Development of solvent-free UV-curable conductive inks for printed flexible microelectronics

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Abstract

Solvent-free UV-hardenable ink formulations for printed microelectronics were designed to retain thermoplastic behavior after UV exposure. Screen printing of conductive inks is a convenient method to rapidly form interconnects in microelectronic devices. At high production volumes, the emissions from solvenborne conductive inks can be significant and require abatement systems. Conventional UV-curable inks can be used to eliminate the solvent since the ink can be tailored to have a low viscosity for application and then be rapidly converted into a hard, crosslinked film upon exposure to UV light. Since these conventional UV-curable inks form a crosslinked film, they will not flow on the application of heat and pressure, thus cannot be used where a subsequent bonding step is needed to connect the conductive ink to another device or component. Thus, we have developed a UV-hardenable solvent-free ink binder system that remains thermoplastic after application and "curing" so that the conductive ink can be thermally bonded to another device. Conductivity is obtained through a combination of silver particles of different size distributions.

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Introduction

Screen printing is a straightforward, rapid and simple method for applying conductive wiring to printed circuit boards and other microelectronic devices for formation of interconnects. Conductive inks are typically formulated with a polymer binder system, solvent, and contain micro-sized metal particles, such as silver or copper, to provide conductivity. After application via screen printing, the ink cures or hardens either through solvent evaporation or curing at elevated temperature to form a tack-free conductive trace. While the conductivity of the deposited metal-containing ink is much less than that of the metallic material, it is generally sufficient for many applications.[1-2]

Environmental regulations are putting pressure on the use of solventborne inks and, thus, alternatives that do not emit hazardous air pollutants—e.g, organic solvents—are sought. UV curable polymer technology is a viable alternative since these inks are liquid at application conditions, generally contain no organic solvent, and are converted into a hard, tack-free ink in seconds using irradiation from a UV light. The binder system is typically comprised of low viscosity, multifunctional acrylates and a photoinitiator. Under the influence of the UV light, the photoinitiator decomposes to yield free radicals which then initiate the polymerization of the acrylate groups.[3] The multifunctional acrylates polymerize to a highly crosslinked, hard network.

In addition to forming simple interconnects, in many applications screen-printed conductive inks may also be used as a substrate for attachment of another conductive device. For example, a "bond pad" can be printed using the conductive ink and then using heat and pressure this bond pad can be attached to another similar bond pad or metallic conductor. In order for good electrical contact to be formed during this bonding process, the polymer binder system must be able to flow under the influence of heat and pressure. In the case of conventional solventborne inks having thermoplastic polymer binders, this is not a problem. However, for UV cured inks, the binder cannot flow since it is highly crosslinked. Therefore, a need exists for an environmentally friendly, organic solvent-free, screen-printable, UV curable conductive ink that is thermoplastic after treatment with UV.

A novel screen-printable conductive ink that is hardened using UV radiation was developed to meet this need. The binder system consists of low volatility monofunctional acrylate monomer, a thermoplastic polymer, and a photoinitiator. Conductivity is provided by silver particles. The polymerizable monomer functions as a reactive diluent for the thermoplastic polymer and upon UV radiation, polymerizes to a linear polymer. Thus, the final ink remains thermoplastic and can be heat bonded to another conductive material.

Experimental

Materials

The monomers, photoinitiators, their respective suppliers' name and the abbreviations used in this paper are shown in Table 1. Solid PMMA resin having a MW= 120,000 was purchased from Aldrich. Silver flakes having dimensions less than 10 micron was purchased from Aldrich. Glass spheres coated with silver and having average diameter 14 micron were purchased from Potters Industries. Silver nano-powder having average diameter 150 nm, and raspberry shaped silver particles (silver acorns) were obtained from Inframat Advanced Materials. The average dimension of the latter was 0.7 –

1.5 µm. All of the materials were used as received. For comparison purposes, two different commercial conductive inks were selected, namely, Acheson Electrodag 479SS and Allied Chemical UVAG0010, designated as Commercial Ink 1 and 2, respectively.

Table 1. Monomers and photoinitiators used in this study.

