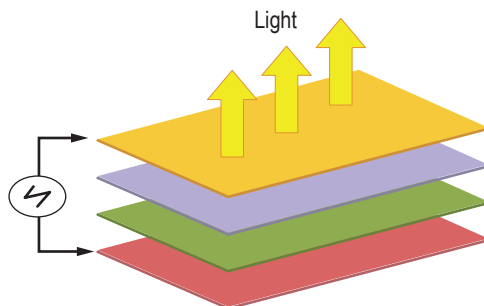


Figure 1. Example of TDEL construction.

There have been other developments in the creation of conductive inks with various advantages and disadvantages. For example, NASA's Kennedy Space Center (KSC) is seeking commercial applications of conductive carbon nanotube inks for inkjet printing technology.² This ink combines carbon nanotubes with metallic nanoparticles to use in standard inkjet printing. As stated in the paper, "the conductive materials are composed of electrical conductors such as carbon nanotubes (including functionalized carbon nanotubes and metal-coated carbon nanotubes), graphene, polycyclic aromatic hydrocarbons (such as pentacene and bisperipentacene), metal nanoparticles, inherently conductive polymers (ICPs), and combinations thereof."² The ink has been characterized to have resistance in the kilohm range and can be printed on surfaces such as paper and textiles. However, the ink is not transparent, and a more complex preparation regimen is required. Figure 2 shows samples of the carbon nanotube ink.²



Figure 2. Ink containing carbon nanotubes.

Another conductive ink is one that uses nanometer-size indium-zinc-tin-oxide (IZTO) particles. The IZTO nanoparticles must have an average size of 20–30 nm.³ A production process similar to that reported here is followed. However, IZTO nanoparticles are challenging to find and purchase, given the novelty of the material. There are few distributors in the market, making it more expensive to obtain. Figure 3 shows an example of IZTO ink.³



Figure 3. IZTO ink.

In contrast to those mentioned previously, the Marshall Space Flight Center (MSFC) produced ink is cost effective, transparent, and a particle free process. MSFC originally worked from reference 4. Experiments were conducted to exactly replicate the process described in the paper. However, this process resulted in less-than-desirable and, in some cases, explosive solutions. Attempts were made to contact the authors to better understand the process, but a response was not received. MSFC decided to conduct experimental trials where certain variables and quantities stated in the paper were altered. Examples of changes included increasing final molar concentrations and evaluating colors seen during the process. A process was developed whereby successful results were obtained. Resistance measurements of films were confirmed in the kilohm range, the magnitude of which is as good as that reported at KSC for carbon nanotube ink.

2. PROCEDURE

2.1 Substrate Preparation

One-inch glass slides were used as substrates and were prepared according to the process in reference 4. They were prepared using this method to ensure that they were clean. The technique involved sonication for 10 min in acetone, followed by 10 min of sonication in isopropyl alcohol. They were then dried with a nitrogen gas gun and stored in a dust-free flowing nitrogen cabinet for future use.

2.2 Chemical Reaction to Create Ink

The inks were prepared first by weighing 1.76 g of indium(III) acetate (99.99%, Aldrich) and 0.24 g of tin (IV) acetate (Aldrich). These acetates were then mixed with 67 mL of acetylacetone ($\geq 99\%$, Sigma-Aldrich) in a 100-mL glass beaker. The color of the resulting solution had the appearance shown in figure 4(a) when dissolved at room temperature. The acetates were dissolved using a glass stirring rod. Figure 4 demonstrates how color can change in time as the concentration increases. Reference 4 states the final solution should be a reddish-brown color, which could be interpreted as sample color figure 4(c) or figure 4(d).

