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Effect of Butanol and Terpinol as a Solvents in GNP/SA Conductive Ink

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ABSTRACT

Silver hybrid inks have garnered significant attention in the realm of flexible electronics due to their remarkable conductivity and compatibility with various substrates. The selection of solvent profoundly influences the ink's properties and performance, encompassing SEM characteristics and electrical conductivity. This paper undertakes a comparative analysis of silver hybrid inks formulated with two distinct solvents: butanol and terpinol. The study delves into how the choice of solvent impacts pigment distribution within the ink and subsequently affects its electrical conductivity.

1. Introduction

Flexible electronics is a rapidly expanding field that synergizes electronics and materials science to create bendable, conformable, and flexible electronic devices [1,2]. These devices offer enhanced mechanical properties, lightweight design, and seamless integration with curved or irregular surfaces, setting them apart from conventional rigid electronics. They find applications in diverse industries, including biomedical applications, where they hold the potential to revolutionize healthcare through enabling biosensors, electronic skin patches, and implantable devices. The purpose of this research is to investigate and comprehend the effects of solvent variations, specifically using butanol and terpinol, in silver hybrid ink formulations on the morphological and electrical properties of conductive patterns deposited on flexible substrates.

Conductive inks play a pivotal role in these emerging technologies by facilitating the deposition of conductive patterns on flexible substrates using printing techniques [3,4]. The traditional soldering method employed in the electronics industry poses environmental and health risks due to the use of lead-based solders [5]. Soldering operations emit toxic fumes and contribute to environmental pollution [6]. Conductive inks offer an alternative to soldering by enabling the deposition of conductive particles on substrates without the need for high-temperature procedures or hazardous

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materials. They mitigate the hazards linked to lead-based soldering, reduce worker exposure to toxic fumes, and enable precise patterning and customization of electrical circuits. Ink formulation significantly impacts the achievement of desired ink properties and print quality. Solvents like butanol and terpinol are commonly utilized in silver hybrid ink formulations [7-9]. Butanol aids in the dispersion of metallic nanoparticles and boasts excellent solubility for silver compounds. Its high boiling point ensures controlled ink drying and improved adhesion on substrates [10]. Terpinol, derived from natural sources, offers distinctive properties such as lower toxicity, solubility for silver compounds, improved pigment flow, and potential ink stability enhancement [11]. Both solvents contribute to the dissolution and dispersion of conductive elements, ensuring ink homogeneity and stability. The solvent choice can impact the electrical properties of conductive inks, and optimizing the solvent composition and concentration permits precise tuning of electrical performance. The utilization of butanol and terpinol as alternatives to hazardous solvents renders electronic manufacturing processes more environmentally friendly.

2. Methodology

The methodology employs a hybrid ink formulation incorporating Graphene Nanoplatelets (GNP) characterized by particle sizes of 25µm and a surface area ranging from 120 to 150 m2/g. The ink also includes silver flakes with particle sizes of 10µm, ensuring a minimum purity level of 99.9% based on trace metals analysis. Additionally, the ink composition contains silver acetate with a trace metals basis purity of 99.99%. For the organic solvents, denatured ethanol (99% purity), 1-butanol (99.9% purity), and terpineol (approximately 65% alpha, 20% gamma, and 10% beta) were used. The methodology employs an ultrasonic bath as the primary tool for incorporating all these materials (Table 1).

Table 1
Materials used in formulation of hybrid ink

Name	Material details
Graphene nanoplatelets (GNP)	Particle surface of 25µm with a surface area of 120 to150 m2/g
Silver flakes	Particles of that have properties of electrical with the with size of 10 µm, ≥99.9% trace metals basis.
Silver Acetate	99.99% trace metal basis acid silver salt
Ethanol	Denatured Ethanol 99%
1-Butanol	99.9% butyl alcohol
Terpineol	Pine oil contain of ~65%α,~10%β,~20%γ substances