Monomer/ Photoinitiator	Commercial name	Supplier's name	Abbreviation used
Tetrahydrofurfuryl acrylate	SR 285	Sartomer	THFA
Isobornyl acrylate	SR 506D	Sartomer	IBA
Alkoxylated tetrahydro furfuryl acrylate	CD 611	Sartomer	ATHFA
Acrylate ester	CD 277	Sartomer	ACES
Cyclic trimethylol propane formal acrylate	SR 531	Sartomer	CTMPFA
Oxyethylated phenol acrylate	Ebecryl 110	UCB Chemicals	OEPA
2-(2 ethoxyethoxy) ethyl acrylate	SR 256	Sartomer	EOEOEA
Combination of phosphine oxide, trimethyl benzophenone, methyl benzophenone and other oligomeric ketone based compounds	SR 1135	Sartomer	PI 1
Combination of alpha-amino ketones and blends	Irgacure 369	Ciba	PI 2
1-Hydroxycyclohexyl phenyl ketone	Irgacure 184	Ciba	PI 3
Benzophenone	Darocur BP	Ciba	Benzophenone
Reactive amine acrylate synergist	CN 373	Sartomer	AASYN

Procedures

The binder formulation recipes containing monomer(s), photoinitiators and with or without polymer were prepared by mixing using a magnetic stirrer with occasional heating to accelerate the dissolution of the polymer. The silver-containing ink paste formulations were prepared by mixing the respective ingredients using a mortar and pestle until a visibly homogeneous mixture was obtained.

For the solidification / tack-free time study, the liquid binder mixture was cast onto glass panels with a doctor blade having a 4 mil (101.6 µm) gap. Curing was accomplished by Dymax EC-20 lamp at 365 nm, and 35 mW/cm^2. For studying the tack-free time of the ink pastes, films were cast on glass panels using a 2 mil (50.8 µm) gap doctor blade and curing was done as before. For the composition containing silver nano powder and silver flakes (formulation E4), the film was cured by 10 minutes UV curing followed by 10 minutes oven curing at 125°C.

Glass transition temperatures of the polymers were determined using differential scanning calorimetry (DSC). Tests were carried out by heating the samples at a rate of 10°C/ minute in a TA Instruments Q-1000. Thermogravimetric analysis (TGA) was carried out under nitrogen, at a heating rate of 10°C/minute up to 300°C in TA Instruments Q-500. Dynamic mechanical analysis was carried

out using a TA Instruments Q-800 DMA. The samples were tested under tension from - 70°C to 110°C at a heating rate of 3°C/minute.

For measuring surface resistivity (Ω/ square), the following procedure was used. First, a rectangle was scribed using a razor blade on the cured ink film (glass panel) and its length and width were measured in mm. Approximate dimensions of the scribed area were 50 mm length by 1-2 mm in width. The length divided by the width gives the number of "squares." Resistance of the rectangle was measured at its two ends using probes and a Wavetek meterman multimeter. Finally, surface resistivity was obtained by dividing the resistance value by the number of squares. Multiplication of the surface resistivity value by the thickness of the film (in mil) would give the volume resistivity (Ω/ square/mil). All the volume resistivity values presented in this paper were measured on screen printed lines.

For SEM (scanning electron microscopy) experiments, samples were mounted on aluminum mounts and coated with gold using a Technics Hummer II sputter coater. Images were obtained using a JEOL JSM-6300 scanning electron microscope.

Screen printing was carried out using a Milara Semitouch Semiautomatic Screen Printer using the following parameters: squeegee speed of 1.5 to 3.0 in/sec; squeegee pressure of 15 to 25 lb./sq.in.; snap off of 0-10 mils; and squeegee hardness of 70-90 durometers. The substrate for screen printing was an FR4 board.

Results and Discussion

Binder System

A typical binder system for a UV curable coating or ink composition includes a multifunctional oligomer, multifunctional diluent(s) and a photoinitiator. Upon exposure to UV light, the photoinitiator initiates polymerization and, since the oligomers and diluents are typically multifunctional, a highly crosslinked film is produced. Due to the crosslinking, the ink film will not reflow on the application of heat, thus, in applications where it is desired to thermally bond the ink to another conductive material, a good bond cannot be formed. Thus, a new type of binder system is needed that will initially be liquid for deposition using screen printing, rapidly harden to a tack-free ink following exposure to UV radiation, but then maintain thermoplasticity so that it can be thermally attached to another conductive material.