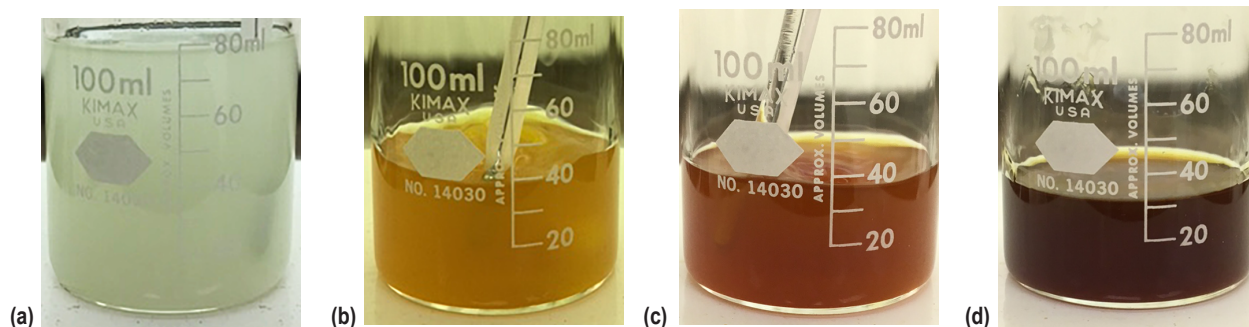


Figure 4. Color change of experimental solutions due to concentration increase in time.

A magnetic stirring bar was placed in the beaker, which was positioned on a hot plate with a magnetic stirring accessory. To stir the solution, the magnetic stirrer was set to 300 rpm. The hot plate was set to 165 °C. The paper states that the solution must be maintained at 120 °C. Several experimental runs indicated that the MSFC hot plate had to be set at 165 °C to ensure that the solution was maintained at 120 °C. One observation made during the course of experimentation was that the hot plate temperature decreased as the solution started to evaporate through heat and

fume hood ventilation. To control this, the temperature was constantly monitored using a thermometer clamped to a metal stand and the hot plate adjusted accordingly (fig. 5). A glass titration burette was also affixed to the metal stand above the beaker. The purpose of the burette was to add hydrogen peroxide (30 weight percentage in water, Sigma-Aldrich) to the solution, drop-wise. Reference 4 states, "...added drop-wise in 6 aliquots at 30-min intervals into the solution to prevent phase separation due to a re-crystallization." Therefore, 1 mL of hydrogen peroxide was added drop-wise to the stirring solution in intervals of 30 min 6 times for a total of 6 mL.

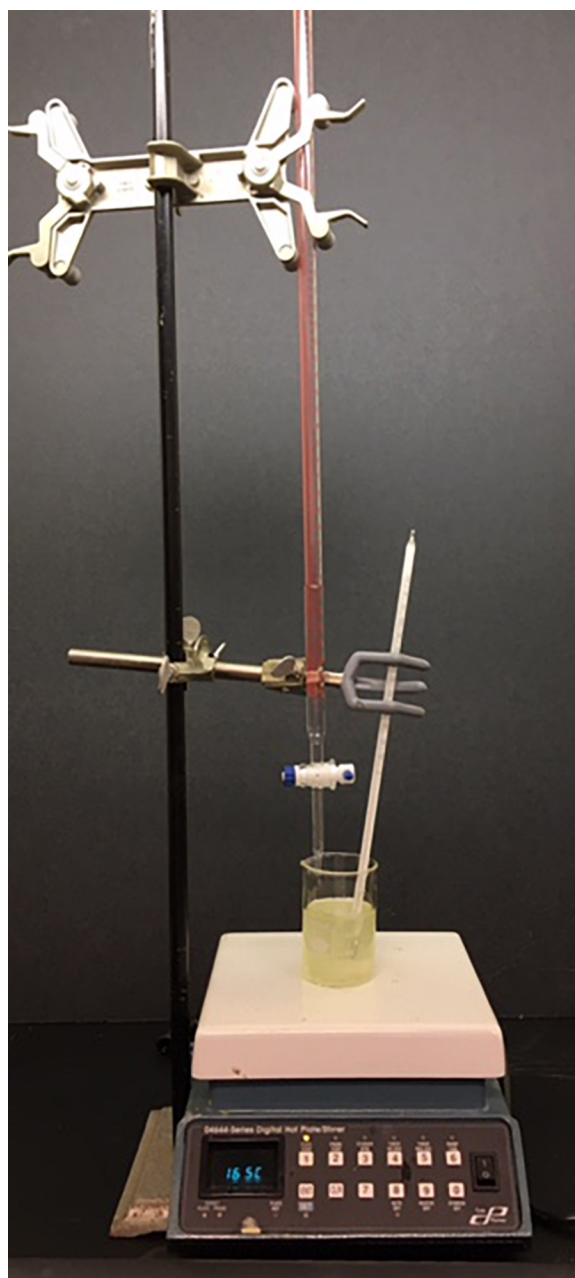


Figure 5. Lab setup.

