SCHOOL OF SCIENCE
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Effects of low-environmental impact graphene on paints: chemical and physical properties

Experimental degree thesis

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Abstract

Paints and varnishes industry is a well know sector of chemical industry and its importance is due to the need of surfaces colouring and protection (metals, wood, concrete) from many natural or artificial chemical or physical agent.

This work is based on the formulation of new graphene-based paints and the analysis of their physical and chemical properties.

Graphene is the bidimensional sp^2 carbon nanomaterial with extraordinary properties as electron mobility, thermal conductivity, mechanical strength and large surface area [(1), (2), (3), (4), (5)]. Due to these properties, it's used as additive in paints formulations to improve mechanical properties.

Graphene-XT produces graphene by Liquid Phase Exfoliation (top-down approach) with a mechanical exfoliation in water environment, using only graphite and a non-toxic exfoliating agent/solvent, avoiding the common toxic solvents as 1-methyl-2pirrolidone (NMP) or cyclopentanone (CPO).

Self-produced graphene was added to two types of paint to obtain products with different properties one from each other. In particular acrylic and teflon paints were used as bases with the addition of powder-graphene/graphene-ink.

During this experimental thesis, three graphene-based paints were formulated:

1. The first with the goal of improving hardness, adhesion, lubricant properties and mechanical resistance of the virgin teflon paint;
2. The second was an adhesive and electrically acrylic conductive paint;
3. The third was a formulation that increases some mechanical performances of a virgin acrylic paint.

All the formulations were created and tested inside Graphene-XT laboratory, except for some test on the first formulation (third-part requested product).

1. Introduction

1.1 Paints and varnishes

1.1.1 Market overview

Paint is a mixture of chemical products which, applied in more coats through a well-defined sequence of operations, forms a solid coating with mechanical and chemical resistance that protect the support from chemical and physical agents present in the environment. Its features of colour, roughness and uniformity change the aspect of the painted-support.

Paints and coating industry is a mature and well established component of global economy. Almost half of the market is covered by only ten suppliers, with Sherwin-Williams Co. at the n°1 position (Fig.1).

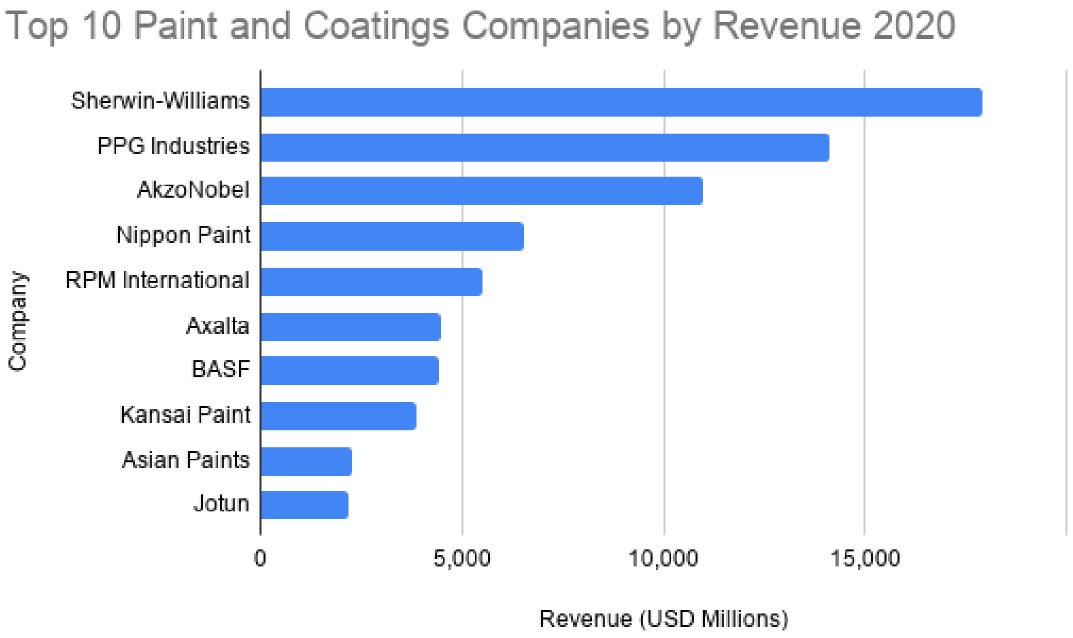


Fig.1 Top 10 paints and coatings companies in 2020 (6)

From year 2000 paints and coatings market increases 2%/year (7) leaded by the acceleration of building construction spending, especially for residential buildings.

In 2017 paints and coatings market has a value of 130 billion euros, equal to 42 billion litres (7) with a forecast of an annual 5% increase.

Italian market is a very fragmented sector, in which mostly small and medium companies are present, with only the exception of Mapei and some multinational subsidiaries as Sherwin-Williams and Basf. According to Assovernici, in 2018 Italy has the third biggest market in Europe, only after Germany and France, with 500 million litres of products, equal to 1,2 billion euros.