While a number of binder system designs were considered, a system where the photopolymerization of a liquid monofunctional monomer to a linear polymer having a sufficient T_g to be tack free appeared to be a reasonable approach. A large number of potential monomers are available, however, commonly used monomers such as butyl acrylate or methyl methacrylate, while having extremely low viscosity, are also highly volatile at ambient temperatures. Thus, these are not suitable for this application. In addition, these monomers also have noxious odor. Several monomers, however, were identified that have low volatility. These are illustrated in Figure 1.

Since these monomers have relatively low viscosities, a material that can impart a higher viscosity to the ink is also desired as a component of the binder system. Thermoplastic acrylic copolymers are readily available commercially. Thus, the binder system consists of a blend of a

thermoplastic polymer, PMMA in this case, along with the monomer(s) and the necessary free radical photoinitiator(s).
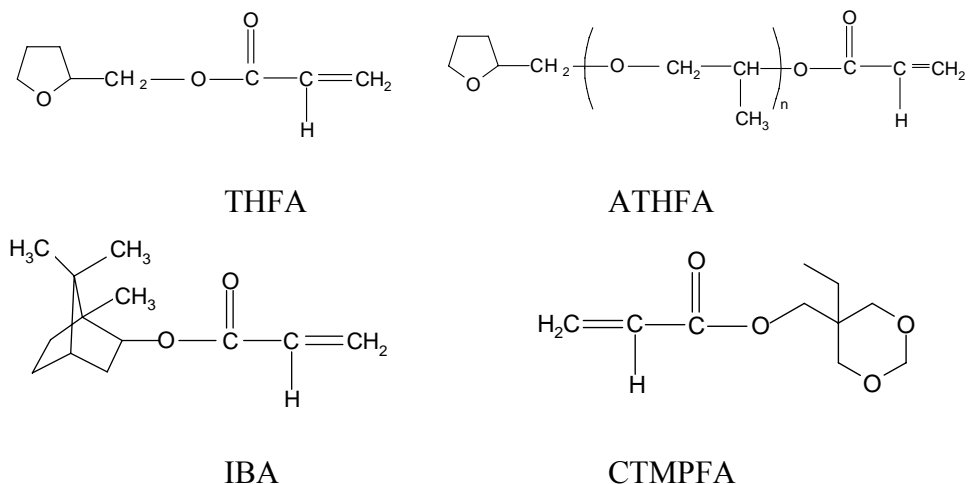

Figure 1. Structures of monofunctional acrylate monomers.

In the following discussion, the time taken by the liquid monomers to form solid film under the influence of UV radiation has been described as tack-free time or solidification time, rather than the commonly used phrase 'cure time.' While the term curing generally indicates that a liquid coating or ink has been converted to a dry material, often the term indicates that a cross-linking reaction has occurred. In this case, however, the system undergoes photoinitiated linear free radical polymerization giving a thermoplastic polymer chain. Thus "tack-free time" indicates the time needed by the system when the monomers has reacted enough to give solid film.

Initial formulations were prepared to determine the effect of monomer and photoinitiator combinations on the solidification or tack-free time of the binder system (Table 2). It can be readily seen that the photoinitiator system consisting of PI 1, PI 2, and the amine acrylate synergist gave the shortest tack free time compared to the other combinations. It is also apparent that among different monomers THFA polymerizes faster than the other monomers under the test conditions. Also, IBA and CTMPFA showed reasonably fast tack free times. In the studies of the binder system alone, we wanted to achieve an extremely short tack free time since it was believed that the addition of the silver particles would serve to scatter the UV light and extend the time for curing.

Five different binder systems were developed based on the results of the screening experiments to be used with the silver particles. The binder system compositions are listed in Table 3. A range of tack free times and glass transition values of the binders was achieved depending on the composition of the binder. Comparatively higher T_gs were observed when the CTMPFA was present in the formulation. Figure 2 shows the thermal stability of the hardened binder systems from the TGA experiments under nitrogen. Comparison of the monomer combinations in Table 3 and the TGA curves in Figure 2 readily indicates that the binder film has less thermal stability when CTMPFA was present in the formulation. However, even the least thermally stable polymer also retained more than 95% of its original weight at temperature around 140°C, which is the proposed processing temperature of the hardened inks.