At this point in the process, color was monitored, and concentration was altered compared to the paper. In one trial, concentration was maintained by adding appropriate amounts of acetone as needed. The maintained concentration, 0.1 M, was reported in reference 4. In other trials, fluid changes from evaporation were permitted resulting in higher concentrations of the acetates. Samples were taken at different time intervals to determine resistance for a given color.

2.3 Post-Processing of Ink

Rheology optimization was not part of this experiment, so the ink was not adjusted for inkjet or aerosol jet printing. Instead, a simpler process for depositing the ink was used. Ink was applied onto a glass substrate as one-layer and two-layer specimens. The glass substrate was maintained at 80 °C, as recommended in the paper, by setting the hotplate to 85 °C.⁴ Ink was removed from the solution using a 1-mL glass pipet in order to track volume for subsequent concentration calculations. The ink was deposited using a glass dropper, glass pipet, or spray bottle. These applications were used to determine the best material deposition method. After each application of ink, the film was dried in a box oven at 150 °C for 10 min in air to evaporate solvents. The dried films were then annealed in a tube furnace at 500 °C for 2 hr in flowing oxygen to burn off any remaining organic components. Table 1 shows the set points and dwell times of the tube furnace. The ramp rate was ≈ 8 °C/ min.

Table 1. Tube furnace set points and dwell times.

Set Point Temperature (°C)	Time Held at Temperature (min)
50	0
300	30
500	25
300	30
50	0

For creating two-layer specimens, another layer of ink was added onto the dried film and placed back into a box oven for 10 min. The film was annealed in the tube furnace at 500 °C for 2 hr in a flowing oxygen gas. These two-layer samples were then annealed for 2 hr at 500 °C in a flowing nitrogen gas because data from reference 4 indicated improved results with nitrogen gas annealing. A multimeter was used to measure the deposited film resistance in ohms. The film was probed in different areas of each sample, and the lowest resistance measurement was recorded.

2.4 Preparation of 2- by 2-Inch Slide

Initially, a 2- by 2-in developmental slide was prepared so that four experiments could be compared side by side. It aided in understanding deposition pitfalls and minimized error introduced by different glass substrates, which may be different textures and still have contaminants irremovable by the Fang cleaning process. Additionally, variables such as concentration, thickness, and annealing were tested. To understand concentration effects, the 2- by 2-in glass slide was prepared similar to sections 2.1–2.3. Four distinct samples with different ending time intervals, but after the sixth aliquot, were deposited. The glass slide was marked with a high resistive heat marker to distinguish the different samples. A 1-mL glass pipet was used to add the ink onto the substrate at the different time intervals. Removing the ink at different time intervals resulted in films with different concentrations due to evaporation.

Secondly, testing was conducted to understand effects of the film's additional layers. The first trial was to deposit a single layer of ink onto the substrate. Then a second layer was added depending on results observed in the first trial. Samples were taken out of the final solution at the same time interval as the first experiment and layered on top of the first film. Finally, the best annealing process was determined. The one-layered film was annealed at 500 °C for 2 hr in flowing oxygen and measured. The two-layered film was placed in a box oven at 150 °C for 10 min in air, then 500 °C for 2 hr with flowing nitrogen gas in a tube furnace.

3. DATA AND ANALYSIS

Valuable data were gathered from the 2- by 2-in developmental slide. Multiple experiments were performed and yielded different results, which provided feedback for optimization. This experiment allowed direct comparison of resistances at different concentrations, thicknesses and annealing.

Figure 6 shows the developmental slide with a one-layer film annealed in oxygen gas for 2 hr. Figure 7 shows sample colors taken in time and images of resulting ink depositions. Box 1 shows a one-layer film after oxygen annealing and box 2 a two-layer film after oxygen and nitrogen annealing.

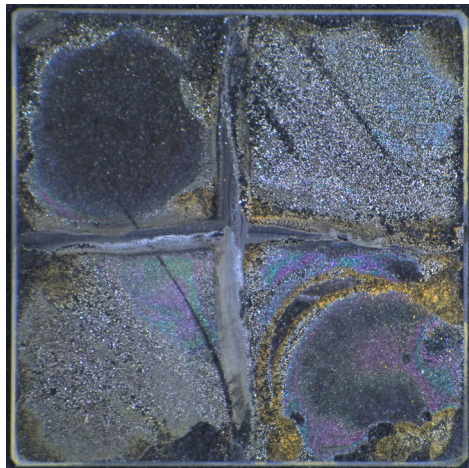


Figure 6. 2- by 2-in developmental slide image.