1.1.2 Definition and classification

Paints and coatings are liquid substances, or in dust, able to create a solid, continuous and adherent film if deposited onto a surface. Their main targets are the protection of the covered surfaces, meaning that a surface treated with a paint or a coating is more protected from external agents, and colour or decorate them.

Supports that are usually subjected to this treatment are metals, plastics, external and internal house walls, wood and others. The mixtures used to perform this treatment take different names as paints, varnishes, primers, lacquers, enamels according to the final use and composition, as well as the common language in use in the development phase of the preparation, making them often hard to categorize.

An important division that is crucial is between paints and varnishes:

- Paints: are mixtures in which there are pigments and the coating is not transparent, covering the colour of the substrate;
- Varnishes: there are no pigments and the colour is transparent. Usually are used to make the original aspect of the substrate more visible, not covering it.

Not all the products of these classes have the same mechanism to create the protective film, for that reason another classification is possible on the basis of the film-creation type:

- Solvent evaporation, in which there are no chemical reactions between the components of the formulation;

- Reaction (crosslinking) between two reactive components, in which a chemical reaction occurs between two components and forms the film;
- Reaction (crosslinking) between one component and the atmospheric oxygen as crosslinking agent, without reactions between components itself or solvent evaporation.

The previous classification shows that film-creation can be due to a reaction between two chemical species (called "reticulation or crosslinking", which can occur between two resins or one resin and oxygen). It's important to have a close look at the principal components of a paint/varnish in order to understand better the chemistry behind.

The Paint and the vanish are formulations of several components. Fig.2 shows what are the main components of a painting product and what are their volume percentage, referring to the year 2017 in the global scale.

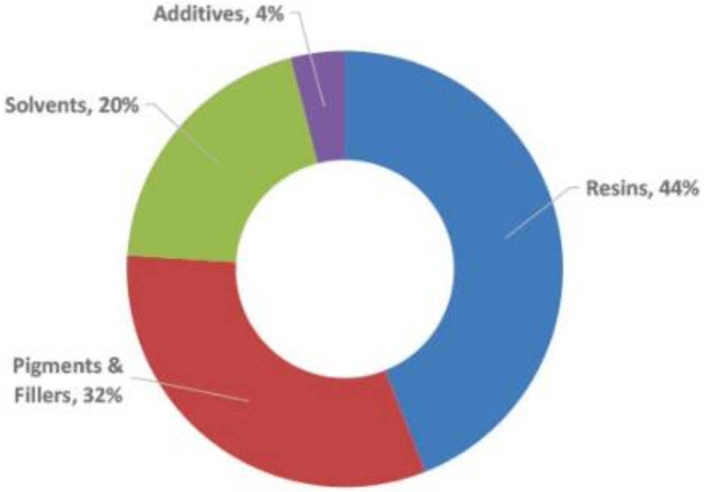


Fig.2 Volume percentages of the component of a painting product (8).

Each one of these components have its precise features and tasks:

1) Polymeric ligand (or its precursor).

It's the resin and its properties are the one with the most impact on the product's final properties.

Its task is to create the homogeneous film, incorporating all the others components in the film structure. They can be thermoplastic or thermosetting: the first ones can be melted every time the temperature reach the melting temperatures and they are formed by high-molecular weight polymers, meaning high viscosity and high solvent quantity, and create the film by solvent evaporation; the second ones are formed by low-molecular weight polymer precursors which react together when the solvent evaporates, meaning lower viscosity and lower solvent quantity with the possibility to develop painting products with higher solid percentage.

They are polymers soluble in organic solvents or in water and their nature depends on the basic monomer. Common resin types are represented in Fig.3-8:

- A) Alkyd:

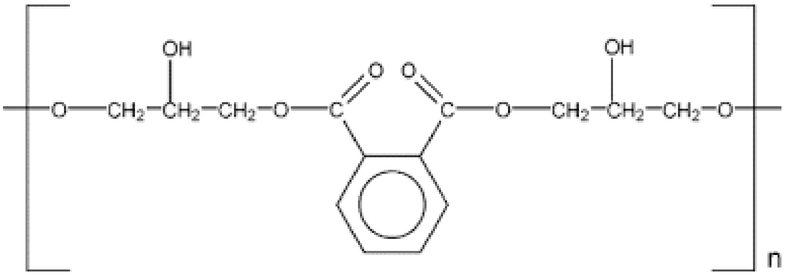


Fig.3 Alkyd resin structure (9)

Alkyd resin is a thermosetting polyester resin formed by polycondensation of dicarboxylic acids or anhydrides and polyols, in presence of triglycerides (which release fatty acids that gives flexibility).

This type of resin are commonly used in paints and varnishes and their synthesis includes two of three raw materials (glycerol and triglycerides) coming from renewable sources, making the production easy and cheap.

They can have different oil percentage, from more than 60% to less than 40% and for that reason the properties and time stability change a lot from one resin to the others.

