Final Report –

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Subject: Conductive Inks

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CE PROJET EST COFINANCÉ PAR
LE FONDS EUROPÉEN DE DÉVELOPPEMENT RÉGIONAL

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Acknowledgments

First, I would like to thank Guy MASSE to offer me this professionalisation contract in the company Encres DUBUIT.

I would like to thank all the staff for their warm welcome as soon as my arrival. Thank you to them for their good mood.

It's a great pleasure to work with the R&D team under the direction of Guy MASSE. I especially want to thank him for giving me the opportunity to work freely and to be able to carry out my research as well as possible.

I would also like to thank all the persons who helped me during my work. I am thinking of my R&D colleagues, Maria, Amandine, Christelle, Jessica and Julie, for their technical help about the inks. Thanks to them for their good atmosphere.

I also thank the people from the workshop who are indispensable for the proper functioning of the company, who helped me a few times when I needed materials.

Introduction

For more than a decade, optoelectronic devices are more present in our daily. Mobile phones, touch tablets, television screens or photovoltaic panels are the best known. These devices require at least a conductive layer. Nowadays, the main materials used for the creation of conductive inks is silver. Silver is the most conductive material in the world. The issue now is that silver is expensive. As the Economy is always based on more competitive prices, the coating industry develops new conductive inks with less silver or without silver in some applications. The discovery of conductive polymers in the 1970s, for example, turned the world of conductive materials. For those years, the conductive ink development is in perpetual growth. So, to approach a growing and potential market, a research work is being done within the company Encres DUBUIT. This French company, specialized in printing inks for more than 50 years, is always looking to increase the covered fields of applications. For Encres DUBUIT, the current question is to know if the company can integrate the innovative and functional inks market.

In a first part, the company Encres DUBUIT will be introduced. Its history, its international dimension, its values and associated markets will be presented, as well as the objectives fixed in the framework of the conductive inks. Then, in a second time, an introduction about conductive inks in general and the vast area will also be presented. The main conductive materials and the applications that result from them will be developed. Finally, the third part is dedicated to the experiments performed, including the tests of raw materials in different varnishes with the different hypothesis that we have made, as well as the conclusions that we have drawn.

1. The host organization

1.1. For the little story…

Encres DUBUIT is a French company established in 1970 and located in Mitry-Mory in Seine et Marne department (close to Roissy – Charles de Gaulle Airport). Known as one of the world leaders in the design, manufacture and sale of technical and industrial inks for screen printing, pad printing and digital printing, Encres DUBUIT has been certified ISO 9001 since 1994. Encres DUBUIT remains at the forefront of technology by offering high quality and innovative customized solutions, in UV and solvent. Satisfying customers, respect, ethics and environment base the values of the society Encres DUBUIT.

***Figure 1**: External view of the company*

1.2. An international presence

Present and active on the international market, Encres DUBUIT has three factories located in France (Mitry-Mory), Spain (Barcelona) and China (Shanghai), three distribution centres in Belgium (Brussels), in the United States (Chicago) and in the Middle East, as well as six technical supports in Belgium (Publivenor), in the United States (DUBUIT America), in Spain (Tintas DUBUIT), in China, in the Middle East and in India. Encres DUBUIT is also represented through a distributor network in more than 50 countries around the world.

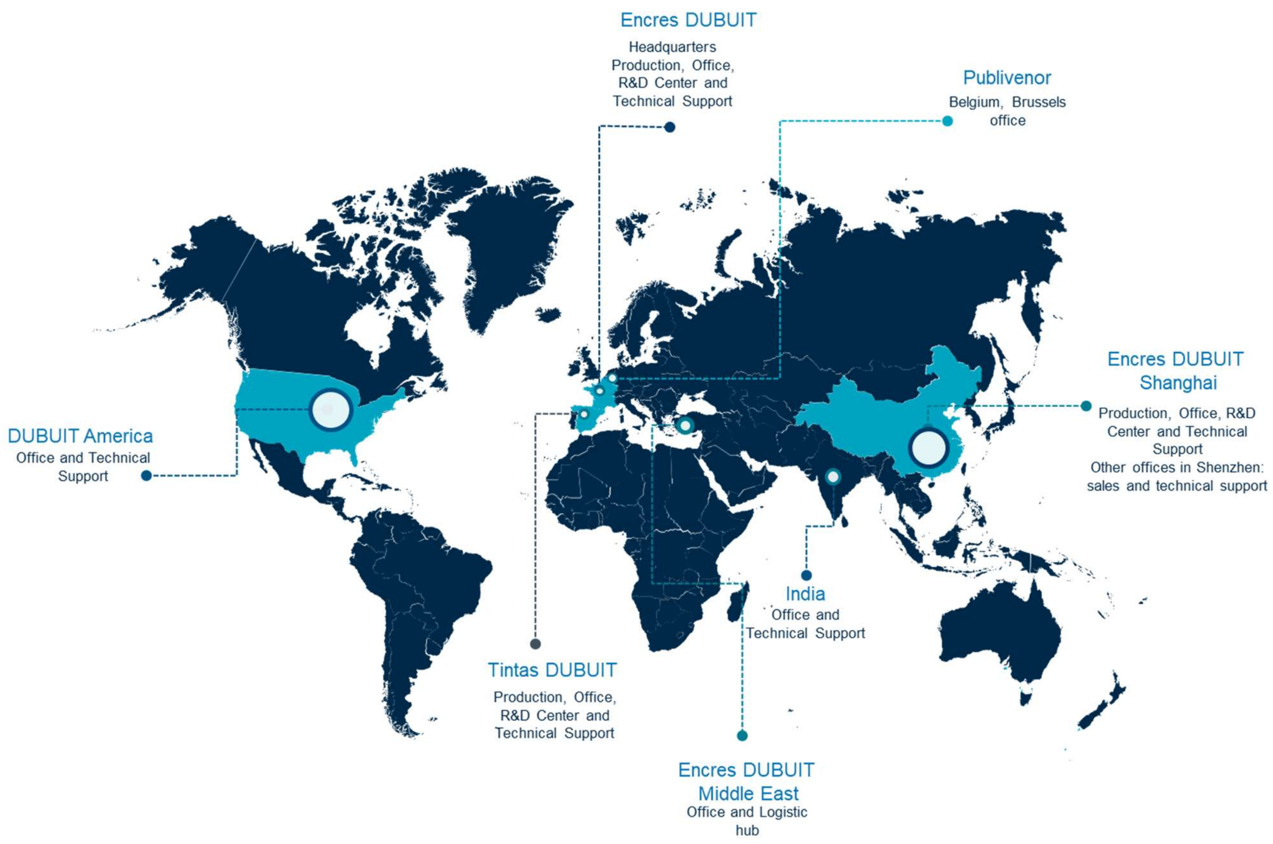


***Figure 2**: Encres DUBUIT locations*

1.3. The market

Encres DUBUIT is a specialist in high-tech inks dedicated to printing market, ranging from simple visual communication to industrial marking and to the use of functional inks. Encres DUBUIT addresses to a diversified international clientele which operates in a wide variety of sectors [1]:

- ➔ Building & Construction (furniture, home appliances, interior decoration, flat glass decoration, …)
- ➔ Consumers goods (small home appliances, phones, identification and banking cards, optical discs, …)
- ➔ Electric & Electronic (membrane switch, touch panels, electrical households, car dashboard)
- ➔ Graphical applications / Visual communication (bus shelter, displays, billboards, art screen printing, …)
- ➔ Packaging (plastic and glass containers, labels, perfume glass bottles, …)
- ➔ Textile (belts, luggage, leather products, …)
- ➔ Transport (vehicle decoration, dials, oil filters, security tags, …)

1.4. A willingness to be innovative

1.4.1. A new conductive inks potential market

If the digital printing inks represent a rather new technology, this is not the case for the screen printing inks which exist for several decades. Currently, the screen printing process is used in many fields of applications and tends to evolve. But, in volume, the production is decreasing which can represent a potential issue for the company. Under this point of view, the conductive inks can be considered as a new opportunity.

1.4.2. The markets targeted by the company

To try to integrate the conductive inks market, Encres DUBUIT, and more specifically my tutor Guy MASSE, offered me to work on this subject. A very large subject in which the company had not an important background. Among the different applications covered by conductive inks, we have chosen to focus first on RFID tags, sensors, membrane switches… The other applications like Organic Photovoltaics (OPV) being too difficult to set up in the production workshop (inadequate processing equipment), and like Organic Light Emitting Diodes (OLEDs) being too expensive to develop.

1.4.3. My objectives

In Encres DUBUIT, my first goal was to collect some information on the different existing conductive inks (coating, materials, …). Then, I search the associated applications for each type of ink and the different suppliers and customers involved in this market. Finally, I follow the technical publications and data sheets of our potential competitors to become aware of the novelty which are tested, or which are commercialized.

We order some conductive materials to start developing some formulations based on the data sheets of our potential competitors. In the end, we will perform few tests (conductivity, printing, adhesion, lifetime, …) to check the quality inks. Currently, customers trials have not yet been done because first, the phase of requesting samples from suppliers is quite long, and secondly, we need many formulations to be evaluated. Of course, testing the chosen inks with the final customers is a logical next step in the marketing process of a product. Moreover, we didn't develop only one ink, we developed a complete range of conductive products (ink more or less conductive, transparent or not, solvent-based or UV inks, with different conductive materials, …).

Now, we will talk about conductive ink in general and its large applications field in printed electronics. A high potential market that constantly grows.

2. The conductive inks

2.1. Background

In recent years, conductive inks have become a new market with a high potential in the field of printed electronics. It consists to deposit various conductive materials by classical printing processes such as screen printing, flexographic printing, or more recently by ink jet process. The screen printing process allows to print a large range of inks on a large range of substrates. Thanks to this process, we can deposit a thick film with a good repetitiveness. Screen printing is sufficient for small production and the resolution is limited by the amount of ink deposited through the mesh. In the contrary, ink jet printing allows to print a thin film with a very good resolution. For this process, very small particles (less than 1 micron) are used to avoid blocking nozzles.

Conventional inks are usually composed of organic vehicle, inorganic fillers, coloured pigments and can also contain some additives. Conductive inks drive the electrical current. They contain metallic particles, or conductive organic compounds other than pigments [2-6].

Nowadays, screen-printable conductive inks on the market are solvent-based or water-based inks. Indeed, the vehicle used to mix the conductive particles are composed of some resins and a solvent or water. It allows to transfer these conductive particles on the substrate. Then, after a heating process, the solvent or the water is eliminated leaving only the conductive particles distributed in the resin. At this moment, the concentration of metallic particles increases. If this concentration is above percolation limit, the electronic charges will pass from a particle to another. The **figure 3** illustrates the principle.