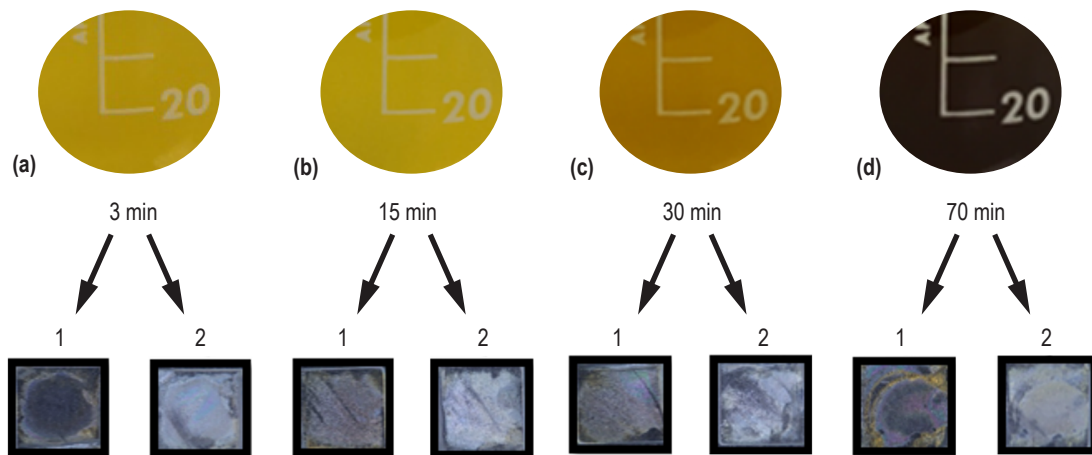


Figure 7. Developmental slide results.

There were several observations made during the course of this effort. First, the best product color had to be determined and was observed to be dependent on concentration. An experiment was performed where acetylacetone was added to replace evaporation and maintain a constant 0.1 M concentration. This resulted in an unusable ink that did not change color. However, when evaporation was allowed, volume reduction created a more concentrated solution that eventually turned a darker color in the range that was discussed in reference 4. When assessing if the paper's description of "reddish-brown" resistance characteristics were in figure 4(c) or figure 4(d), an initial separate experiment confirmed it was not figure 4(c). Although this solution is more of a reddish-brown color, it exhibited high resistance.

Additionally, the ink in figure 4(c) was not stable, which caused it to crumbled off after the 500 °C oxygen annealing process. Therefore, no further testing was performed on solutions removed at this interval. Table 2 shows the best result was obtained with sample D2, which was a brownish-red solution with a concentration of approximately 0.2 M. This concentration was calculated by neglecting the volume error due to evaporation up until the 70-min mark after the sixth aliquot. This volume reduction would tend to increase the concentration.

Table 2. 2- by 2-in slide results.

Sample	A1	A2	B1	B2	C1	C2	D1	D2
Layer	1	2	1	2	1	2	1	2
Resistance (MΩ)	∞	1.98	∞	∞	∞	∞	8.87	0.01619

Secondly, the paper states that two layers had better conductivity, likely due to linking between conducting islands. This was proven by the A solution and the D solution. It was observed that after adding a second layer to the samples and annealing it in nitrogen gas, a finite resistance was measured. The best resistance was in areas where the film had two, thinly applied layers that were transparent. This was typically near the slide edges where the ink rolled off after application of drops or spray. The transparent film is shown at low magnification in figure 8 and high magnification in figure 9.



Figure 8. Film in low magnification.