- B) Acrylic:

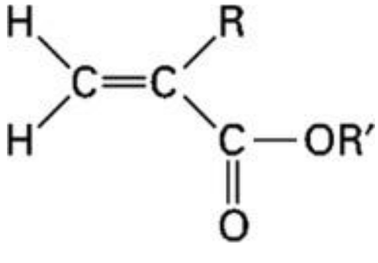


Fig.4 An acrylic monomer of general formula (10)

This class includes different polymers differing each other’s according to the starting monomer (acrylic, methacrylic, etc..). Different monomers means different properties and applications as resistance to chemical agents(alkali) and UV, water resistance and good adhesion, this is why these resins are used in many field ranging from automobile to building industry, in every case mostly used as paint component.

- D) Epoxy:

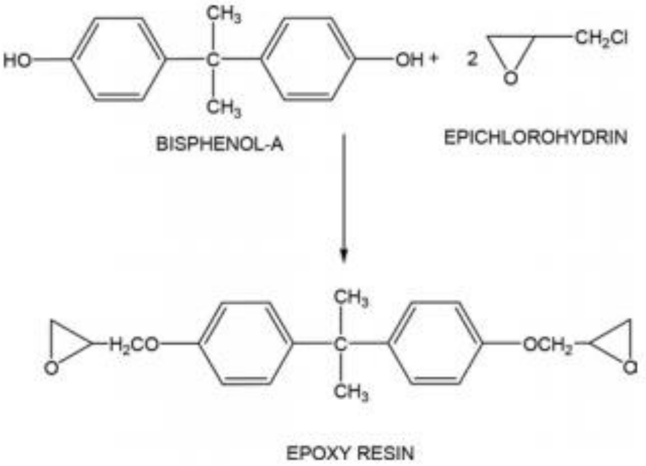


Fig.5 Epoxy resin structure with Bisphenol-A as nucleophile (11)

It’s a class of polymers containing an epoxy group and it’s formed by reaction between an epoxide (epichlorohydrin) and an acidic hydroxy group (commonly bisphenol-A).
The crosslinking occurs usually for reaction with a second component (polyfunctional aliphatic or aromatic ammines, anhydrides, thiol) at ambient or hot temperature, creating the tridimensional structure which increase the mechanical and chemical properties of the final resin. This process is usually called curing.
This type of resins have good adhesion to the substrate and chemical resistance, but are subjected to yellowing and for this reasons they are not used in external applications.

- E) Polyester:

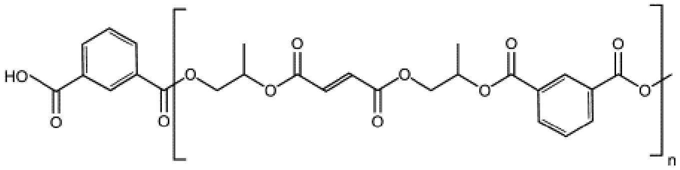


Fig.6 Polyester resin structure (12)

They are polymers that include the ester bond between the monomers and are widespread mostly in clothing and furniture industries, alone or in combination with other vinyl monomers (eg. Styrene).

Can be used also in painting industry reaching an high solid percentage (70%) in the paint / varnish.

- F) Polyurethane:

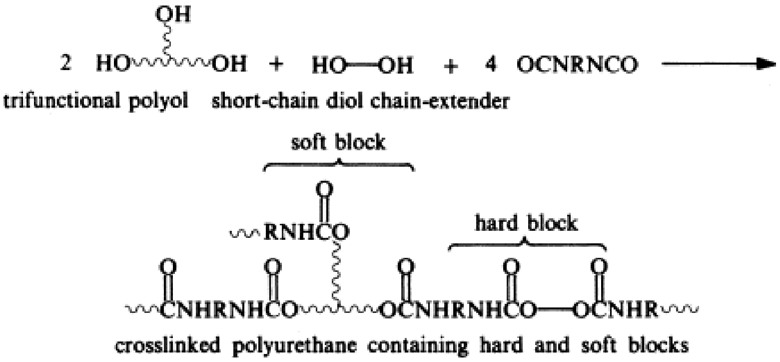


Fig.7 Polyurethan resin formation and typical structure (13)

This class includes all the polymers with an urethane bond, -NH(CO)O- which is formed by reacting of an di-isocyanate and an alcohol (or polyol, to make the crosslinking process).

The use of aliphatic isocyanates ensure an high resistance to yellowish and solar aging (but are more costly), making these resins very suitable for applications in which the aesthetic properties are the most important ones.

Moreover, the possibility to choose different isocyanates and polyols gives the possibility to create product with very tuneable properties.

- G) Teflon:

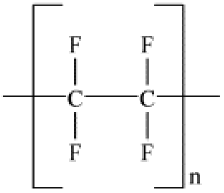


Fig.8 PolyTetraFluoroEthylene resin structure (14)

PolyTetraFluoroEthylene (PTFE), commonly known as Teflon, is a fluorinated homopolymer deriving from the radicalic polymerization of TetraFluoroEthylene.
It’s a completely inert material (exceptions are alkali metals in a fused state), it’s insoluble in water and organic solvents and has a very low friction coefficient.
The most common utilization is in kitchen as coating for non-stick pans, but is also used in a huge range of applications in every industry, from the gasket fabrication and mechanical parts to lab applications for glassy parts, moreover, expanded teflon is used in dental applications to create membranes.