2.1 Hybrid Ink Preparation

The methodology employs a hybrid ink formulation incorporating Graphene Nanoplatelets (GNP) characterized by particle sizes of 25µm and a surface area ranging from 120 to 150 m2/g. The ink also includes silver flakes with particle sizes of 10µm, ensuring a minimum purity level of 99.9% based on trace metals analysis. Additionally, the ink composition contains silver acetate with a trace metals basis purity of 99.99%. For the organic solvents, denatured ethanol (99% purity), 1-butanol (99.9% purity), and terpineol (approximately 65% alpha, 20% gamma, and 10% beta) were used. The methodology employs an ultrasonic bath as the primary tool for incorporating all of these materials.

In this experiment, a mixture was prepared by combining 0.005g of GNP (graphene nanoplatelets) with 0.429g of silver flakes (SF) and 0.042g of silver acetate (SA) in 5ml of ethanol. The methodology involved sequential steps of sonication and solution preparation. Initially, GNP powder underwent sonication in ethanol for a duration of 10 minutes. Subsequently, the sonication process was extended for an additional hour after the introduction of SF into the solution. The mixture underwent the addition of SA and subsequent sonication for another hour. The heating process involved elevating the mixture's temperature to 70°C. Simultaneously, a magnetic stirrer maintained constant stirring at a speed of 200rpm. Ethanol evaporation was achieved by continuing the process. The drying process involved curing the solution in an oven for 1 hour at a temperature of 250°C. Subsequently, the cured solution was pounded until it reached a fine powder texture. The process is shown at Figure 1 below.