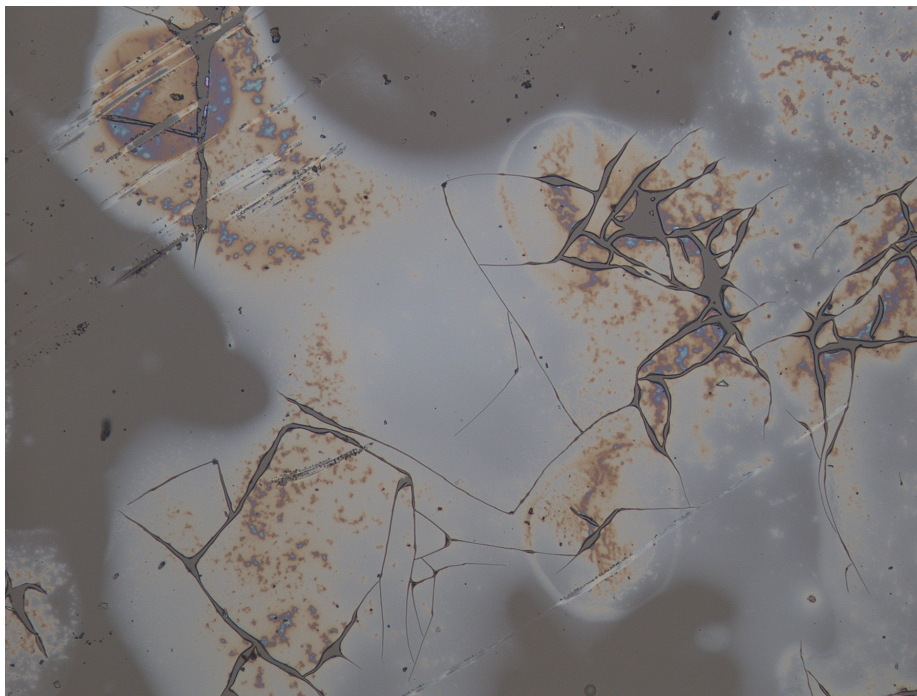


Figure 9. Film in high magnification.

Finally, annealing the samples in oxygen gas for 2 hr at 500 °C resulted in multimeter readings that were either infinite (∞) or in the tens of megaohms. However, after the nitrogen gas annealing, A2 was observed to have a new spot that had a slightly lower resistance. This indicated that a nitrogen anneal was beneficial. After application of this anneal for sample D, the resistance was observed to go from megaohms down to kilohms. Optically comparing square 1 and 2 in figure 7, it was found that the lowest resistance film in square 2 is more transparent.

3.1 Subsequent Experiment

Data from the D2 sample clearly exhibited the best results. To ensure the process was repeatable, a subsequent experiment was performed following the D2 process. Observations directly from lab notes of the D2 repeatability run are shown in table 3. Two 1-in glass substrates were prepared at the 70-min mark when the ink was brownish-red. Two samples were taken out of the solution and deposited on the glass substrates. They were then placed in the box oven at 150 °C for 10 min in air and subsequently layered with ink a second time. After the second layer was applied, the glass slides were placed in the box oven at 150°C for 10 min in air. Both slides were then annealed in oxygen followed by nitrogen.

Table 3. Subsequent experiment lab observations.

Aliquot Interval	Starting Temperature	Ending Temperature	Observation and Notes
1	120 °C	117 °C	As the solution gets hotter, it becomes clearer because the solids are dissolving. No reaction when added H ₂ O ₂ . The color is a clear yellow. Hot plate is set at 165 °C.
2	120 °C	117 °C	Solution is still clear. After adding H ₂ O ₂ , the solution bubbled and fizzed toward the end of the 1mL addition. Hot plate is set to 160 °C.
3	123 °C	119 °C	Bubbling and fizzing when adding the H ₂ O ₂ . The solution is starting to look like a more concentrated yellow such as lemonade. Hot plate is set at 150 °C.
4	120 °C	116 °C	Reaction observed when H ₂ O ₂ is added into the mixture. The color is now a concentrated yellow, but still a lighter version. Hot plate is set at 145 °C. Precipitate is on the walls of the beaker.
5	120 °C	115 °C	Now an even more concentrated yellow. When adding H ₂ O ₂ precipitate was observed on the walls and steam came off. Hot plate was set at 140 °C.
6	118 °C	114 °C	A deeper concentrated yellow with a hint of brown. Reaction observed when H ₂ O ₂ was added. Hot plate is set at 140 °C.
-	-	-	Wait 70 min after the sixth aliquot to obtain the brownish-red ink color to take a sample.

The subsequent experiment of D2 produced a 4.88-kΩ transparent film. The actual multimeter reading is shown in figure 10. This second run not only confirmed repeatability but also resulted in the best material produced. When testing the slide, the lowest resistance was found to be in the transparent area. This area was located near the edge of the substrate where the liquid rolled off the side.