2) Solvent.
Its task is to make the application of the product easier by keeping the resins in solution, mix all the components in an effective manner and, once the product is applied to a surface, evaporate letting the solid coating on the surface.
The evaporation process must be rapid (to avoid dripping) but not too much (causing a fast cooling and consequently creation of breaks in the film.
Most common solvents are organic ones, having good properties (mostly the volatility which gives very fast evaporation) and conferring adhesion to the products. In the last years the use of water as solvent is increasing, due to its environmental performance (no VOC emissions, no problems of handling, no risks for health and safety). The only drawback is in the evaporation phase because of the higher temperature required.
The second generation water paint products are formulated with resins in emulsion / suspension and allow to create products with only 10% of solvents. Use of water is going to continue its ascent because of the many environmental and economic advantages, in addition to the possibility to create a 90% solid painting products using very low amount of solvents.

3) Pigments.
They are solid products used in powder and insoluble in the painting products. Their tasks are to absorb certain wavelengths in order to confer the right colour to the product and to hide the substrate.

They influence the mechanical, chemical and aesthetic properties of the painting product and can be present in a large range of concentrations.

They are light and heat resistant and chemically stable (inert towards the other components), moreover, they can be organic or inorganic (mineral).

Organic pigments are organic compounds extracted from living organisms or synthetically produced and the most common are based on flavonoids and anthraquinones ("biological"), or on hydrazones, aromatic rings and condensed heterocycles (synthetic).

Organic pigments can be transformed in colourants by making them soluble in the solvent, by reacting parts of their structure.

Inorganic pigments are pigments in which carbon can be present only in the form of carbonates and include silicates, oxides and salts. This type of pigment is commonly produced by grinding and sedimentation, but can be also prepared by other techniques as calcination or sublimation.

4) Fillers.

They are cheaper than pigments and are used to bring some aesthetic improvement and to reduce the quantity of pigment needed. They are useful to reduce the costs by increasing the percentage of solids with a cheap material.

Usually they are inorganic insoluble salt like sulphates, silicates, and carbonates.

Their principal tasks are to control solvent evaporation and don't allow pigments to float.

5) Additives.

They are substances added in low quantity in a precise process step and their goal is to change, tune or improve a specific feature of the product.

They can be: plasticizers, dispersants, accelerators, siccatives, anti-yellowish.

Usually the percentage of additives does not exceed the 4%.

1.2. Graphene

1.2.1 Features and state of the art

Carbon is one of the most important elements of the periodic table being involved in the carbon cycle through atmosphere-hydrosphere-lithosphere-biosphere allowing the life of organisms, acting as reservoir of energy and providing the lands on which we live.

This element was the motor of human evolution in the last centuries starting from the industrial revolution up to now. Coal was the first way of utilizing carbon as energy source and it was the real power of those times, while going on with the decades new form of carbon as energy source was becoming dominant: hydrocarbons. They were exploited and are still exploited in a huge way by the entire world as effective fuel for machines, electricity and many different applications.

Carbon is present in nature in many allotropic forms (15) with properties very different from each other's. Diamond and graphite are known from ancient times, while newly discovered nano-structures like carbon nanotubes (single or multi wallet), fullerenes and graphene are taking much interest from chemists and physicists (Fig.9).

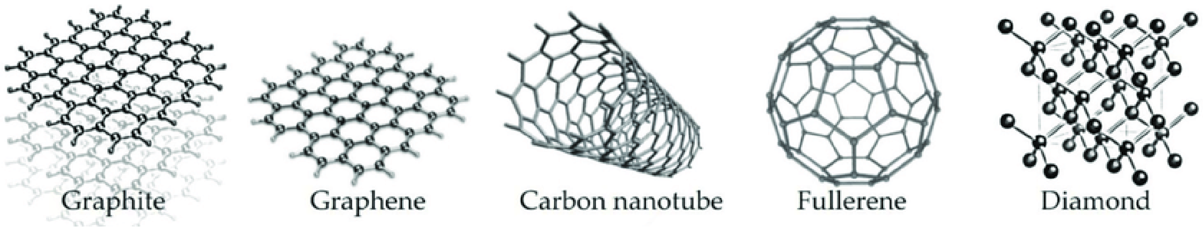


Fig.9 Allotropic forms of carbon (16)

The possibility to form so many structures with different properties is due to how the chemical bond between every atom and the entire structure itself are oriented into the space. For example, in graphene and in carbon nanotubes the chemical bonds between the atoms are the same, but the arrangement in the space change from planar sheet to tridimensional tubes.

Carbon has six protons and six electrons, two of them occupy the 1s orbital while the remaining four partially occupy the 2s and 2p orbitals. Orbitals 2s and 2p can undergo a process called hybridization that rearrange these orbitals in different ways (sp, sp^2, sp^3) and that's the reason why carbon (and many other elements) can make bonds in such a different way.