Table 2. Screening formulation compositions using monomer and photoinitiator combinations

No.	Monomer		Polymer (PMMA resin) (g)	Photoinitiator		Solidification time (s)
	Type	Amount (g)		Type	Amount (%)	
1	THFA	10	1.0	PI 2	5.17	30
2	THFA	10	2.5	Benzophenone	2.84	5
				AASYN	5.68	
				PI 2	2.84	
3	THFA	10	2.5	Benzophenone	2.84	25
				AASYN	5.68	
				PI 3	2.84	
4	THFA	10	2.5	PI 1	2.84	3
				AASYN	5.68	
				PI 2	2.84	
5	IBA	5.0	-	PI 1	5.0	10
				AASYN	8.33	
				PI 2	3.33	
6	ATHFA	5.0	-	PI 1	5.0	15
				AASYN	8.33	
				PI 2	3.33	
7	ACES	5.0	-	PI 1	5.0	10
				AASYN	8.33	
				PI 2	3.33	
8	CTMPFA	5.0	-	PI 1	5.0	6
				AASYN	8.33	
				PI 2	3.33	
9	THFA	5.0	-	PI 1	5.0	2
				AASYN	8.33	
				PI 2	3.33	
10	OEPA	5.0	-	PI 1	5.0	15
				AASYN	8.33	
				PI 2	3.33	
11	EOEOEA	5.0	-	PI 1	5.0	30
				AASYN	8.33	
				PI 2	3.33	

The thermo-mechanical properties of representative binder films C and E are illustrated in Figure 3. Comparison of the two curves indicates that for the lower T_g polymer, the modulus of the system at ambient temperature is also lower. Additionally, it can be seen for both the curves that above the T_g, the elastic modulus quickly dropped to zero indicating melt flow and verifying the inherent thermoplastic nature of the polymer binder system.

Table 3. Binder Formulations and Key Properties.

Formulation ID	Monomer(s)	Wt. % of monomer	Wt% of PMMA resin	Wt% of photoinitiator combination[a]	Tack free time (s)	DSC T_g (°C)
A	THFA	76.27	8.47	15.26	6	- 24.42 ºC
B	THFA	31.75	7.94	12.69	5	- 23.52 ºC
	CTMPFA	31.75				
	ACES	15.87				
C	THFA	55.11	7.87	13.40	10	- 28.67 ºC
	IBA	11.81				
	ACES	11.81				
D	THFA	31.50	7.87	13.39	5	- 22.78 ºC
	CTMPFA	31.50				
	ATHFA	15.74				
E	THFA	28.22	6.45	12.91	10	-2.77 ºC;
	CTMPFA	32.26				
	IBA	20.16				

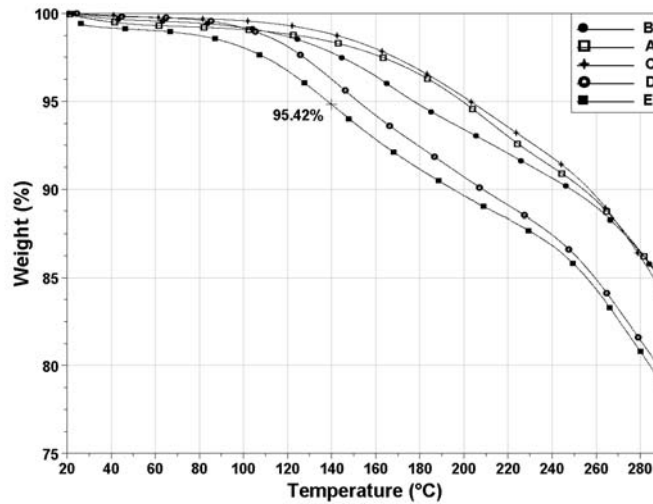[a]A mixture of PI 1, PI 2, and AASYN was used.