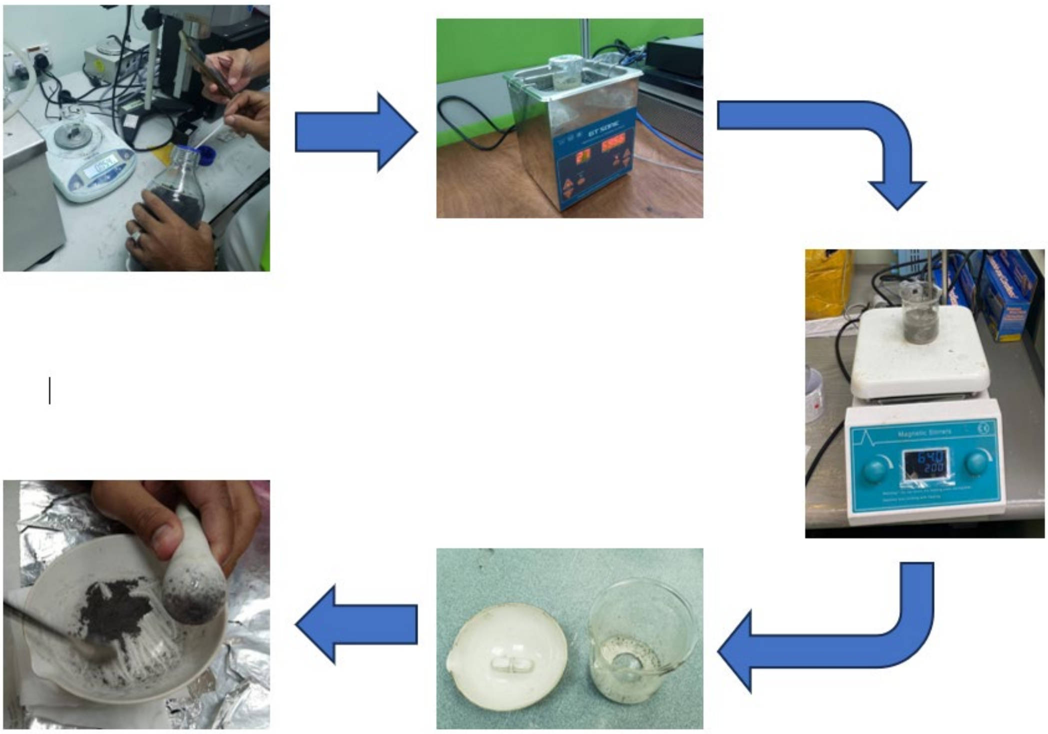

Fig. 1. Process for preparation of hybrid ink

2.2 Conductive Paste Fabrication for Different Ratio of Butanol and Terpinol

The methodology involves the crucial step of weighing the hybrid powder, which is essential for determining the appropriate ratio of terpineol and butanol required to produce the desired paste. The methodology utilizes reference [12] to determine the proper quantities of butanol and terpineol required for a given amount of granules. Specifically, for every 0.1733g of granules, it is recommended to add approximately 1 drop of butanol, which is roughly equivalent to 0.02g, and 1 drop of terpineol, approximately equivalent to 0.03g. Vigorous agitation of the mixture will be conducted for five minutes using a high-powered agitator. The following methodology describes the utilization of the resulting paste for printing on a substrate.

To investigate the effects of varying ratios of butanol and terpineol, a series of pastes will be meticulously prepared. Each paste will be formulated with a distinct combination of these two substances, ensuring a wide range of ratios is covered. The experimental procedure involves the preparation of five samples with varying ratios of butanol to terpineol. The ratios of the samples are as follows: 5:10, 10:10, 10:15, 10:5, and 15:10, respectively.

2.3 Test Sample Preparation using Printing Techniques

The employed methodology involved the utilization of a silkscreen printing technique, where a silkscreen containing a pre-printed pattern was utilized. The methodology employed a squeegee to trace the pattern, ensuring the deposition of ink with the highest accuracy and precision [13]. In this method, the dimensions of the printed ink measure 3mm x 3mm. Furthermore, a spacing of 3cm is maintained between each printed point. The ink application will be executed on a copper substrate with dimensions of 12cm x 1cm, as depicted in the accompanying Figure 2.

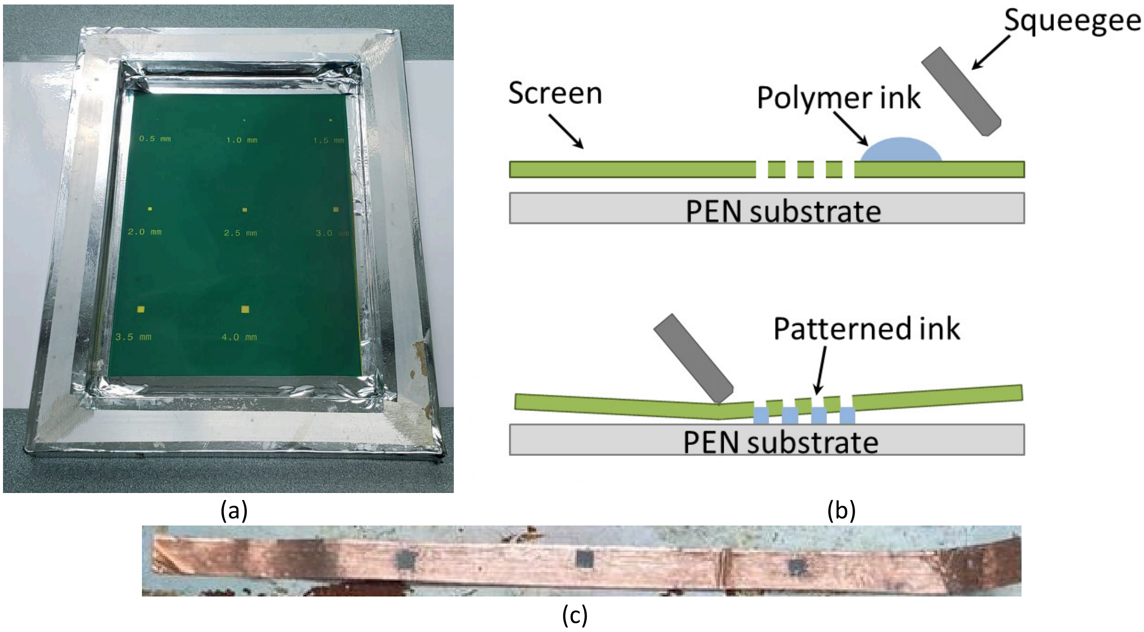

Fig. 2. (a) silk printing mesh (b) printing techniques using squeegee on substrate and (c) printed hybrid ink on copper substrate