Sp carbon creates a linear structure forming carbyne molecule, sp^3 carbon makes bonds in four directions creating a tetrahedral and tridimensional structure like diamond, and finally, sp^2 carbon makes bonds in three directions with a 120° angle creating a planar structure (Fig.10). This structure is the one of graphene, carbon nanotubes and graphite (which is made by graphene layers packed together).

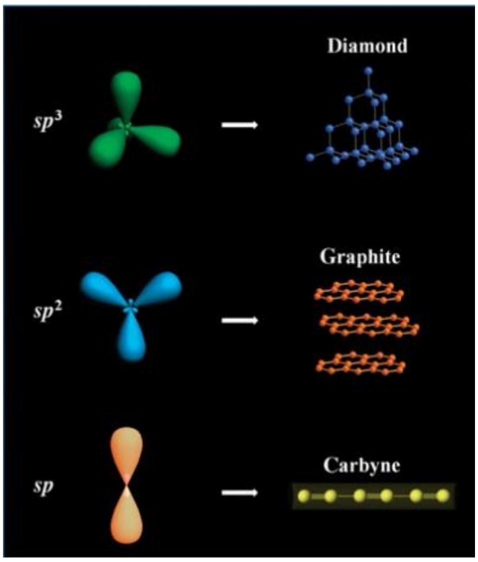


Fig.10 sp, sp^2 and sp^3 hybridizations of Carbon (17)

Among all the allotropic forms of carbon, graphene is the one with the biggest expectations, with many companies, universities and research centres working on its possible application.

Graphene was discovered in 2004 in Manchester University by the physics A. Geim and K. Novoselov. They isolated a single layer of graphene by the so-called scotch-tape method in which a scotch tape is attached and removed (many times) on graphite, resulting in a graphene sheet isolation. This discovery gives them the Nobel prize for physics in 2010.

In graphene, carbon atoms are arranged in a hexagonal honeycomb structure, where every atom is linked with three adjacent atoms, with the distance of 1,42 Å and 2,46 Å (18) respectively between carbon-carbon and hexagon centre- hexagon centre, as shown in Fig.11.

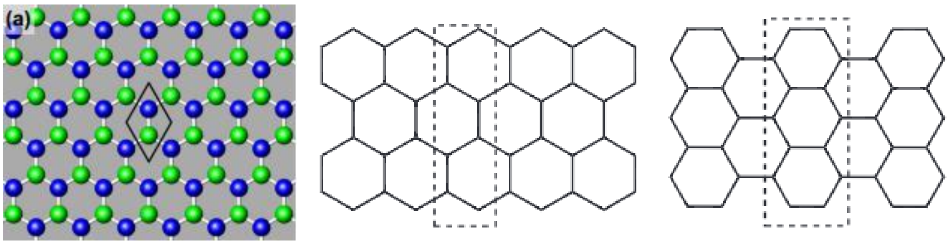


Fig.11 (a) graphene honeycomb structure (18) *, (b) zig-zag structure and armchair structure* (19)

The repetition of the hexagonal unit forms the graphene sheet that can be longer or shorter, larger or narrower, depending on the number and disposition of the single units. The structure can be a zigzag structure (only the angles are externally exposed) or an armchair structure (half of the hexagon is exposed).

Sp^{2} strong bonds and graphene aromaticity give it very interesting properties as high charge mobility, high mechanical resistance, high thermal conductivity and large surface area.

In Tab.1 is showed how graphene mechanical properties are theoretically comparable (and in some cases superior) to other metals is use nowadays.

	Graphene	Comparison
Young modulus (Gpa)	1000	200 (inox steel), 1050 (diamond) (1)
Thermal conductivity (W/mK)	4840-5300 (2)	386 (copper), 419 (silver) (3)
Electrical conductivity (S/m)	100x10^{6} (4)	59,6x10^{6} (copper), 63x10^{6} (Silver) (5)

Tab.1 Mechanical performances comparison between graphene and the best alternative

In particular, it has a higher thermal and electrical conductivity than copper and silver, and young modulus comparable to diamond.

Data about electrical conductivity are due to the fact that graphene is a semiconductor with a very tiny overlap (20) that allows a very high charge mobility.

Moreover, graphene is a conductive solid, which can be used as electrode in many applications. Nowadays the most common transparent electrodes used in is ITO which has good performances, but is fragile and costly (due to Indium scarcity in nature).

Fig.12 show a transmittance comparison between graphene, ITO (most used transparent electrode) and others. Single-layer graphene, due to the higher transmittance, hardness, flexibility and lower raw-material problems, is a real alternative to common ITO electrodes.