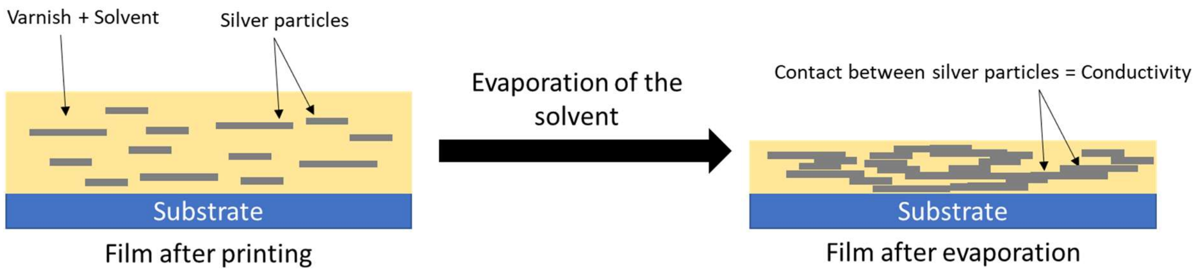


***Figure 3**: Printing principle of solvent-based inks*

Most of the time, UV inks, which are hardened under UV lamp (curing process), are not used because the UV raw materials (acrylates) are completely 100% solid content. After printing and hardening (curing), there are less contacts between the conductive particles and so, a good conductivity cannot be obtained with this type of ink. The principle is described in **figure 4** below.

However, these UV varnishes are widely used in many fields because curing process under UV lamp is very fast (a few seconds) without the need of solvent or water evaporation.

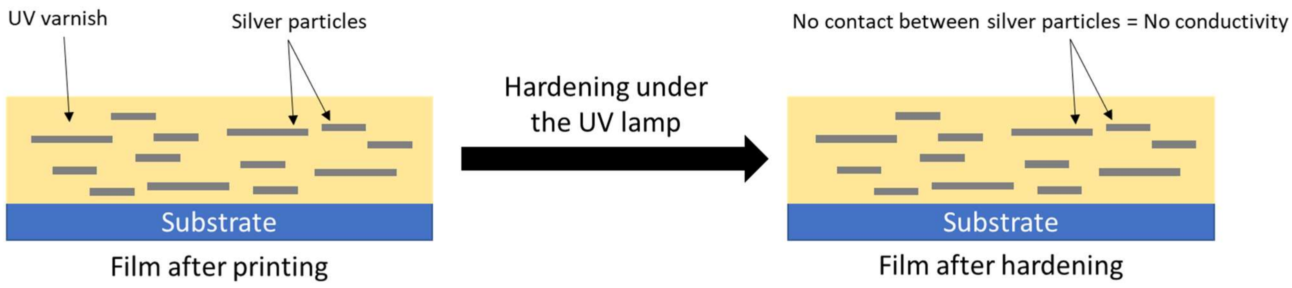


Figure 4*: Printing principle of UV inks*

Some industries have developed a method to combine UV inks with solvent to reduce the drying time to evaporate the solvent, and to decrease the process time. For example, to get a very matt UV coating (glossiness < 1), it is necessary to add solvent in the UV formulation. Compared to solvent-based inks, this combination also decreases the conductivity of the films, but it depends of the desired application.

2.2. The conductive materials

Conductive materials include metals, of course, but also semiconductor materials, conductive polymers and organic compounds (graphene, graphite, carbon black) [7-8]. For metals, the most used is silver, whose conductivity is around 10^4 S/cm. Nowadays, even if silver is expensive, it remains the most used conductor and finds an interest at nanometric scale. A lot of manufacturers develop conductive inks with silver nanoparticles for printed electronics by ink jet printing [9]. Other metals such as gold, copper and aluminium are also used, but not as much as silver. Today, for screen printing, the manufacturers try to decrease the amount of silver or to avoid silver because silver is expensive. They meet the same problem with ITO (Indium Tin Oxide), used as transparent conductive electrode. Due to the scarcity of Indium, ITO is expensive. In any case, these metallic particles can be used either in pastes (silver paste for example) or in powders with micrometric or nanometric particles sizes.

Other conductive materials such as conductive polymers may also be used. Conductive polymers, or precisely conductive intrinsic polymers, are almost always organics and have a conjugated system most of the time composed of aromatic groups. Almost all the known conductive polymers are semi-conductors thanks to their bands structure. Their conjugation facilitates the fluorescence phenomenon, allowing their use for the development of organic light emitting diodes (OLEDs) or organic photovoltaic panels (OPV).

The main advantage of conductive polymers is their ease of production. These ones are simple plastics, so compared to metals which are more conductive, polymers are flexible, resistant and elastic. The most conductive polymers are polyaniline (PANI), polypyrrole (PP) and polythiophene (PT). Nowadays, polythiophene derivatives stay the conjugated polymers the most conductive, among which the best known and the more effective is poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) sodium (PEDOT: PSS) [10-11].

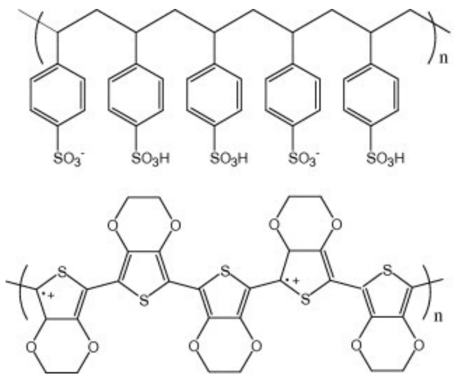


Figure 5*: PEDOT : PSS structure*

Conductive organic particles such as carbon black, graphite and graphene, can be added to the list of materials that can be used to formulate a conductive ink.

Carbon black is a form of paracrystalline carbon. We obtain carbon black by incomplete combustion of heavy petroleum products. Thanks to it high surface area to volume ratio, carbon black is conductor[12-13].

Graphite, like diamond, is one of the natural carbon allotropes. It is the stable form of carbon at normal pressure and temperature. The graphite structure is composed of hexagonal layers called graphene. Each layer, composed of aromatic carbons, has covalent bonds (σ and π bonds). Between layers, there are weak interactions with Van der Waals bonds. Thanks to the aromaticity of graphene layers, graphite has a vast electron delocalization. These valence electrons are free to move, so can conduct electricity [14].

As graphene is a layer of graphite, graphene is bidimensional. We can produce graphene by exfoliation or epitaxy. Thanks to its electronic band structure, graphene is a semi-conductor with a draw gap. It conducts current almost like copper and it is 200 times more resistant than steel to the traction. With its physical and electric properties, graphene is often used in electronics and energy storage fields [15-16].

2.3. The conductive ink markets

Currently, the two main fields of application of conductive inks are the smart packaging and the printed electronics [17-22]. In the printed electronics market, conductive inks make it possible to manufacture:

- ➔ RFID antenna (Radio Frequency IDentification)
- ➔ Membranes switches
- ➔ Sensors
- ➔ Heaters
- ➔ OLEDs
- ➔ OPV panels
- ➔ And so many others…

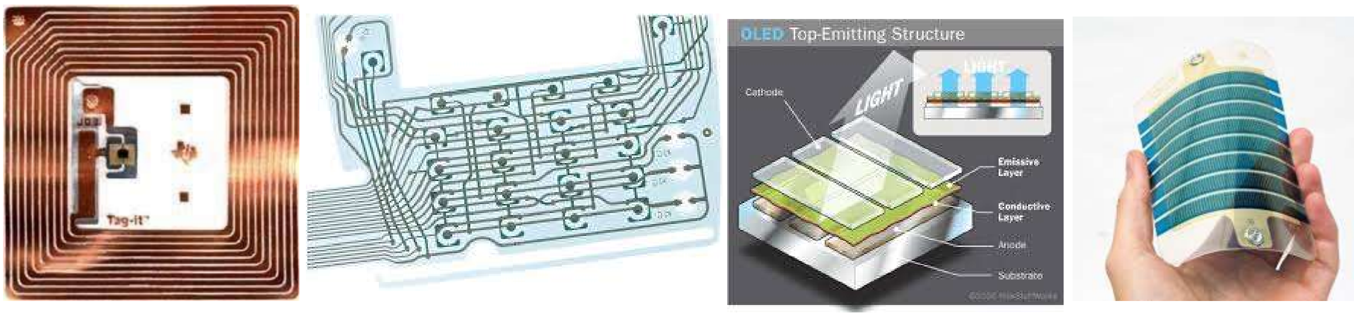


***Figure 6**: Pictures of RFID antenna, membrane switch, OLED and OPV*

RFID antenna: a RFID system is composed of a RFID microchip (or tag) and one or several transmitters. A RFID tag is composed of a chip with the data, and an antenna. Transmitter produces radiofrequencies to give sufficient energy to the tag to work. When the tag is activated, the data are exchange and the transmitter can read the data. Between transponder and transmitter, there is an interface. And in the case of RFID system, the interface is air. There are three types of RFID tags: Low Frequency (LF) at 125 kHz, High Frequency (HF) at 13,56 MHz and Ultra High Frequency (UHF) between 865 and 868 MHz [23].

Membrane switch: corresponds to a printed electronic circuit for turning a circuit on and off by using pressure. Most of the time, membrane switch is printed by screen printing. The ink used for screen printing process is usually silver, copper or graphite. Usually, a membrane switch is composed of 7 layers: the graphic overlay, the overlay adhesive, the top circuit layer, the circuit spacer, the lower circuit layer, the rear adhesive layer and the rigid support. The devices with membranes switches are user interfaces (man-machine interfaces) [24-25].

Sensor: a sensor is a device for transformation from a physical quantity observed to a usable quantity, like electric tension, temperature, or pressure… A sensor is different from a measuring tool. A measuring tool is an independent device with a data storage system. Sensor is a simple interface between a physical phenomenon and a usable information.

Heater: printed heaters are warming elements that are printed by screen printing. Most of the time, printed heaters are made on flexible substrates such as polyester (PET), polyimide (PI), polycarbonate (PC) and thermoplastic polyurethane (TPU). The functional ink used is a combination between conductive, resistive and positive temperature coefficient (PTC) inks [26-27].

OLED: is a component which produces light. Its structure is relatively simple with the superposition of several semi-conductive organic layers between two transparent electrodes (or at least one). The base structure of OLED has 4 layers: the transparent substrate (glass or plastic), the transparent anode which creates holes during the current passage (most of the time anode is in ITO), the metallic cathode (mainly composed of aluminium, calcium or magnesium) which emits electrons, and the organic conductive layer between anode and cathode. The organic conductive layer is composed of conductive layer which transports the holes generated by the anode, and an emitter layer which transports the electrons generated by the cathode. Finally, there is a protective layer, called " seal ", on the top (glass or plastic). Light source is obtained by combinations of excitons (electron-hole pairs). During these combinations, luminous photons are emitted and go through the substrate. This technology aims to replace liquid crystals technologies (LCD), or plasma used for the manufacture of screens [28-30].

OPV: photovoltaic solar cell is component allowing to convert solar energy to electricity. It is composed of several layers deposited by spin coating or ink jet: the absorbent photoactive layer, the charge transport layers and two electrodes (anode and cathode). The transparent substrate is usually glass or plastic. The photoactive layer is composed of an electron donor and an electron acceptor printed in bilayer or blend. The absorption of photons by the photoactive layer creates excitons. These excitons diffuse at the interface between donor and acceptor, then dissociate in one electron and one hole. Electrons and holes are transported respectively by acceptor and donor towards the electrodes to be collected. There are two different architectures of solar cells, the "normal" structure, used since the first research, and the "inverted" structure. Today, a lot of researchers work with the inverted structure because normal structure is not very stable to air [31-33].

First focused on solvent-based conductive inks, several preliminary tests have been performed to observe what was happening. Then, conductive inks with an entirely UV system have been created. A last part will present the experiments tested with a combination of solvent-based and UV systems.