2.4 Methodology Testing

The test samples will undergo thermal curing in an industrial UF55 oven maintained at a constant temperature of 250 degrees Celsius. The investigation aims to explore the impact of curing temperature on electrical resistivity by analyzing the paste samples. These samples are formulated with varying ratios of butanol to terpinol, specifically in the ratios of 5:10, 10:10, 15:10, 10:5, and 10:15. The structural analysis of the paste will involve the utilization of a scanning electron microscope (SEM). Furthermore, the electrical performance evaluation of each formulation will involve measuring the resistance using a multimeter (Figure 3).

To assess the cross-section of the printed samples, scanning electron microscopy (SEM) will be employed. An automated fine machine will be utilized for a coating process to prevent potential charge accumulation on the printed samples. The methodology employed in this study utilizes scanning electron microscopy (SEM) to gather comprehensive nanoscale data from materials. The primary signals detected during SEM imaging include backscattered electrons (BSE) and secondary electrons (SE), which generate grayscale images of the material at high magnification [14]. The method employs a raster-like beam motion to scan the sample, capturing signals from secondary electrons and backscattered electrons. This approach provides valuable insights into the sample's topography and composition. SEM imaging is widely used for in-depth surface analysis across various

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scientific fields. The procedure involves using a JEOL JSM-5050PLUS/LV scanning electron microscope (SEM) with an accelerating voltage of 20 kV [15-17].

(a) (b)

Fig. 3. (a) sample for SEM (b) SEM to observe the cross-section

3. Results

3.1 Optimization Ratio of Organic Solvent for Hybrid Paste

In this experiment the organic solvent of paste was used are N-butanol and terpinol based on the referred conducted by Saleh et al., [18]. The base paste formulation, which served as the reference, demonstrated a best appearance of hybrid ink paste of the ratio of 10:10 also 5:10 and 15:10 provide same appearance but for the ratio of 10:5 show the paste a dry and 10:15 slightly dry the illustration as shown in Table 2.

Table 2
The droplet of N-Butanol and Terpinol

GNP Powder	N-Butanol, no. of droplet	Terpinol, no. of droplet	Observation
0.173g	10	10	
0.173g	5	10	
0.173g	15	10	
0.173g	10	5	
0.173g	10	15	

In contrast, the Terpinol formulation exhibited a different distribution of precipitates compared to the N-Butanol-based formulation, indicating that Terpinol played a significant role in the changes observed. The performance of each paste was measured in terms of sample sheet resistance measurement where the sample was prepared on the Cu substrate and cured on the same temperature of 250°C in the oven.

3.1.1 Electrical characteristics

Table 3 and Figure 4 present the sheet resistance measurements of the hybrid ink paste with different ratios of organic solvents, specifically 5:10, 10:10, 15:10, 10:5, and 10:15 of N-butanol to terpinol. The baseline data, represented by the base paste, showcases a resistivity value of 0.828E-04 Ω/sq. This baseline serves as a reference for evaluating the electrical performance of various mixed ink formulations. The resistance value reflects the overall electrical conductivity of the ink, while the resistivity value quantifies conductivity per unit area. These results of electrical characterization provide the foundation for assessing how solvent composition, ink formulation, and curing conditions influence the electrical properties of the hybrid ink formulation.