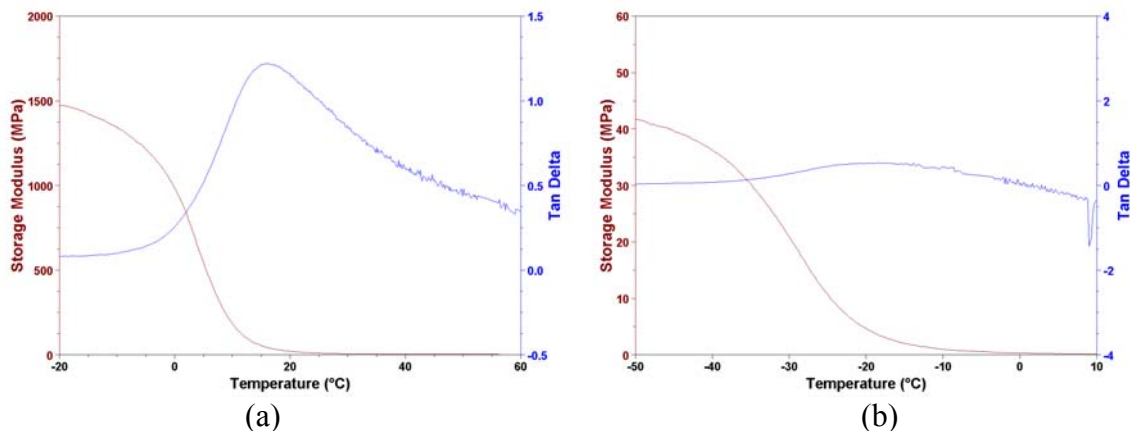**Figure 2.** TGA curves in N_2 of different binder films. Formulations refer to Table 3.

Figure 3. (a) DMA of formulation C; (b) DMA of formulation E

Conductive Ink Properties

While making conductive ink with different binder formulations, the main objective was to obtain the highest possible conductivity, good screen printability at a minimum tack free time. Four types of conductive silver particles were evaluated and SEM micrographs are shown in Figure 4. The silver-coated glass microspheres (Figure 4a) range from 8 to 20 μm in diameter, have a mean particle diameter of 14 μm and possess a density of 2.7 g/cm^3 with an overall silver content of 12 weight percent. The silver flakes (Figure 4b) are irregular in shape with diameters less than 10 μm and thickness estimated at 100 nm to give an aspect ratio of 100:1. The acorn-shaped silver nanopowders (Figure 4c) appear to be sub 100 nm particles in micron-sized agglomerates. Finally, the silver nanopowder (Figure 4d) has particles sizes ranging from 100 nm to 1 μm with some 2 μm agglomerates present.

Table 4 shows ink paste formulations where glass micro-spheres coated with silver and silver flakes were used as the major conductive fillers. The formulation E3 also contains silver acorn-shaped particles as an additional conductive filler. It can be said that the electrical properties of the final composite film depend both on the type and amount of individual filler and also on the binder composition. The tack free time for the compositions described in Table 4 varied between 15 sec. and 60 sec. It has been reported that flake shaped fillers imparts unsatisfactory cure.[4] Hence, in each case a combination different types, shapes, and sizes of fillers were evaluated. However, the main disadvantage of the conductive composites containing glass micro-spheres coated with silver as one of the conductive filler was that resistance value was always too high for the required application for all the formulations. None of the systems explored provided the level of conductivity desired for this application.
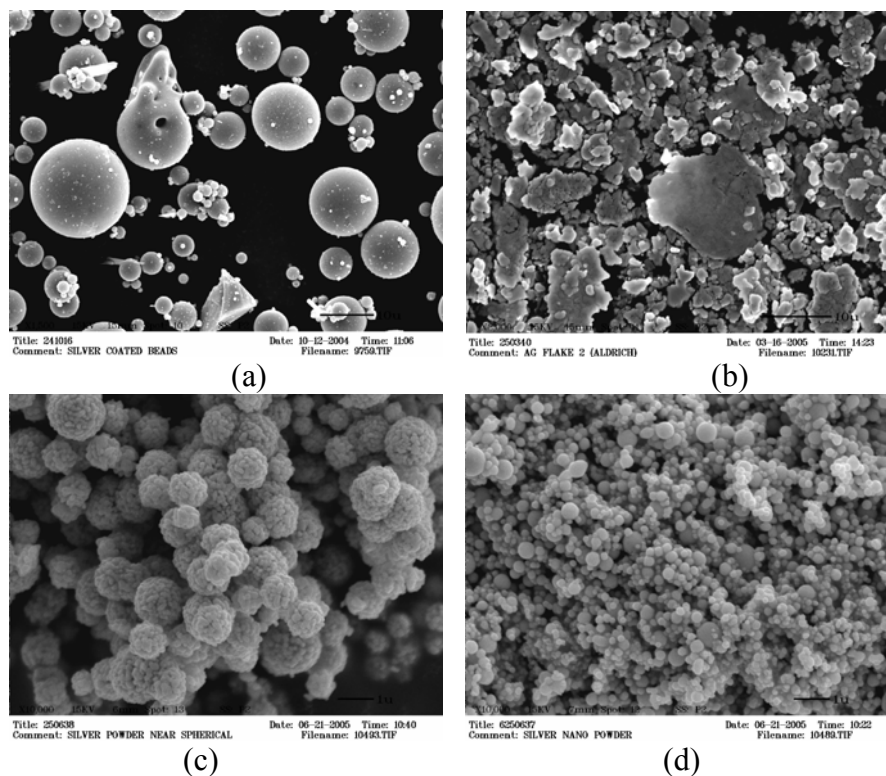
Figure 4. SEM images of conductive fillers: (a) glass micro-spheres coated with silver; (b) silver flakes; (c) silver acorns; (d) silver nano powder.