3. The experimental part

3.1. Solvent-based inks

The first tests realized concern only the conductive raw materials. A few months ago, before my arrival, some bibliographic research has been performed about the conductive inks, just to tell you that this project emerges in the society. Some samples of conductive compounds from suppliers (Graphene, Carbon black, silver-coated copper powder and silver-coated glass powder) have also been asked.

To formulate our inks, the varnish 24800, which is one of the most varnish used by the company to create solvent-based inks, is used. This varnish is based on a mixture of acrylic and vinylic resins. The solvent of this varnish is Dipropylene Glycol Methyl Ether (DOWANOL DPM) which corresponds to a hydrophilic glycol ether.

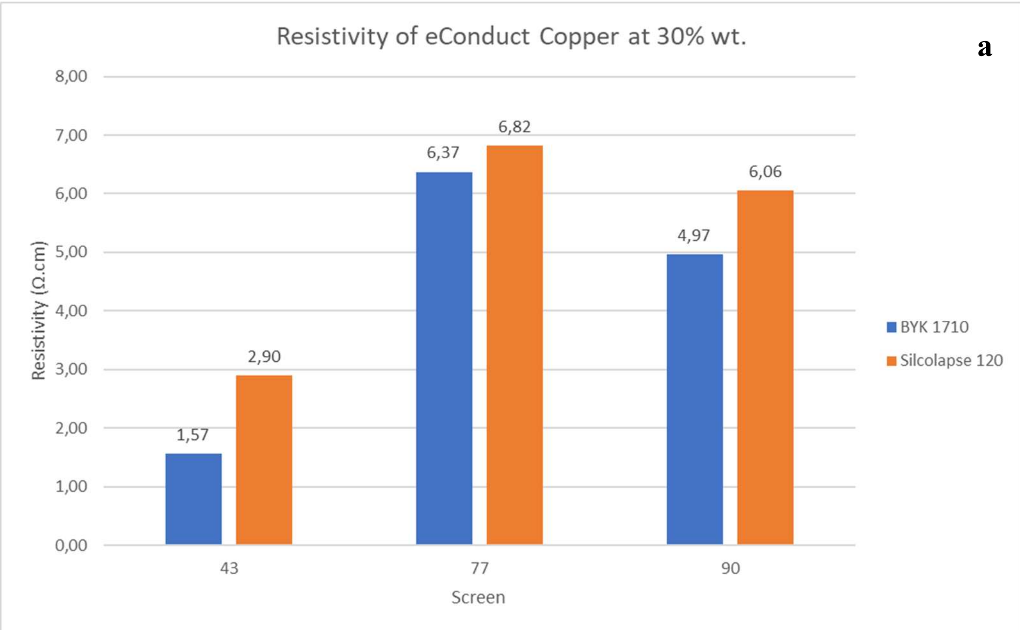
The use of DOWANOL DPM allows to heat enough without problem to easily evaporate it. For all the samples tested, the total weight has been fixed at 30 g, the drying temperature at 80 °C, the drying time at 15 min and the printing substrate which is Polycarbonate (PC). We used 4 printing screens mesh (43; 77; 90 and 120 lines per centimetre). The number associated to the screen corresponds to the number of threads per centimetre. In other words, when the number of threads increases, the quantity of deposited materials decreases and so, the thickness of the film also decreases.

At the same time, the same experiment with a modified formula of varnish 24800 has been performed. To get through the mesh, the screen printing ink must contain a tension modifier. This additive has two effects: anti-foam effect to eliminate bubbles inclusion and surfactant effect for a good spreading of the deposited film. Usually in decorative inks, the tension modifier contains derivative silicone (Polydimethylsiloxane PDMS). Here, the tension modifier used is a non-silicone one (BYK 1710), but we wanted to know if a silicone tension modifier (Silcolapse 120) can change the conductivity. In theory, the silicone has an insulating effect. The experiment tested will try to confirm the theory. **Table 1** below summarizes the results obtained.

In the R&D lab, a Digital Multimeter 8808A is used to measure the resistivity (Ω.cm) of the film. The resistivity is inversely proportional to the conductivity (S/cm). The **figure 7** shows an example of results obtained for silver-coated copper and silver-coated glass particles powders (eConduct Copper and eConduct Glass). The graphs for the other conductive materials are indexed in **Annex 1**.

Table 1*: Resistivity (Ω.cm) of raw materials*

Samples	Wt. % raw materials	Tension modifier	Screen 43	Screen 77	Screen 90	Screen 120
Graphene	2%	BYK 1710	106 103	332 000	170 663	2 590 000
		Silcolapse 120	64 550	420 667	392 000	10 703 333
Carbon black	10%	BYK 1710	57 350	548 333	257 667	1 184 333
		Silcolapse 120	38 297	401 333	365 667	883 667
eConduct Copper	30%	BYK 1710	1,57	6,37	4,97	69 163
		Silcolapse 120	2,90	6,82	6,06	149 740
eConduct Glass	30%	BYK 1710	0,13	0,48	0,17	No value
		Silcolapse 120	0,22	0,70	1,31	No value



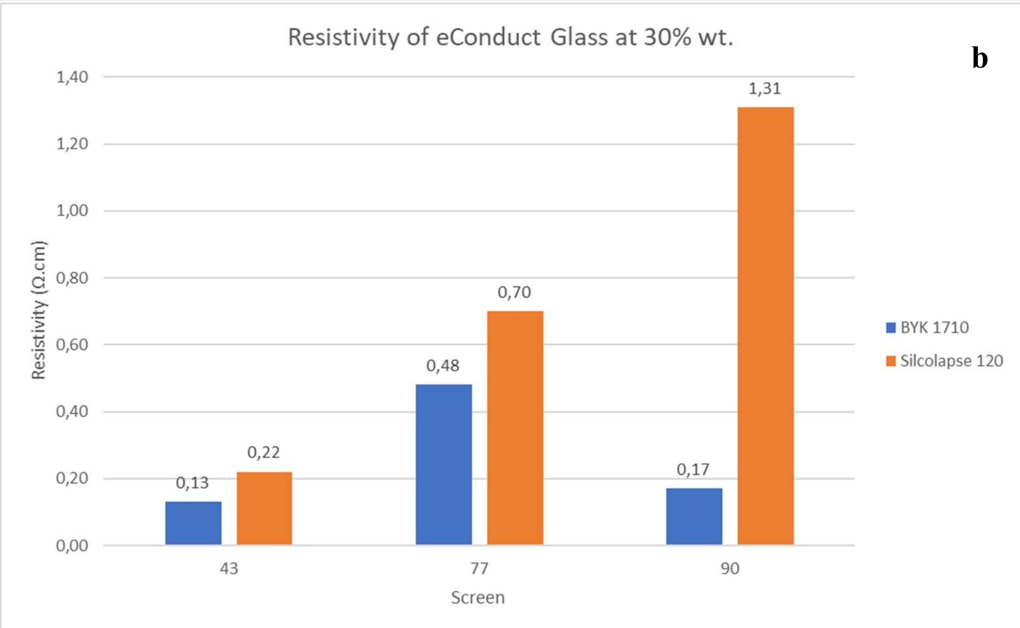


Figure 7*: Resistivity of eConduct Copper (****a****) and eConduct Glass (****b****)*

Several materials have a very good conductor behaviour, like the eConduct Copper and Glass, while others are not so good like Graphene and Carbon black. In parallel, we also confirm that the effect of silicone in the tension modifier reduces the conductivity of raw materials. This difference allowed us to say that BYK 1710 will be the tension modifier chosen for the next experiments on solvent-based inks. Moreover, as the conductivity values for graphene are unsatisfactory, graphite has been tested instead of graphene. Graphite corresponds no more, no less to a stack of graphene sheets. The same experiment has been performed with graphite. The **figure 8** shows the results obtained. Results are significantly better than those for graphene. To increase the conductivity, a bigger part of solvent could allow to put more conductive materials in the final coating.

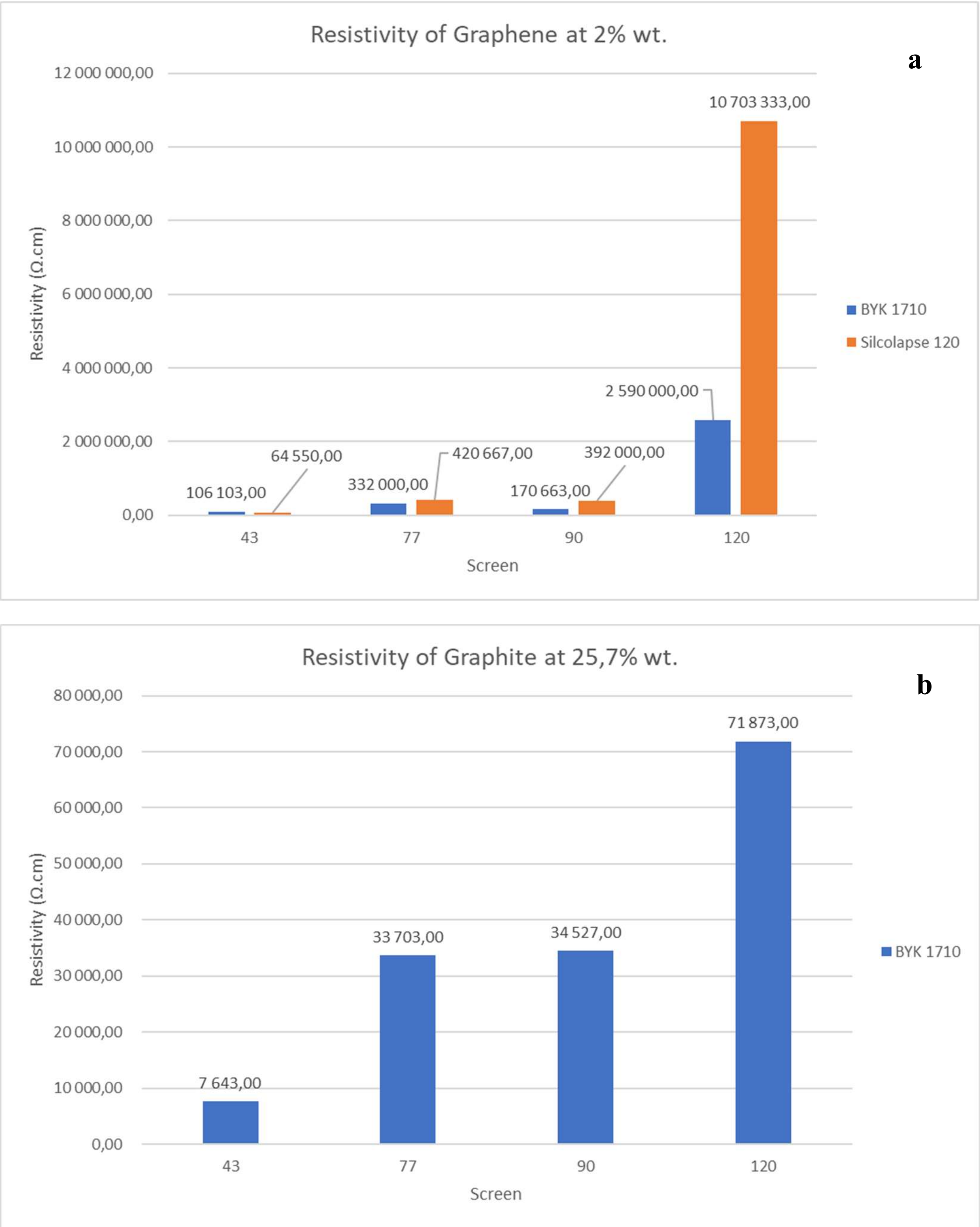


***Figure 8**: Resistivity of Graphene (**a**) and Graphite (**b**)*

The varnish 24800 formulation has been modified by putting 25% wt. of DOWANOL DPM instead of 5%. For this experiment, conductive Carbon black has been chosen. Thanks to this modification, the quantity of Carbon black increased from 10% wt. to 15% wt. The results obtained for different formulations are indexed in **Annex 2.** The **figure 9** shows the results obtained under the conditions described above.