Table 3
Result of sheet resistance

Hybrid Ink	Curing Temperature of 250°C	
	Resistance, Ω	Resistivity, Ω/sq
Base	2.0333	0.828×10^{-4}
5-Butanol	2.4667	1.562×10^{-4}
15-Butanol	2.0000	0.69×10^{-4}
5-Terpinol	1.7333	0.5459×10^{-4}
15-Terpinol	2.0000	1.18×10^{-4}

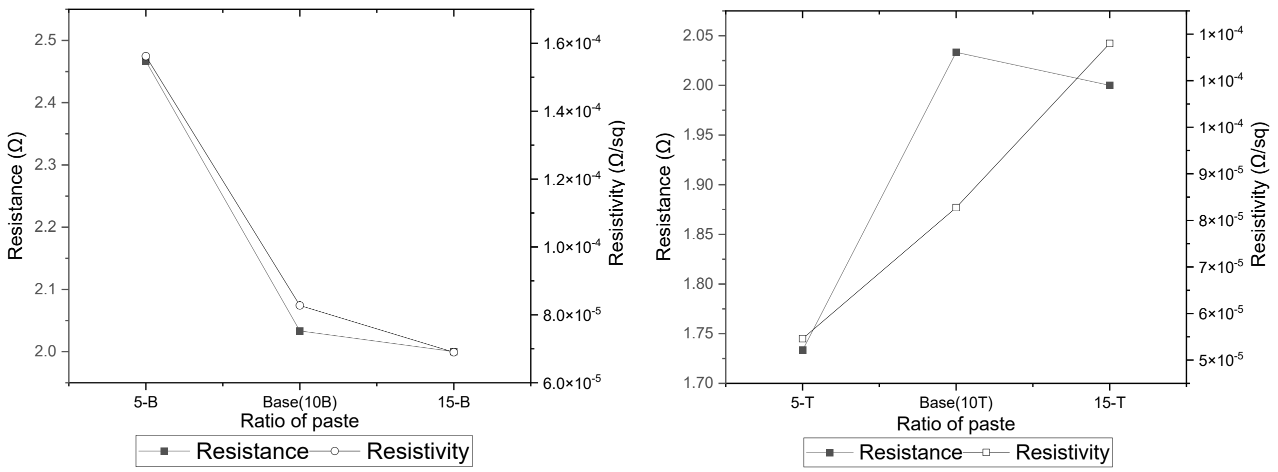


Fig. 4. Resistant and resistivity measurement (a) butanol (b) terpinol

The inks based on 5-Butanol and 5-Terpinol displayed marginally lower resistance values compared to the inks based on 15-Butanol and 15-Terpinol, indicating enhanced electrical conductivity or reduced resistance. In terms of resistivity, the 5-Terpinol-based ink demonstrated the lowest value of 0.5459E-4 Ω/sq, closely followed by the 15-Butanol-based ink with a resistivity of 0.69E-4 Ω/sq. These outcomes suggest higher conductivity, characterized by lower electrical resistance per unit area, for these ink formulations.

Conversely, the 5-Butanol-based ink exhibited a resistivity of 1.562E-4 Ω/sq, while the 15-Terpinol-based ink displayed a resistivity of 1.18E-4 Ω/sq, indicating elevated resistivity and diminished conductivity for the 15-Terpinol-based ink. The curing temperature's influence on ink drying behavior, particle sintering, and overall ink morphology can affect the electrical properties of printed patterns. Therefore, when evaluating ink conductivity, it is vital to consider the impact of curing temperature.

3.1.2 Morphologic

The enhancement of properties is strongly correlated with the nanocomposite microstructure. Effective characterization of morphology is important to establish a structure-property relationship for these materials. Scanning electron microscopy (SEM) has been employed to assess the dispersion of graphene and to examine the surface for filler pull-out, which could provide insights into the strength of interfacial adhesion. Figure 5 illustrates the cross-section obtained for all the printed samples of conductive ink.