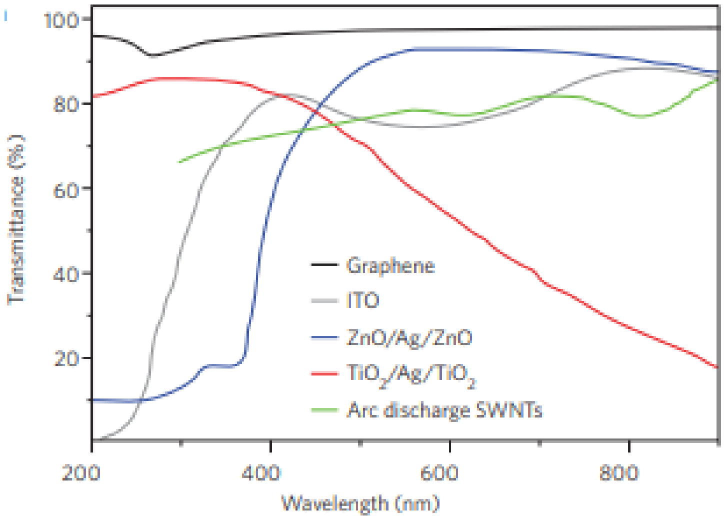


Fig.12 Transmittance comparison between graphene, ITO, ZnO/Ag/ZnO, TiO_2/Ag/TiO_2, SWNTs (21)

Many field (electronic, optoelectronics) are developing faster and faster and they require every time better materials, for that reason all the properties showed in this paragraph are those which put major interest in this material.

1.2.2 Production processes

All the properties and features described in the previous chapter are related to Single Layer Graphene (SLG) but it is not the only graphene available, also Few Layer Graphene (FLG) exists. FLG is composed of many (usually between two and ten) single sheets of graphene (SLG) overlapped one over the others and connected by Van der Waals forces, whose properties are tuneable changing the number of sheets (22).

Obviously quality and layers number of graphene influence the production methods and costs, which can change a lot from very cost-effective to high-costly production.

Graphene can be produced by two different approaches:

- top-down
- bottom-up.

Top-down methods start from graphite and separate its layers through thermal / mechanical / electrochemical exfoliation or sonication. Usually, these methods produce Few Layer Graphene (FLG).

Top-down methods break the Van-der-Waals forces between graphene layers inside the main graphite structure, liberating them. The most important techniques are:

- Mechanical exfoliation (Fig.13); it generates shear forces that exfoliate graphite. This can be done by some machines as ball mill, mixer, etc, and can be performed with or without a liquid solvent. Advantages are facility and relatively low production costs, while low graphene quality is the main disadvantage (23).

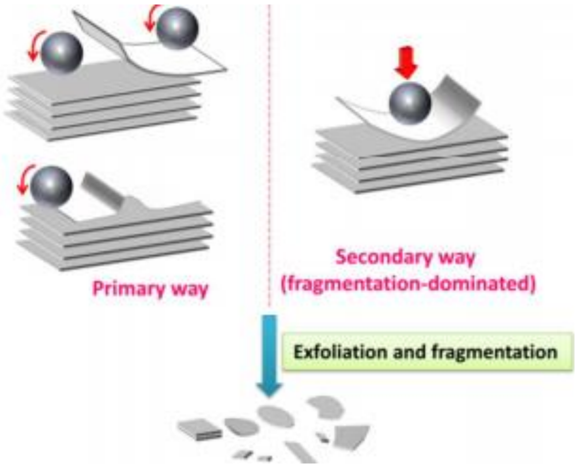


Fig.13 Mechanical exfoliation method (23)

- Electrochemical exfoliation (Fig.14); graphite is charged by the application of an external voltage and, once charged, it attracts opposite charged ions.

  This principle is exploited to attract ions of opposite charge to be intercalated between the layers and expanding the interlayer space. At this point the intercalated graphite layers can be exfoliated to produce pristine graphene, which in turn can be functionalized to create graphene derivatives (24).

  This route has the advantages of low prices for mass production (25) avoiding harsh condition/chemicals during the process and the possibility to produce also functionalized graphene. Disadvantage is the quality because is not a controllable process yet in terms of number of layers, meaning that few layer graphene is the product.