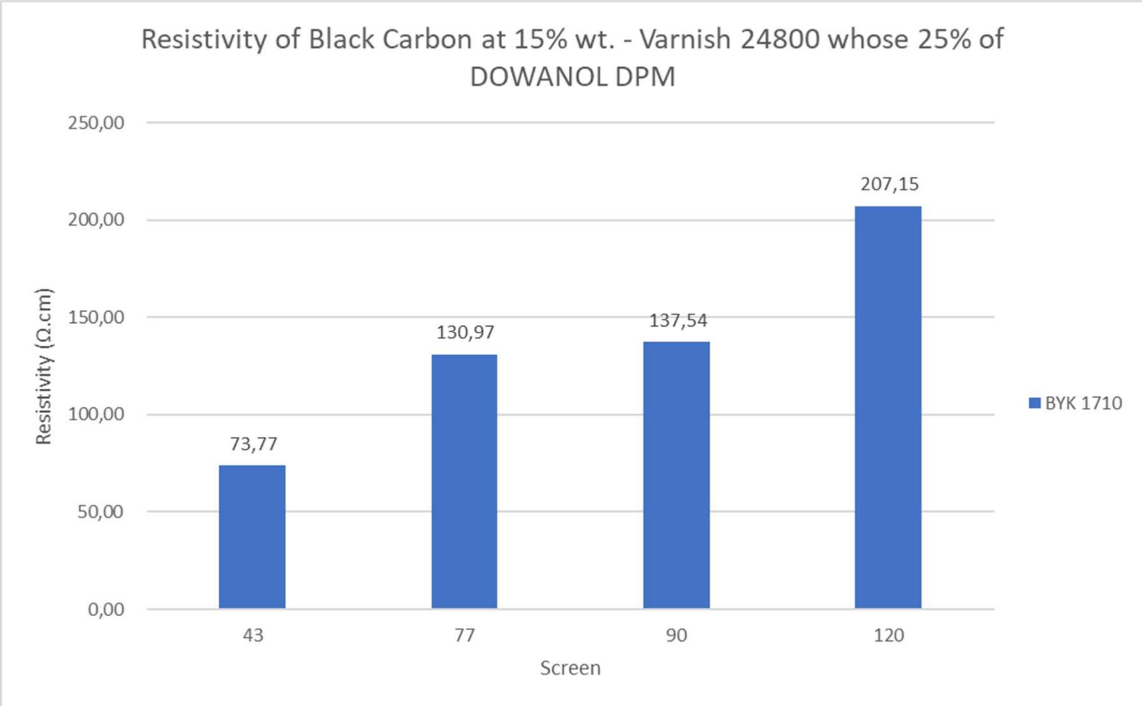


Figure 9*: Resistivity of Carbon black at 15% wt.*

The results obtained are much better. They confirm the hypothesis that the quantity of conductive materials influences proportionally the capacity of the ink to conduct the current.

So, if the quantity of conductive materials allows to increase the conductivity, we have to consider the good printability of the product. Addition of dispersing agent and its influence on the conductivity has been studied. This experiment has been realized with the conductive Carbon black and the eConduct Copper.

The two dispersants used are: Solsperse 32000 which is a very strong dispersant (called hyperdispersant), and Borchigen 911/D60 which is more traditional one. The quantity added are purely arbitrary: 1% wt. in comparison to the weight of conductive compounds for the Solsperse 32000, and 10% wt. for the Borchigen 911/D60. For both conductive materials, the same screen (screen 43 lpcm) and the same substrate (PC) have been used. The resistivity values are listed in **table 2** below.

Table 2: *Resistivity (Ω.cm) of Carbon black and eConduct Copper with dispersant*

Conductive materials	Solsperse 32000 – 1% wt.	Borchigen 911/D60 – 10% wt.
Carbon black	259 330	708 330
eConduct Copper	0,79	0,88

The results show that the desired effect is completely the opposite for Carbon black. This would mean that carbon particles are too far from each other, resulting in bad contacts and therefore, bad conductivity.

However, for eConduct Copper, the addition of dispersant, whatever its nature, increases almost 50% the conductivity (0,79 and 0,88 Ω.cm in comparison to 1,57 Ω.cm). This would also be explained by the fact that eConduct Copper particles are flakes, so after printing, these flakes stack on each other. The dispersant allows to slightly take away them and increases the surface contact between the conductive particles, and therefore increases the conductivity. The scheme in **figure 10** shows this principle.

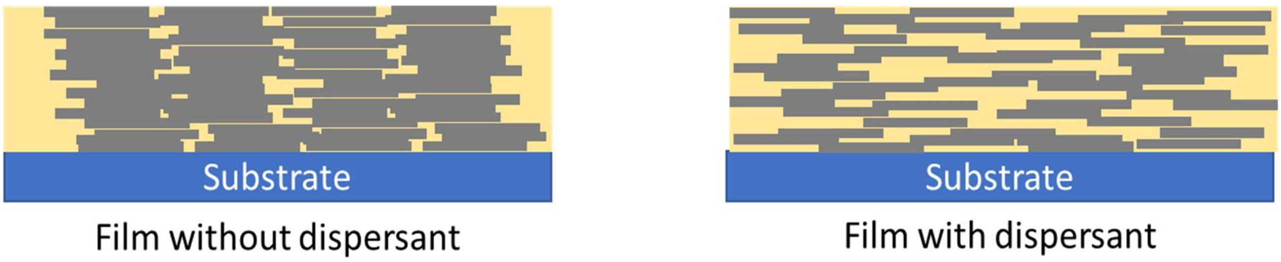


Figure 10: *Role of dispersant*

Finally, the last test realized in this part is the process of "sintering". This process, generally used for the nanoparticles, allows conductive particles to go soft under the temperature effect, which is higher than the drying temperature to evaporate the solvent, during a precise time.

So, this experiment has been performed with the eConduct Copper powder at 30% wt. and the screen 90 lpcm, as well as the eConduct Glass powder at 30% wt. and the screen 43 lpcm because the particles size is too high for the other screens to obtain a good printing quality. For these both samples, a temperature of 150 °C and a time of 30 minutes have been chosen. Glass substrate is used because it's the only substrate which can tolerate this temperature without any degradations. The values are assembled in the **table 3**.

***Table 3**: Resistivity (Ω.cm) of eConduct Copper and Glass powders before and after sintering*

Conductive materials	Before sintering	After sintering
eConduct Copper	2,55	1,84
eConduct Glass	8,64	8,17

Sintering process slightly improves conductivity. But this improvement is too small compared to the costs of equipment (oven price and time required). Therefore, more focused on eConduct products (Copper and Glass) because their conductivity is good, this final step has been removed in the printing process.

3.2. UV inks

As solvent-based inks, the first experiments were to test conductivity of conductive raw materials (Graphene, Graphite, Carbon black, silver-coated copper powder and silver-coated glass powder).

A UV varnish is composed of oligomers, monomers, photo-initiators, additives (wetting, thixotropic agent, defoamer, …) and fillers. Oligomers used are epoxies, polyurethanes and polyesters, but functionalized with acrylates functions. These oligomers are dissolved in acrylates monomers to form the base of the varnish. The addition of photo-initiators allows to initiate the radical polymerization reaction, and so to cure the varnish under UV lamp. To decrease the production cost, the addition of fillers, most of the time neutrals, is conceivable.

For experiments, two different UV varnishes are used: Multiplus and Evopanel. Multiplus is the most reactive but it dries in surface and not enough in depth. Evopanel is the less reactive but the drying is correct in depth. This varnish is most of the time used for thermoforming process because it is flexible and stretchable.

For the first experiment, the resistivity of conductive raw materials has been measured in Multiplus and Evopanel. As in solvent-based system, the maximum amount of conductive materials has been integrated in the ink. The total weight has been fixed at 10 g. For all measurements, the screen 43 lpcm and the substrate in PC are used. To cure samples, the UV mercury lamp of 300 W/inch at 100% (corresponds to the energy maximum of the lamp) is used and the belt speed has been fixed at 10 m/min. The results obtained are listed in the **table 4** below.

Table 4: *Resistivity (Ω.cm) of conductive raw materials in UV varnishes*

Samples	Multiplus		Evopanel	
	Resistivity (Ω.cm)	Number of passages under UV lamp	Resistivity (Ω.cm)	Number of passages under UV lamp
eConduct Copper 45% wt.	591	2	26,75	9
eConduct Glass 40% wt.	No value	1	No value	1
Graphene 2% wt.	3 327 000	5	246 667	8
Graphite 25% wt.	42 433	5	27 000	5
Carbon black 10% wt.	73 687	12	371 667	20

The resistivity values are better in Evopanel. For Carbon black, Multiplus is better because the film in Evopanel is not completely cured. The drying process in Multiplus is faster than Evopanel because Multiplus is more reactive. Even if the Multiplus layer cures faster than Evopanel, the conductivity result is weaker because Multiplus dries at the surface and encapsulates the conductive materials.

The question is: why Multiplus cures faster than Evopanel ? The answer is in the chemical structure. Indeed, the reticulation network in Multiplus is denser than the network in Evopanel because mono and bifunctional monomers are used to make Multiplus varnish and only monofunctional monomers for Evopanel. As the Multiplus network is denser and crosslinked, the number of acrylate functions is higher. When photo-initiator absorbs UV light, it creates a radical. This radical reacts with acrylate functions of oligomers to initiate the radical polymerization reaction. And so, as Multiplus has more acrylate functions than Evopanel, the polymerization speed is faster. Moreover, the lifetime of radical is very short. The presence of amino oligomers in the Multiplus formula allows to increase the lifetime of the radical. Indeed, when photo-initiator creates a radical, there is a transfer from photo-initiator to the amino function, so the radical is more stable, its lifetime increases, and it is more reactive. Now, even if Multiplus reacts easier than Evopanel under UV lamp, the polymerization reaction is too fast and it happens only on the surface. Therefore, the next experiments will use Evopanel to have better results.

Finally, the results showed that eConduct Glass does not work. No conductivity has been measured because the printing quality of the film is too bad. As eConduct Glass doesn't work in Multiplus and Evopanel, it is not a curing issue. The eConduct Glass works in solvent-based system but not in UV system. Maybe the UV system is not suitable for eConduct glass but it works for the other conductive compounds.