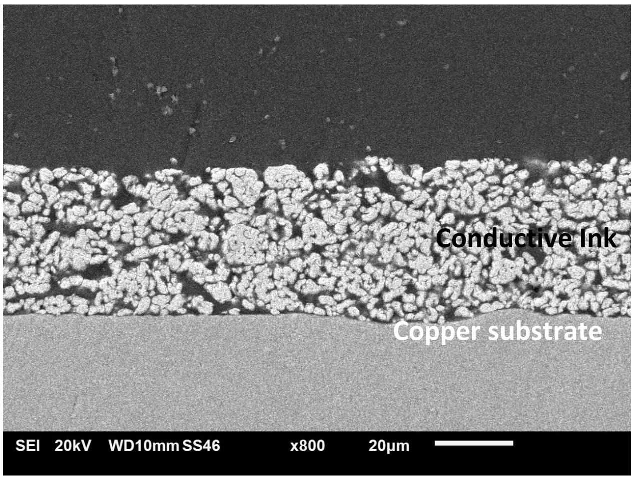
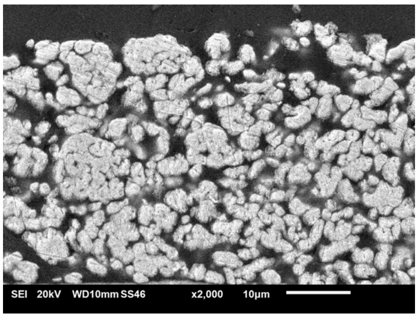


Fig. 5. The image of cross section printed conductive ink using SEM

The SEM images of the paste formulations offer valuable insights into the morphology and particle distribution within the paste matrix (Figure 6). In the base paste formulation, the SEM image reveals an evenly dispersed distribution of metallic particles with a homogeneous morphology, although some particles are clumped together. The particles seem to be uniformly spread across the paste, indicating favorable particle dispersion. This uniform morphology is crucial for achieving good electrical conductivity [18].



(a)

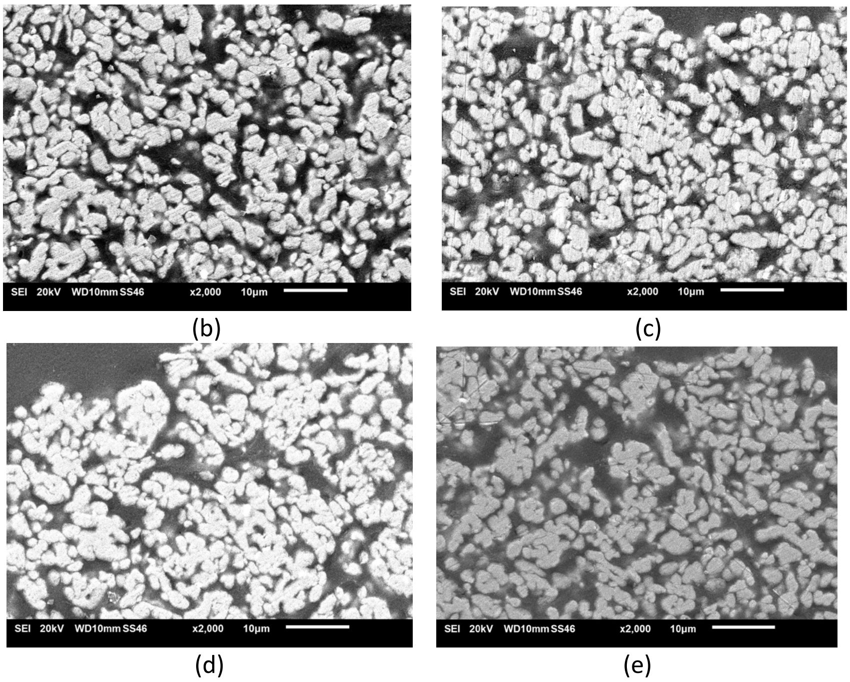


Fig. 6. The morphology of solvent (a) base paste (b) 5-butanol ratio (c) 15-butanol ratio (d) 5 terpinol and (e) 15 terpineol

When compared to the base paste particles, the pastes containing 5-butanol and 15-butanol exhibit a well and evenly dispersed distribution of metallic particles without any clusters or clumps. This suggests that butanol can maintain a uniform dispersion of morphology and particles, reducing clumping. In contrast, the cross-section SEM images of 5-terpinol and 15-terpinol show metallic particles clumped together, with slightly more even dispersion. This indicates that the terpinol substance hinders the dispersion of particles but acts as a binding agent for particles.