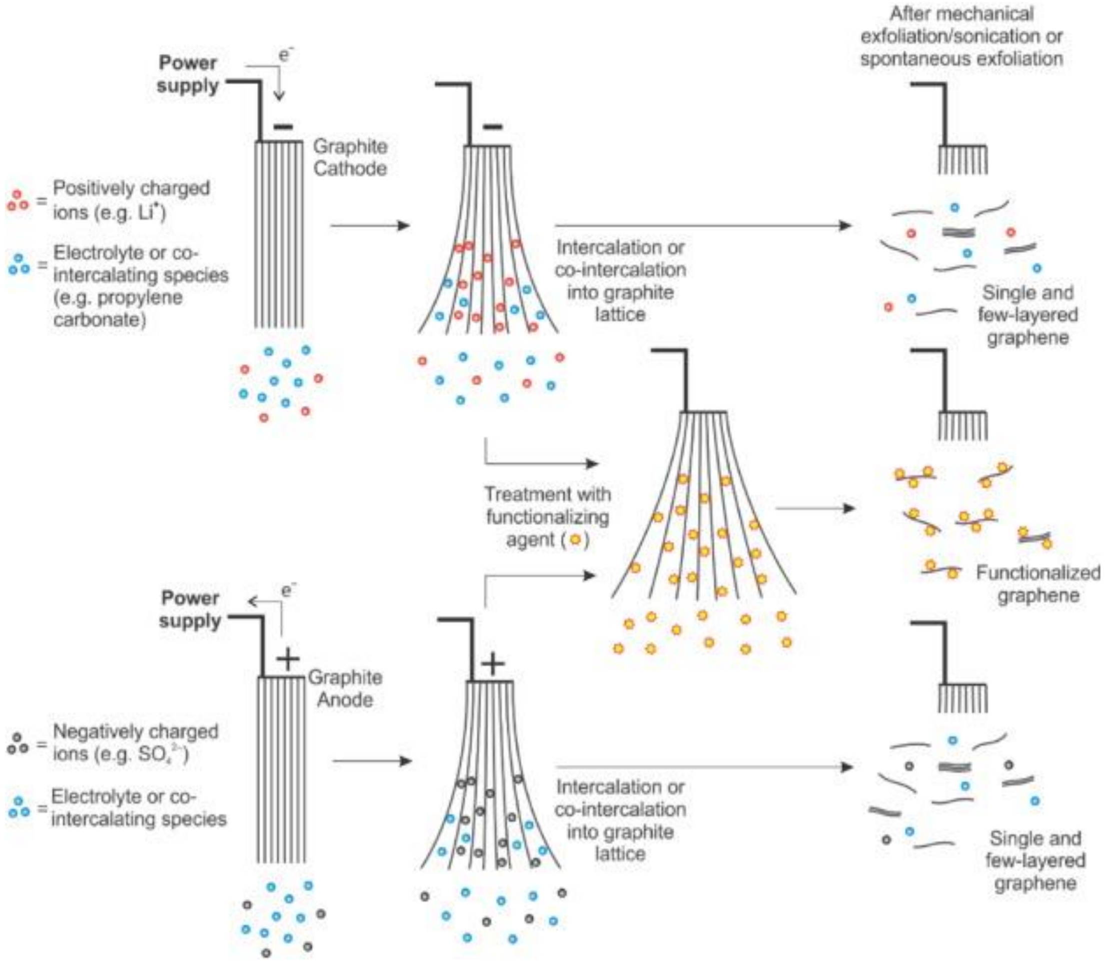


Fig.14 Electrochemical exfoliation method (24)

- Sonication (Fig.15); graphite (commonly used as powder), with the addition of a solvent, are treated with ultrasonication process that generate the cavitation forces that separate the layers. This process needs low amount of energy and produces high-quality graphene, the drawback is the long time required (26).

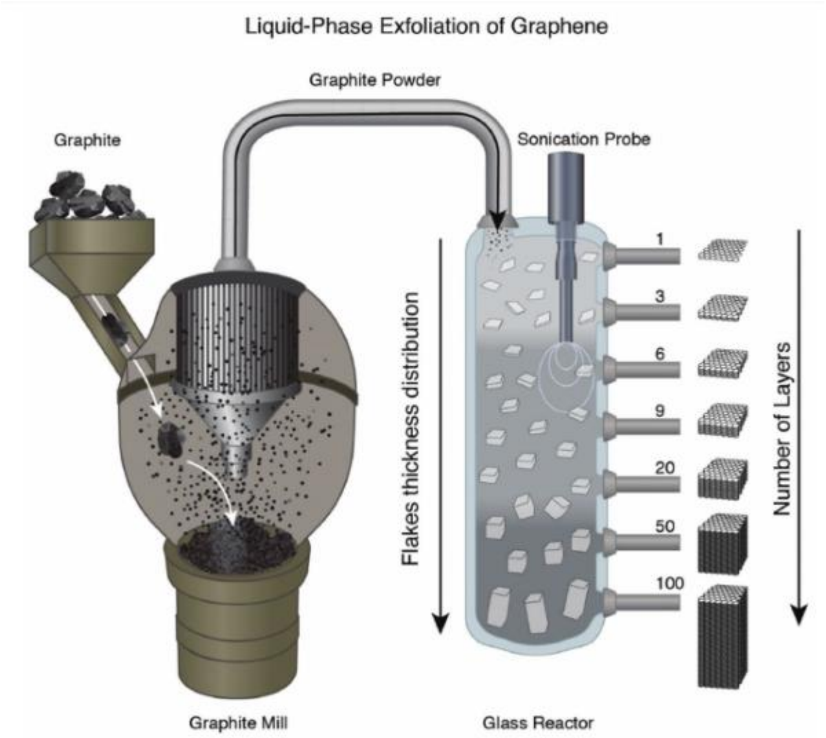


Fig.15 Sonication method (27)

- Graphene-oxide reduction; graphite is first oxidized through the Hummer's process (oxidation with potassium permanganate in concentrated sulfuric acid, stirring and water addition, filtration and washing with chloridric acid) and then exfoliated by ultrasounds. Finally, the reduction of graphite oxide layers is performed by hydrazine hydrate or N,N-dimethylhydrazine depending on the media to give graphene layers (28). This process uses a lot a chemical agents which are toxic, dangerous and difficult to treat as wastes once the process is finished.