Between solvent-based and UV experiments, a new sample of eConduct Glass has been received. The difference between first and second sample is that glass was treated for the first sample but not for the second.

A first hypothesis is that the quantity of eConduct Glass is too important. As solvent-based ink, we put 30% in place of 40%, but no conductivity was measured. Glass flakes are not completely coated with silver, so the second hypothesis is that glass without silver needs to be treated. Addition of hardener, a silane compound called AM9192, can allow the treatment of glass surface of the flakes. Putting 40% of eConduct Glass and 5% of AM9192 in the formula, no conductivity was measured.

With 40% of eConduct Glass, the ink is thick, maybe too thick to be printed. To decrease the viscosity, the Evopanel formula has been modified to be more liquid. Thanks to this new Evopanel, a conductivity equal to 116 Ω.cm has been measured. But curing remains a problem because many passages under UV lamp are necessary to cure properly the film. To overcome this obstacle, the varnish 24800 is tested instead of modified Evopanel with 20% of DOWANOL DPM and 5% of AM9192. Only 30% of eConduct Glass are put in the varnish 24800. The drying is better (15 min at 80°C) and the resistivity is equal to 25,79 Ω.cm.

To go back to UV inks, as the film with eConduct Glass contains many holes, eConduct Copper, with smaller particles, can fill the holes. To do this experiment in Evopanel, the screen 43 lpcm and the substrate in PC have been chosen. The total weight is fixed at 10 g and the total rate of conductive charges is also fixed at 40% wt. Three different ratios between eConduct Copper and Glass are tested: 10%/30% ; 20%/20% ; 30%/10%. **Table 5** below summarizes the results.

Table 5: *Combination between eConduct Copper and eConduct Glass*

Samples	Copper/Glass (%)	Resistivity (Ω.com)
eConduct Copper and eConduct Glass	10% / 30%	44,67
	20% / 20%	71,33
	30% / 10%	192,00

As the results obtained with solvent-based inks, the resistivity value is better with a high concentration of eConduct Glass. For the three ratios, the resistivity values are relatively good. Compared to 116 Ω.cm, a resistivity equal to 44,67 Ω.cm is better. This experiment confirms the fact that eConduct Copper allows to fill the holes and so to increase the conductivity. Moreover, from an economic point of view, this experiment is a success because eConduct Glass is cheaper than eConduct Copper due to a lower quantity of silver. The only problem with eConduct Glass is the size of the particles which is too coarse.

Before the studies on eConduct Glass, a preservation test has been performed. This experiment consists to follow the evolution of conductivity and the evolution of weight over time. The conductive materials tested are eConduct Copper, eConduct Glass and Graphite. The screen 43 lpcm and the substrate in PC have been used to print the film. For 30 days, the ink and the appropriated film have been kept in different temperatures (ambient air, 60 °C, 80 °C and fridge). The resistivity and the weight have been measured each day at the same hour. Of course, no conductivity was measured for eConduct Glass. The curves in **figure 11** show the results for eConduct Copper. The results for eConduct Glass and Graphite are gathered in **Annex 3**.

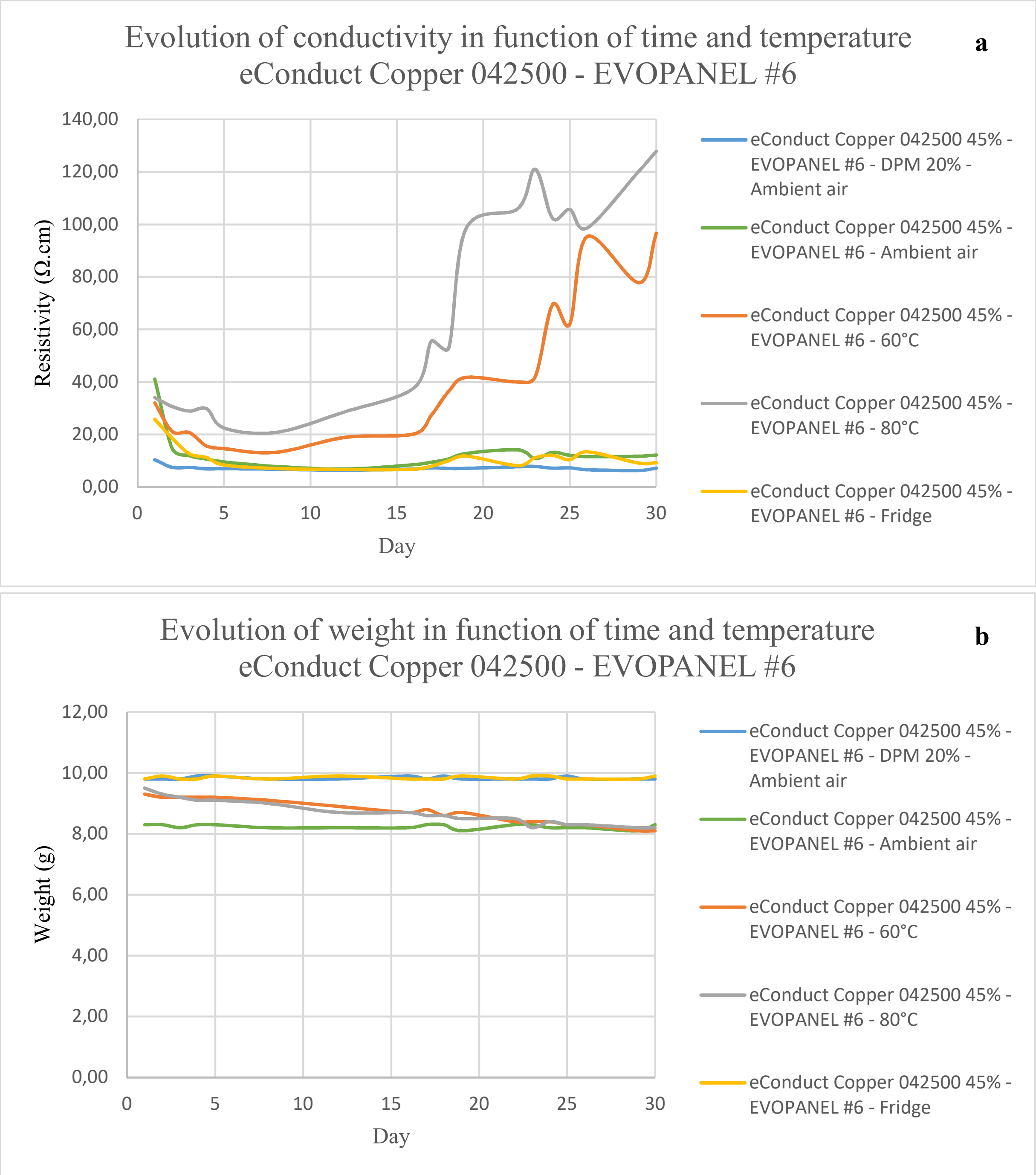


Figure 11: *Evolution of conductivity (a) and weight (b) in function of time and temperature for eConduct Copper sample*

The evolution of weight shows that eConduct Copper is very stable in Evopanel, even combination with DOWANOL DPM. For high temperatures (60 °C and 80 °C), a small decrease is visible. The decrease corresponds to the progressive evaporation of monomers which didn't reacted. Indeed, during the curing process, some monofunctional monomers are not involved in the polymerization reaction. So, at high temperature, the remaining monomers which didn't reacted, can be evaporated.

About conductivity, three different phases can be distinguished. For the 5 first days, resistivity decreases. Like evolution of weight, this decrease is due to the evaporation of non-reacted monomers. Then, conductivity does not change until the end, except for high temperatures (60 °C and 80 °C). After 17 days, resistivity continually increases because of the oxidation of copper, and copper oxide is not conductive. The oxidation of Copper to the air is an evidence, but the process is accelerated by temperature. If the temperature is higher, Copper oxidation is faster. So, after 17 days, temperatures at 60 °C and 80 °C are enough to oxidize Copper. More precisely, this analysis is confirmed by the fact that resistivity at 80 °C is higher than that one at 60 °C, so Copper oxidation is a bit stronger at 80 °C. Normally, if test had continued, samples at ambient air will begin to oxidize, and after more time, sample in fridge will also begin to oxidize.

In global, for all the materials studied in this experiment, the inks are relatively stable in all the temperature conditions. On the contrary, this is not the same for conductivity. For eConduct Copper, film oxidizes after only 17 days at high temperatures, and maybe in less than two months, all the film will be oxidized. So, eConduct Copper films need to be protected. For Graphite, there is no problem of oxidation but it needs to be stored at ambient air in minimum (conductivity is bad in fridge).

3.3. Combination between solvent-based and UV systems

As the results for eConduct Copper in Evopanel / DPM are good, a combination between UV varnish and solvent is studied for Carbon black. Carbon black has been chosen because since the beginning of experiments, its resistivity values are not so good. The first hypothesis is that this carbon black sample is not the best pigment for conductive ink.

The participation at two exhibitions in Paris (Eurocoat and Afelim) allowed us to discuss with customers and suppliers about conductive inks, and more precisely about carbon black. Thanks to the exhibitions, three new samples of Carbon black have been tested (XPB 552, VXC72R and Printex L6). Compared to the first Carbon black sample, these three new samples have lower oil absorption and the particles size is smaller. Improving these properties, the quantity of Carbon black pigment could increase and the conductivity too. Moreover, the grinding process will be easy and the printing quality will be better.

For this experiment, three UV varnishes have been used : Evopanel, Multiplus and Polyflex. The last one is an intermediate between Evopanel and Multiplus in terms of reactivity and curing. These three varnishes have been combined with solvent, and in most of the cases, it is Dowanol DPM, used for solvent-based inks. The screen 43 lpcm and the substrate in cardboard have been chosen. The percentage of solvent has been also fixed at 20% wt.

For drying, two processes are possible. First way is to begin to evaporate solvent in the oven and then to cure UV varnish under the UV lamp. The second is to do the opposite. After testing the two ways, the first option (to begin to evaporate solvent in the oven) gives better results of resistivity. So, the drying conditions to evaporate solvent in the oven are 15 min at 80 °C. For UV varnish, 5 passages at 10 m/min with 100% lamp are the curing conditions.

Table 6: *Resistivity of Carbon black samples in UV-solvent inks*

Sample	% wt.	Varnish	Resistivity (Ω.cm)
XPB 552	12	Evopanel / Dowanol DPM	948
	12	Polyflex / Dowanol DPM	4 573
	13	Multiplus / Dowanol DPM	19 733
	12	Varnish 24800	46 483
	12	Evopanel / Dowanol DPM	1 133
VXC72R	10	Evopanel / Dowanol DPM	3 800
	10	Evopanel / Ethoxy Propanol Acetate (EPA)	4 943
	10	Polyflex / Dowanol DPM	1 056
	10	Polyflex / Butyl acetate	1 523
Printex L6	10	Evopanel / Dowanol DPM	19 877
	10	Polyflex / Dowanol DPM	1 580
	10	Varnish 24800	35 727

First for XPB 552, looking the resistivity values in Evopanel, Polyflex and Multiplus, resistivity increases because films are not very dry in Multiplus, a little bit more in Polyflex and more again in Evopanel.