Figure 10. Multimeter measurement.

4. CONCLUSIONS

Transparent films were produced with resistances in the low-kiloohm range by deviating concentration from the value indicated in reference 4. The paper stated that a 0.1-M concentration solution should be the final concentration, but experimental data demonstrated that the best concentration was a minimum of 0.2 M.⁴ This solution was the darkest observed, exhibited a brownish-red color, and demonstrated the lowest resistance.

Secondly, reference 4 states that two thin layers have better conductivity. Results from this experiment confirmed this statement. This result is most likely due to the deposited material meeting the percolation threshold for conducting islands. The lowest resistance area was found where the ink was layered thinly and near the edge of the slide. This shows that the film must be applied in very thin, but multiple layers in order to have good results.

Finally, the annealing process stated in reference 4 was verified. It suggested to anneal the samples in nitrogen gas after oxygen gas to improve properties. Observations from the A2 and D2 samples indicated this was a necessary step in processing the films. Initial observations showed that oxygen annealing by itself was insufficient to produce the best results.

Future MSFC experiments should follow the D2 method and use a better application method such as aerosol jet printing to achieve thin two-layer films. Aerosol jet printing can produce evenly distributed layers as thin as 600 nm. However, additional studies will have to be conducted to adjust the viscosity of the D2 solution to meet the demands of diverse printing paradigms.

REFERENCES

1. NASA: “2015 NASA Technology Roadmaps,” <<https://www.nasa.gov/offices/oct/home/roadmaps/index.html>>, August 2017.
2. Parrish, L.: “Conductive Carbon Nanotube Ink For Inkjet Printing,” NASA, <<https://technology.nasa.gov/patent/KSC-TOPS-41>>, July 2017.
3. Jihoon K.; Seok-In N.; and Han-Ki K.: Inkjet printing of transparent InZnSnO conducting electrodes from nano-particle ink for printable organic photovoltaics,” *Sol. Energ. Mat. Sol. C.*, Vol. 98, pp. 424–432, doi:10.1016/j.solmat.2011.11.050.
4. Fang M.; Aristov, A.; Rao, K.V.; Kabashin, A.V.; and Lyubov, B.: “Particle-free inkjet printing of nanostructured porous indium tin oxide thin films.” *RSC Adv.*, Vol.42, No. 3, pp. 19,501–19507, doi:10.1039/C3RA40487K, July 2013.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operation and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 01-10-2017		2. REPORT TYPE Technical Memorandum		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Transparent Conductive Ink for Additive Manufacturing			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) X.J. Patlan* and T.D. Rolin			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) George C. Marshall Space Flight Center Huntsville, AL 35812			8. PERFORMING ORGANIZATION REPORT NUMBER M-1444		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITOR'S ACRONYM(S) NASA		
			11. SPONSORING/MONITORING REPORT NUMBER NASA/TM-2017-219690		
12. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified-Unlimited Subject Category 33 Availability: NASA STI Information Desk (757-864-9658)					
13. SUPPLEMENTARY NOTES Prepared by *The University of Illinois at Chicago and the EEE Parts Engineering and Analysis Team, Parts, Packaging, and Fabrication Branch, and Electrical Integration and Fabrication Division, Space Systems Department, Marshall Space Flight Center, Huntsville, Alabama.					
14. ABSTRACT This project focused on using nanotechnology to improve electroluminescent lighting. Specifically, the goal was to produce a conductive-but-transparent printable ink that can be sprayed on any surface for use as an electrode in electroluminescent device design. Using Mei Fang's paper entitled, "Particle-free inkjet printing of nanostructured porous indium tin oxide thin films," attempts at following the paper exactly did not produce desired results. However, by altering certain variables stated in the paper, such as molar concentrations and colors seen during the process, successful results were obtained. Resistance measurements of films confirmed conductivity in the kilohm range.					
15. SUBJECT TERMS electrical, electronic, electromechanical parts, additive manufacturing, nanomaterials, electroluminescence, printable ink					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			STI Help Desk at email: help@sti.nasa.gov
U	U	U	UU	24	19b. TELEPHONE NUMBER (Include area code) STI Help Desk at: 757-864-9658

National Aeronautics and
Space Administration
IS02

George C. Marshall Space Flight Center
Huntsville, Alabama 35812