Table 4. Silver-Containing Paste Ink Formulations

Ink ID[a]	Vol.% of organic phase	Vol.% of Ag-glass beads	Vol.% of silver flakes	Vol.% of silver acorn	Surface resistivity (Ω/ square)
A1	64.63	28.09	7.28	-	1.21
B1	65.00	28.00	7.00	-	5.74
B2	64.37	27.73	7.90	-	2.00
C1	65.38	27.48	7.13	-	7.46
C2	64.84	27.96	7.20	-	2.55
C3	63.65	29.93	6.42	-	4.13
E1	63.40	30.10	6.50	-	0.53
E2	63.00	30.00	7.00	-	0.80
E3	63.00	30.00	6.40	0.60	0.42

[a]The letter in the ID refers to the binder system in Table 3.

Since the silver coated glass spheres did not provide sufficient conductivity, a formulation was developed that eliminated these as the conductive material. Table 5 shows an ink composition containing silver nano powder and silver flakes as the conductive particles with the binder formulation E and the overall composition is designated as E4. Due to the very high viscosity of the system, a solvent needed to be included in the formulation to reduce the viscosity to a level where screen printing could be carried out.   In addition to UV-radiation curing, oven heating was also needed to evaporate the solvent as well as to get the residual monomers to polymerize, initiated by thermal initiator benzoyl peroxide.

This ink was printed on an FR4 board using screen printing along with formulation C3 and commercial solvenborne and UV curable inks. Although here the tack free time was prolonged, the conductivity was greatly improved. Table 6 shows some of the key properties of the experimental formulations compared to few commercial formulations. The conductivity of the formulation containing the silver flakes and nanopowder is significantly better than that of the commercial UV cured ink and similar to the commercial solventborne ink. Additional work with systems containing these silver particles and improved binder systems is currently being carried out. A key goal is to adjust the binder system so that a solvent is not needed for viscosity reduction and to improve the application characteristics when using screen printing.

Table 5. Ink composition containing silver nanopowder and silver flakes (Formulation E4).

Composition	Wt. %	Vol %
Binder formulation E	19.0	71.0
Benzoyl peroxide	0.5	
Silver nanopowder	37.9	14.5
Silver flakes	37.9	14.5
Butyl acetate	4.7	

Table 6. Comparison of different ink properties

Properties	Commercial Ink 1	Commercial Ink 2	Ink Formulation C3	Ink Formulation E4
Curing method	Heat	UV curing	UV curing	UV + heat
Presence of solvent	Yes	Solventless	Solventless	Low
Screen printability	Very good	-	Good	Needs optimization
Resistivity (Ω/sq./mil)	< 0.02	0.285	0.856	0.074

Conclusions

Novel UV-hardenable conductive ink compositions that retain thermoplasticity were explored in order to optimize the conductivity and application properties. Binder systems that are converted from a liquid to a solid upon exposure to UV irradiation were designed and optimized in order to yield short tack free times. Retention of thermoplastic behavior was verified by dynamic mechanical analysis. An ink was developed and screen printed that has conductivity similar to a commercial solventborne ink.

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