But compared to the value in Varnish 24800, the resistivity value is higher than values for UV-solvent varnishes. The same is observed for Printex L6 sample. To be conductive, Carbon black has an organized structure. But maybe in Varnish 24800, Carbon black becomes clusters and loses its organized structure, so the conductivity decreases.

Moreover, for XPB 552, orange value in **table 6** mains that the drying for solvent is 5 min at 120 °C instead of 15 min at 80 °C. A small difference of resistivity is observable. That may be due to a measurement error. Another possibility is that at 120 °C, the drying is too strong and only the surface layer dry and in depth. At the opposite, the drying at 80 °C allows to dry in depth and the surface layer.

Now, looking values for VXC72R and Printex L6, a difference is visible. Polyflex/Dowanol DPM gives better result than Evopanel/Dowanol DPM. Compared to XPB 552, VXC72R and Printex L6 have only 10% of Carbon black. As the two last samples have less Carbon black, knowing that black absorbs light and prevents films to dry correctly, the films dry better than XPB 552. Moreover, as Polyflex is more reactive than Evopanel, it dries better, so the conductivity is better.

The last observation concerns only VXC72R sample. For Evopanel and Polyflex, new solvents which are respectively EPA and Butyl acetate, have been tested instead of Dowanol DPM. These two solvents evaporate faster than Dowanol DPM, so normally, with the same drying time, films dry better and consequently, conductivity increases. But the opposite occurs. Eco rapide and Butyl acetate are very volatile, so maybe during printing, solvent begin to evaporate on the screen and disorganize a little bit the organized structure of Carbon black.

In conclusion, to put maximum quantity of conductive materials is not the best option if the drying is impossible. We must try to find a compromise between conductivity and drying. Finally, the choice of solvent is important because solvent must be compatible with UV varnish and must evaporate at low temperature.

Conclusion

At the end of all these experiments, it first appears that there are different conductive materials with a large conductivity scale. This diversity allows to formulate a range of conductive inks for different applications. These experiments allowed to better understand the influences of the different raw materials used on the conductivity properties. Moreover, the different results allowed to modify the varnish formula more easily because thanks to them, an anticipation on the final properties of printed film is possible.

However, this project is not finished. Other studies need to be undertaken. Indeed, even if we developed different inks, they are not completely approved by the company because many properties (mechanical and chemical properties) need to be studied and/or optimized to have a complete formulation. Furthermore, several projects with customers will be appreciated to test the inks in order to validate it and to incorporate it on the market.

I thank again my tutor Guy MASSE to propose me this project. A very interesting and intriguing project which stimulated more than one time my curiosity. This subject allows me to put several skills learned during the courses into practice. I think to chemometric, formulation and the notions about OPV and OLED which, even if we don't develop anything in these fields, helped me during my bibliographic research like conductive polymers.

More personally, this project also allows me to deal with my knowledges in depth in the world industry, but also in the field of screen printing. As I already had a professional experience in the field of polyurethane squeegees for screen printing, this subject also allows me to see how these squeegees are used, seeing as they come directly from FIMOR company in which I did my internships. Thanks to this professionalization contract, I'm even more sure to make career in industry, in Research & Development.

References

[1] https://www.encresdubuit.com/ : Encres DUBUIT society

[2] http://cerig.pagora.grenoble-inp.fr/memoire/2004/encres-conductrices.htm : Conductive inks

[3] http://fr.methode.com/sensors-and-switches/conductive-and-resistive-inks.html : Conductive and resistive inks

[4] https://en.wikipedia.org/wiki/Conductive_ink : Conductive inks

[5] Black K.; Singh J.; Mehta D.; Sung S. *Sci Rep*. **2016**, 10.1038/srep20814

[6] Berteaud A. J. *Phys Appl.* **1986**, 21, 665-668

[7] K.M. Gupta; N. Gupta. *Advanced Electrical and Electronics Materials* (Chapter 5)

[8] https://www.digitaltechnologieshub.edu.au/docs/default-source/getting-started-years-5-6/makey-makey/list_of_materials.pdf?sfvrsn=2 : List of conductive materials

[9] Dongio K.; Jooho M. *Electrochemical and Solid-State Letters*. **2005**, 8 (11), J30-J33

[10] https://www.electrochem.org/dl/interface/fal/fal12/fal_win12_p061.pdf : Conductive polymers

[11] http://cerig.pagora.grenoble-inp.fr/Note/2007/polymeres-conducteurs.htm : Conductive polymers

[12] www.csst.qc.ca/prevention/reptox/Pages/fiche-complete.aspx?no_produit=14043 : Carbon black

[13] http://www.imerys-graphite-and-carbon.com/5-conductive-carbon-black/index.html : Conductive carbon black

[14] Y.J. Dappe; M.A. Basanta; F. Flores and J. Ortega. *PhysRevB*. **2006**, 74, p. 205434

[15] D. Elias and al., *Science*. **2009**, 323, 610

[16] https://www.futura-sciences.com/sciences/definitions/chimie-graphene-4713/ : Graphène

[17] http://www.genesink.com/fr/nos-applications-1679 : Applications of nano-silver inks in Genes' Ink society

[18] https://www.henkel.fr/ : Henkel society, manufacturer of conductive inks

[19] http://www.dupont.com/ : Dupont society, manufacturer of conductive inks

[20] http://www.agfa.com/specialty-products/ : Agfa society, manufacturer of conductive inks

[21] https://www.appliedinksolutions.com/ : Applied Ink Solutions society, manufacturer of conductive inks

[22] Rao Rama V.K.; Abhinav K V.; Singh S. *ResearchGate*. **2015**, 10.1039/C5RA12013F

[23] http://www.centrenational-rfid.com/fonctionnement-dun-systeme-rfid-article-17-fr-ruid-17.html : RFID principle

[24] https://www.ssi-electronics.com/products/membrane-switches/ : Membrane switch

[25] https://www.pannam.com/membrane-switches/ : Membrane switch

[26] http://www.gsitech.com/heater-and-warming-element-printing-ptc/ : Heater elements definition

[27] https://butlertechnologies.com/flexible-printed-heaters/ : Heater elements definition

[28] https://fr.wikipedia.org/wiki/Diode_électroluminescente_organique : OLED principle

[29] http://cerig.pagora.grenoble-inp.fr/memoire/2010/impression-oled.htm : OLED, principle and applications

[30] http://www.explainthatstuff.com/how-oleds-and-leps-work.html : OLED principle

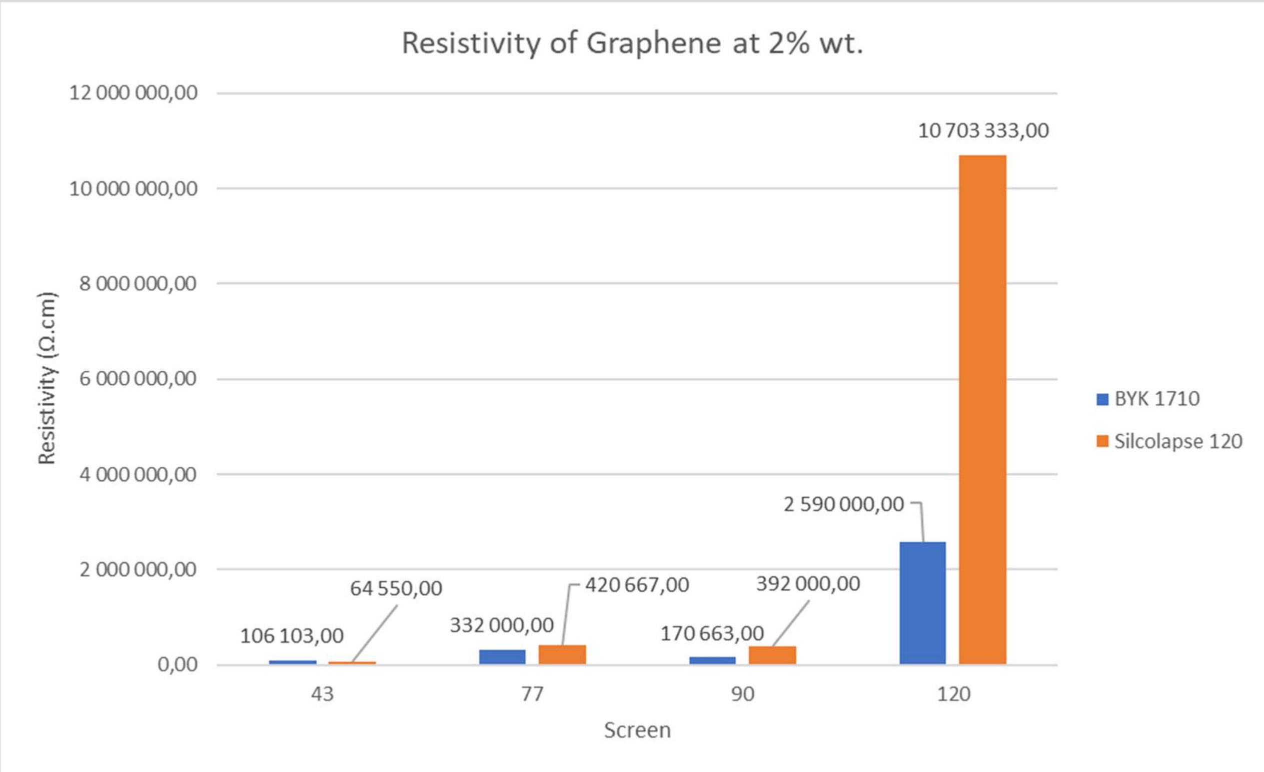
[31] M. Le Bail, *Synthèse et formulation d'encres conductrices imprimables par jet d'encre pour l'électronique organique*, **2015**, p. 151-157

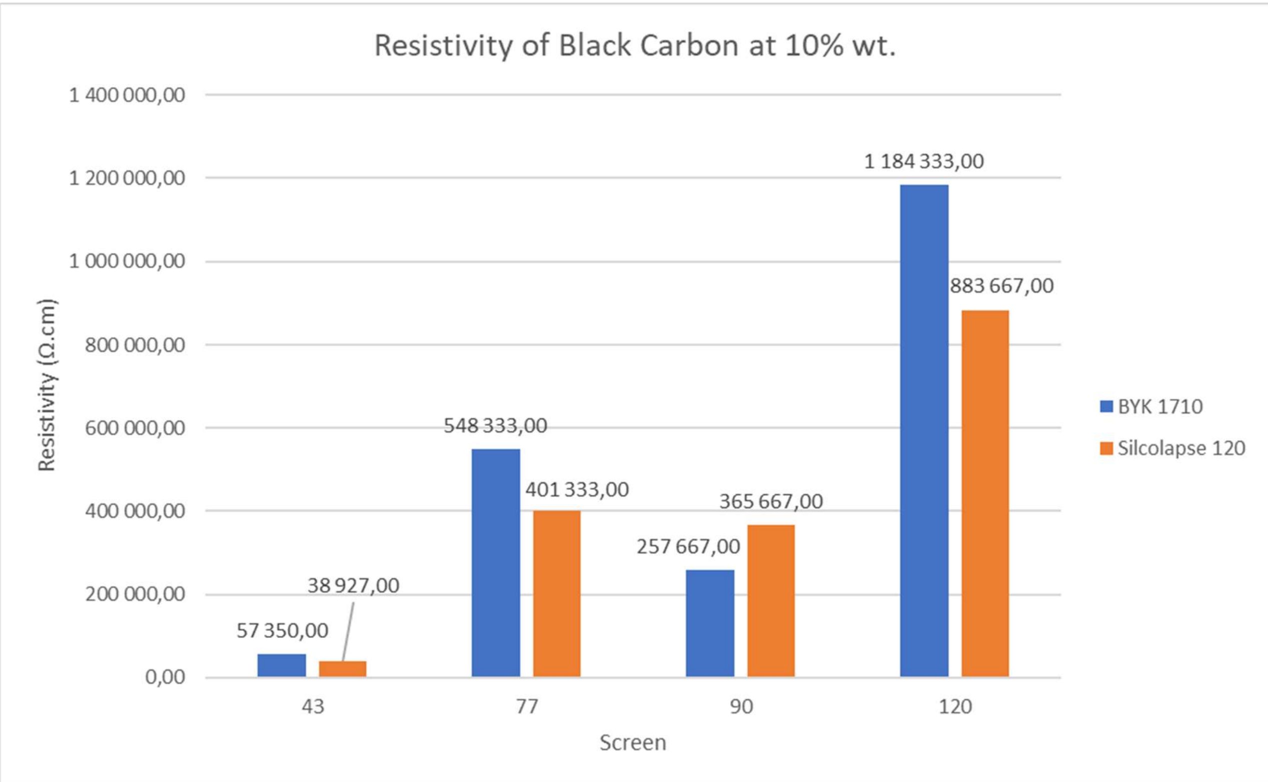
[32] J. Chil, *Chem. Soc.*, **2008**, 53 (n°3), p. 1549-1564