Regarding morphological characteristics, even dispersion of metallic particles contributes to better conductivity. It is evident that butanol leads to better resistivity, as shown in Table 3 previously.

Summary of the hybrid ink of different ratio solvent can be refer to Figure 7. It can be observed that pattern of different solvent was decreased in resistivity for butanol and increase for terpinol. Furthermore, in their research, [19] discovered that silver nanoparticles could be self-generated from the micrometer flake shape of silver particles during the sintering process. These silver nanoparticles are anticipated to offer increased die shear strength in contrast to the micrometer spherical shape of Ag particles [19]. Moreover, earlier studies revealed that a single layer of sintered hybrid Ag paste on a soda-lime glass sheet exhibited elevated thermal conductivity at the sintering temperature of 200°C [20].

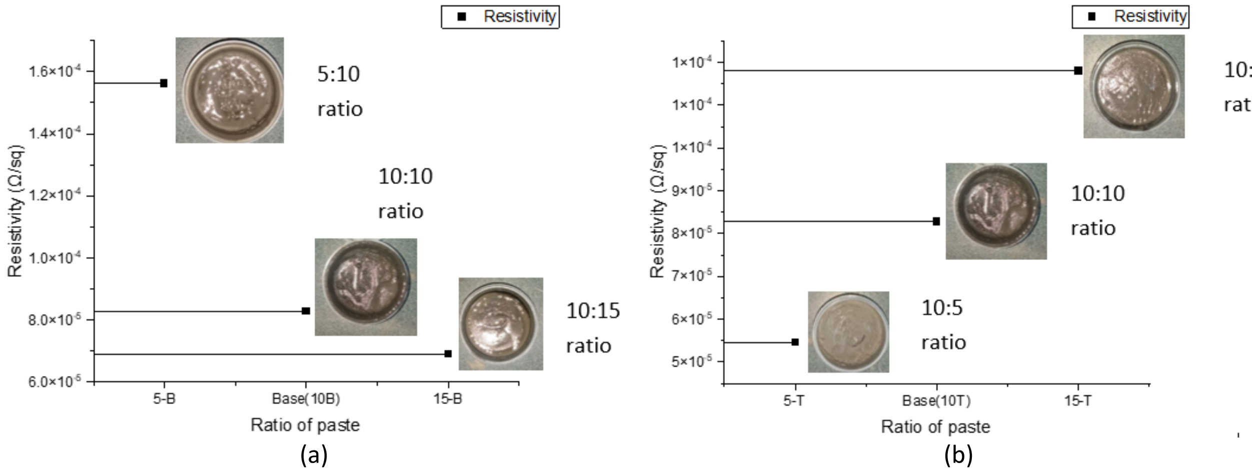


Fig. 7. Summary for solvent different ratio

4. Conclusions

In conclusion, this study thoroughly investigated the effectiveness of silver hybrid inks incorporating both butanol and terpinol solvents, focusing on aspects such as ink stability, printability, and electrical conductivity. Both solvents exhibited commendable conductivity, with a slight advantage seen in butanol-based inks. However, the solvent choice minimally influenced the electrical performance of the printed structures. The research underscored the importance of solvent evaporation, ink morphology, and particle dispersion in elucidating the variations in resistance and resistivity among different formulations.

Moreover, the meticulous selection and fine-tuning of solvent composition were found to be paramount in enhancing the electrical conductivity and overall efficiency of printed electronic devices. The use of terpinol-based inks particularly showcased advantages in terms of viscosity, flowability, resolution, and surface morphology. This further underscores the crucial role of solvent selection in optimizing silver hybrid inks to suit various electronic applications.

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