[33] http://www.solarcell.science/2017/07/29/organic-solar-cells/ : Organic solar cells

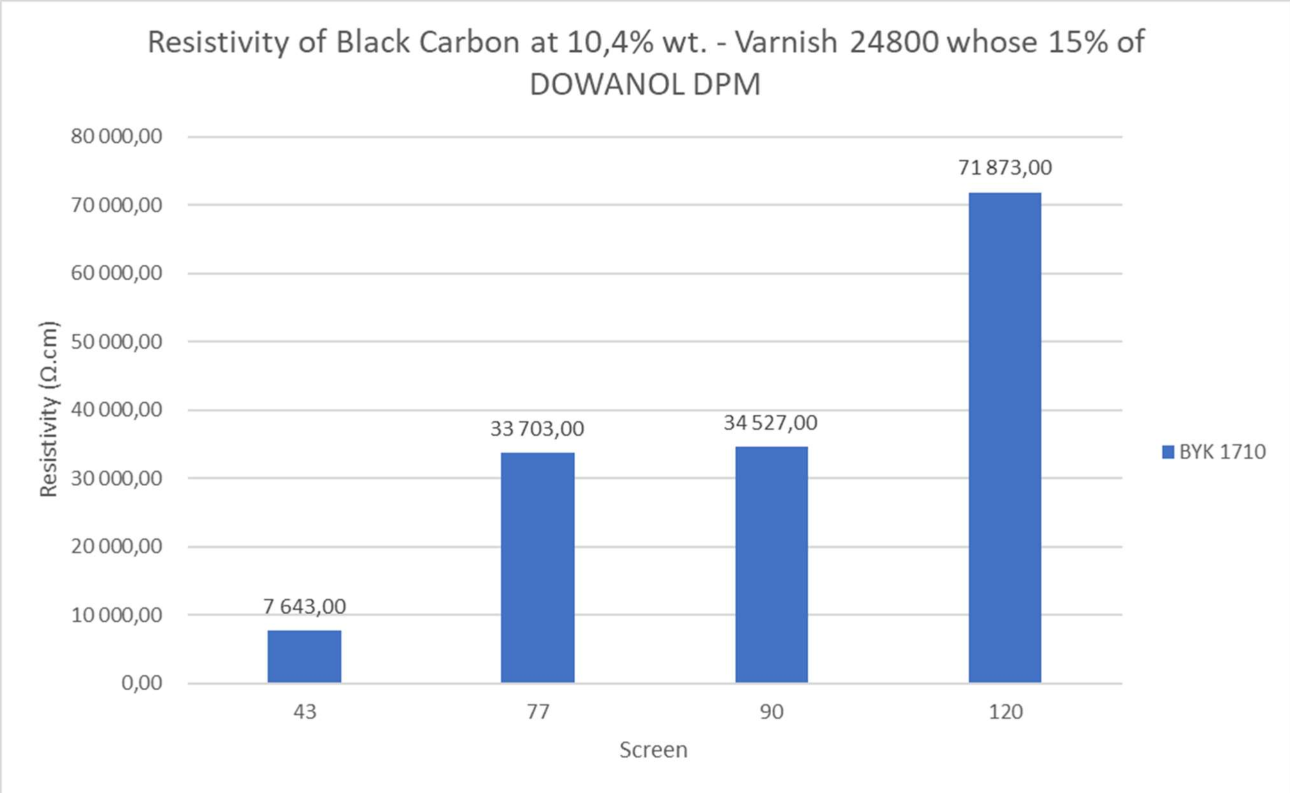
ANNEXES

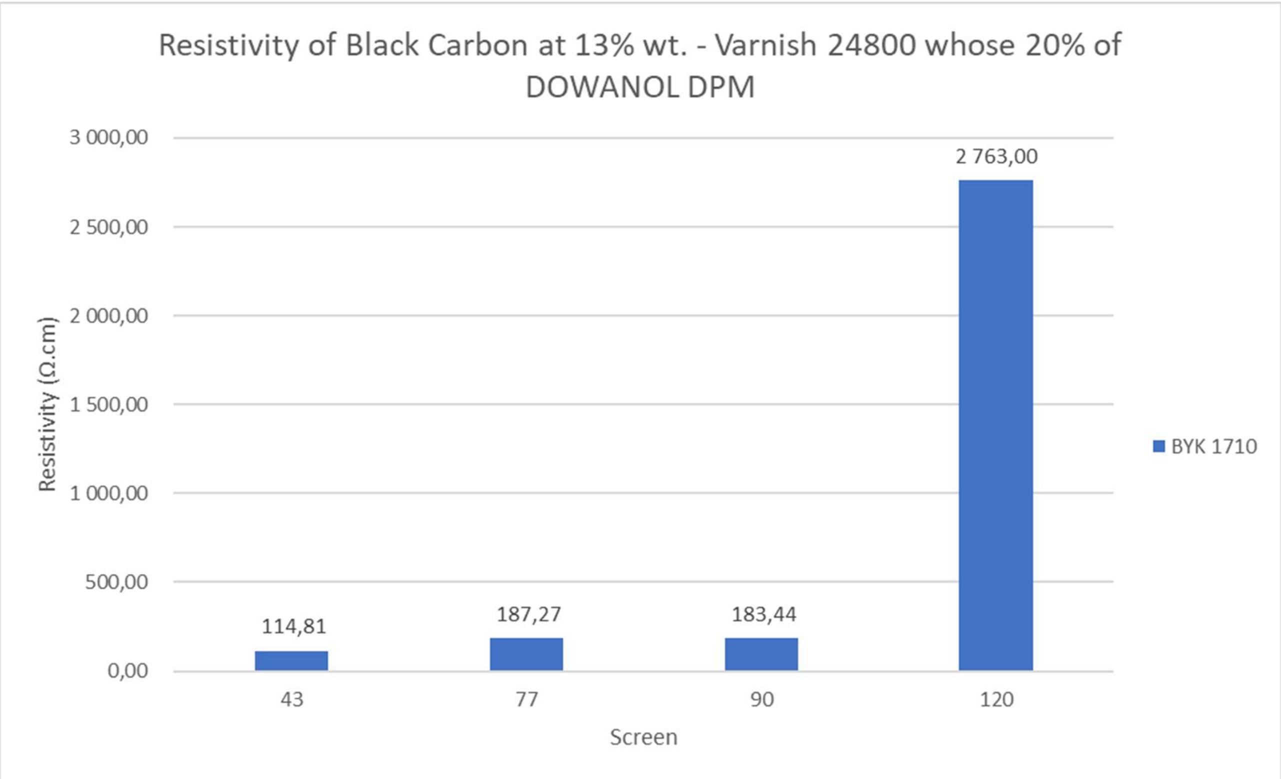
Annex 1: Conductivity of raw materials



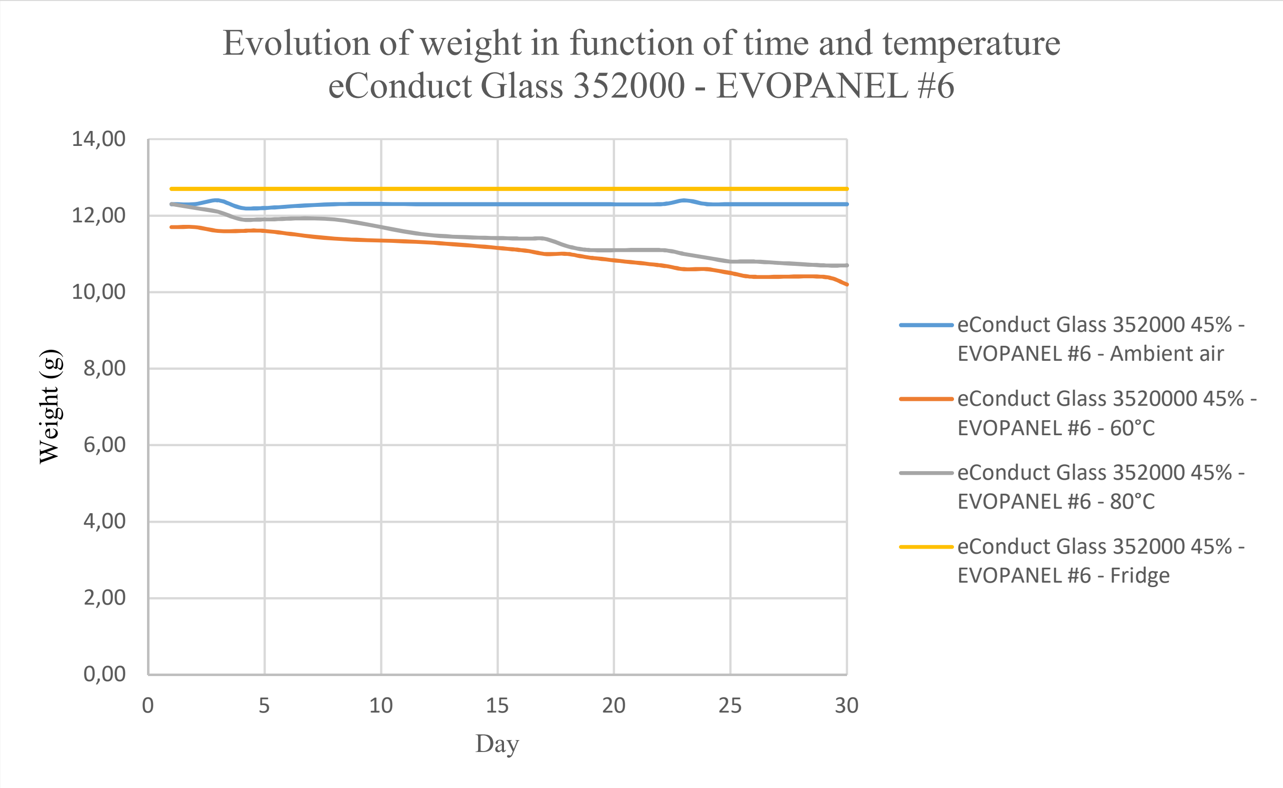


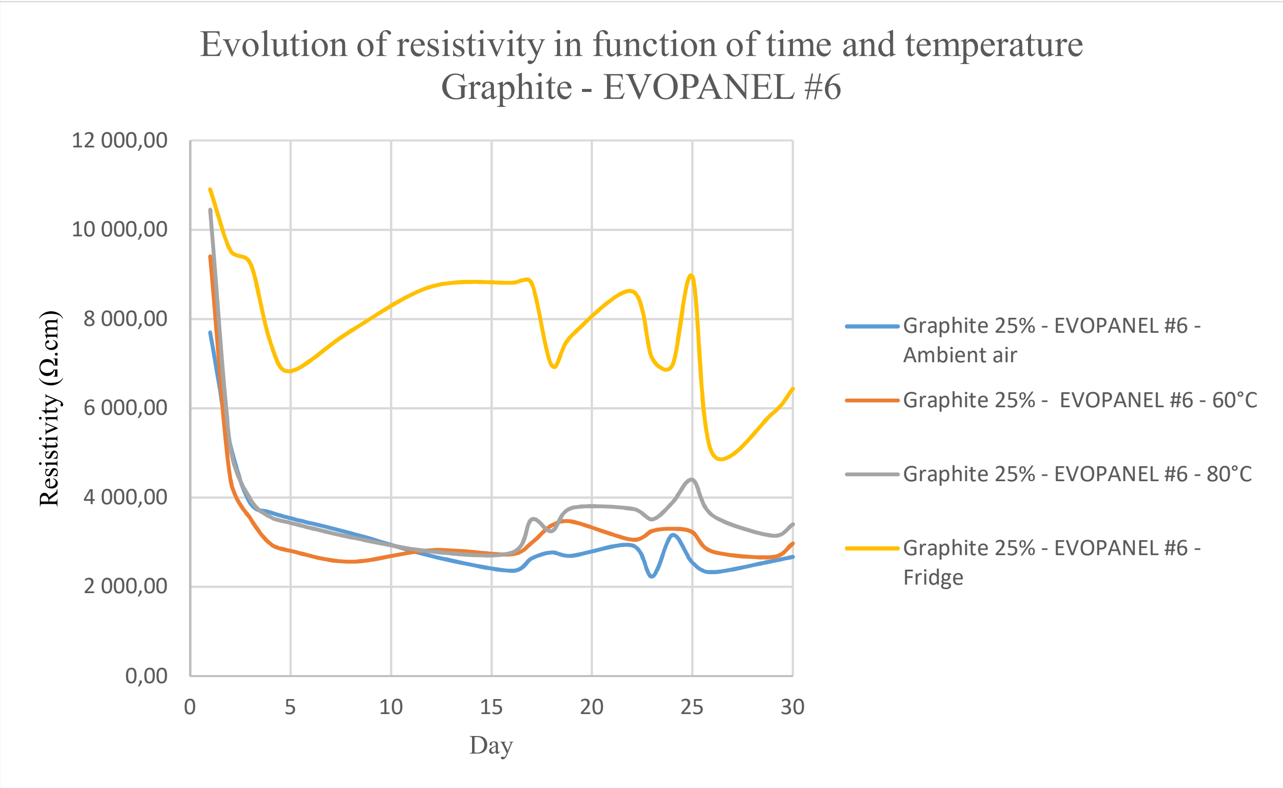
Annex 2: Evolution of the conductivity of Carbon black

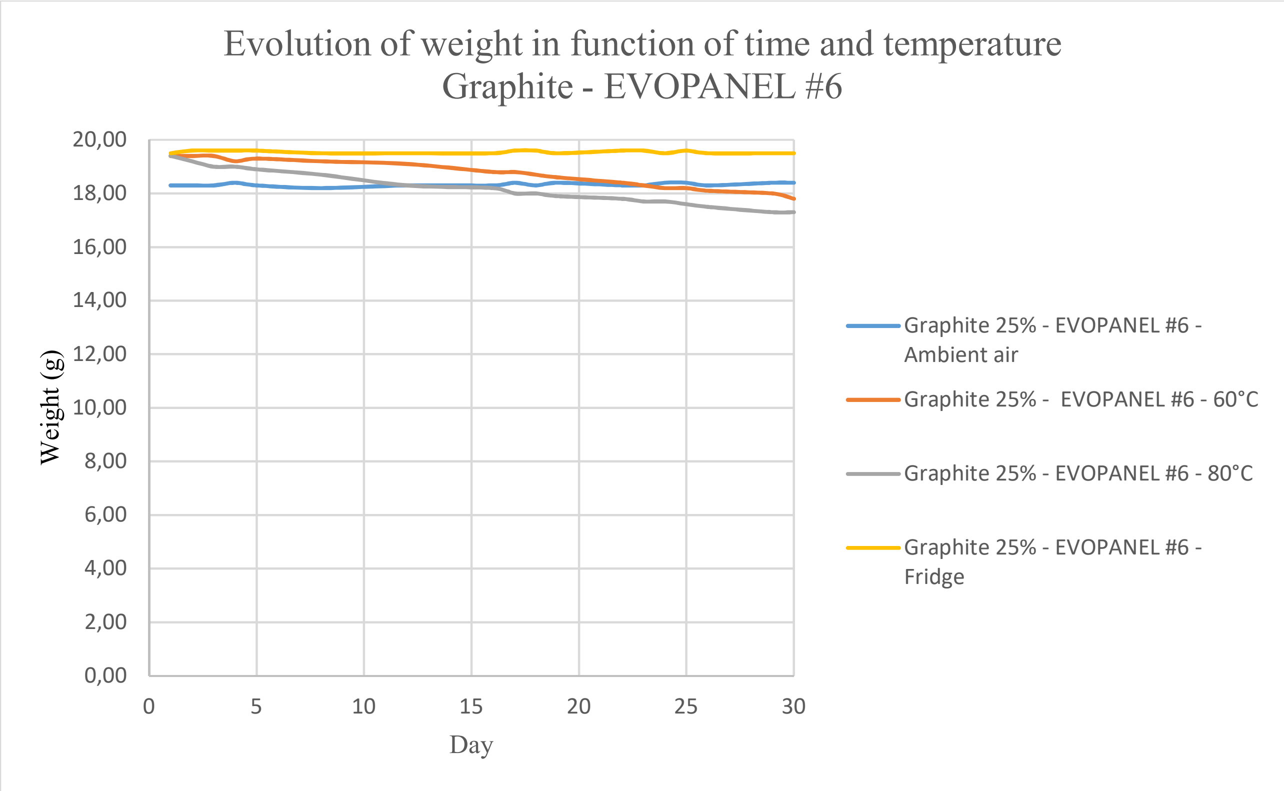


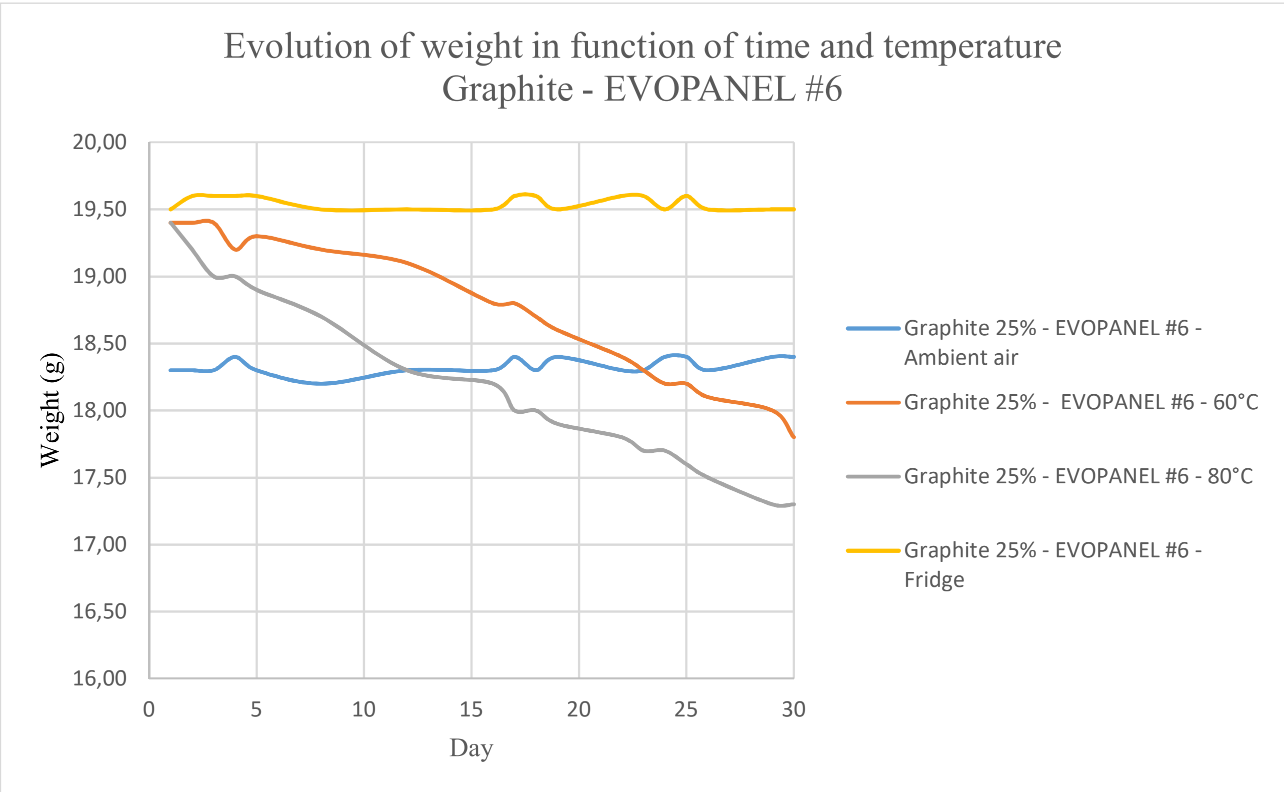


Annex 3: Preservation test – eConduct Glass and Graphite






Evolution of weight in function of time and temperature
Graphite - EVOPANEL #6
Weight (g)
20,00
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
0
5
10
15
20
25
30
Day
Graphite 25% - EVOPANEL #6 - Ambient air
Graphite 25% - EVOPANEL #6 - 60°C
Graphite 25% - EVOPANEL #6 - 80°C
Graphite 25% - EVOPANEL #6 - Fridge


Evolution of weight in function of time and temperature
Graphite - EVOPANEL #6
Weight (g)
20,00
19,50
19,00
18,50
18,00
17,50
17,00
16,50
16,00
0
5
10
15
20
25
30
Day
Graphite 25% - EVOPANEL #6 - Ambient air
Graphite 25% - EVOPANEL #6 - 60°C
Graphite 25% - EVOPANEL #6 - 80°C
Graphite 25% - EVOPANEL #6 - Fridge