- Scotch-tape (Fig.16); this method was the one used by Novoselov and Geim to discover graphene in 2004 in Manchester university. A scotch tape is applied on high ordered pyrolytic graphite (HOPG) removing part of the graphite, then apply scotch tape several times on the removed-graphite to reach the single layer. This method produce large monolayer graphene flakes (sheets) meaning high quality, however, this process is a very labour intensive and time consuming and is only used for lab scale application and does not seem to have a scale-up perspective (23).

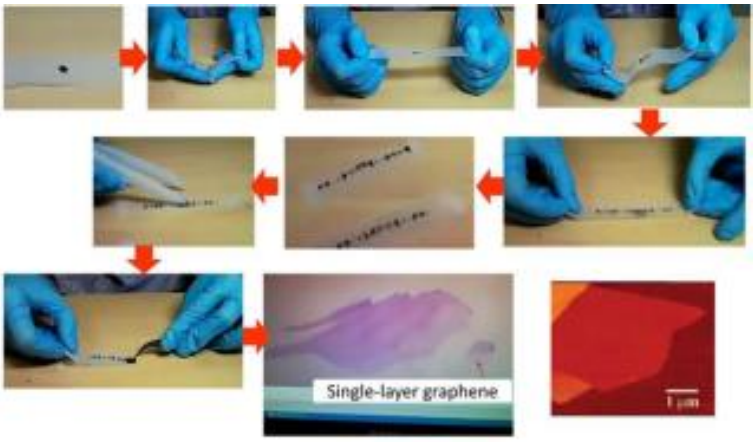


Fig.16 Scotch-tape method (23)

Bottom-up methods start from a carbon source, which usually is different from graphite, to build graphene layers, going in the opposite direction as before: from the atoms to the graphene structure.

Most important techniques in this field are:

- Chemical Vapour Deposition (CVD); a carbon precursor (usually methane) is decomposed at high temperatures (1000°C, A review of chemical vapor deposition of graphene) in a chamber with appropriate substrate (Cu, Ni and other transition metals) (29). Methane enters in the chamber with an inert gas that allows a better and uniform distribution of carbon atoms to form graphene layers.

With this method high-quality single layer graphene is produced and is mostly used in electronic applications (30). The only drawback are the cost and the separation of graphene from the metal, which is performed at the end of the process (Fig.17).

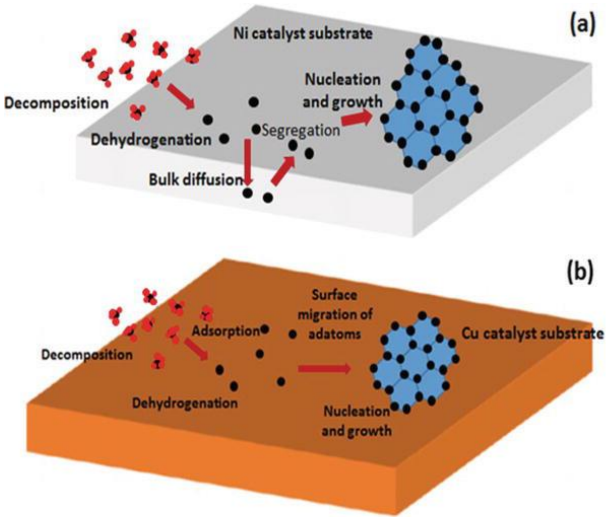


Fig.17 Chemical vapour deposition on Cu and Ni catalyst (29)

- Growth on silicon Carbide (SiC) (Fig.18); a wafer of SiC can be heated at >1000°C in ultra-high vacuum in order to evaporate Si atoms and let the carbon atoms rearrange in graphene sheets. The same process can be done by a molecular beam to growth epitaxial graphene sheets.
  Drawbacks are that the thickness of sheets is not uniform and the cost of SiC wafers is high. Moreover is a very expensive technique in terms of heating energy and vacuum (31).

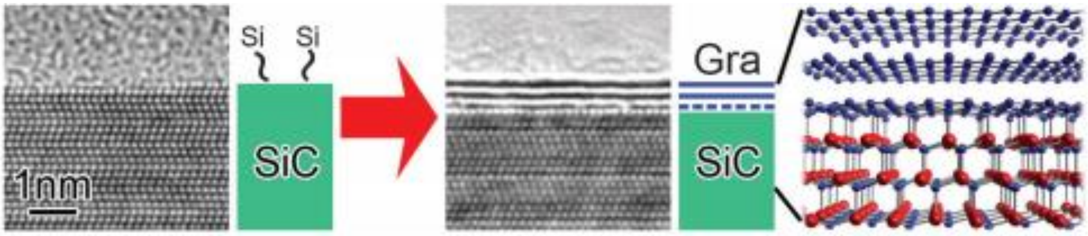


Fig.18 Growth on SiC (32)

On the basis of all the production methods described in this chapter it is possible to understand that top-down methods have an higher productivity and simplicity, and lower production costs, for that reason they are easier to scale up in an industrial plant, as showed in Fig.19.

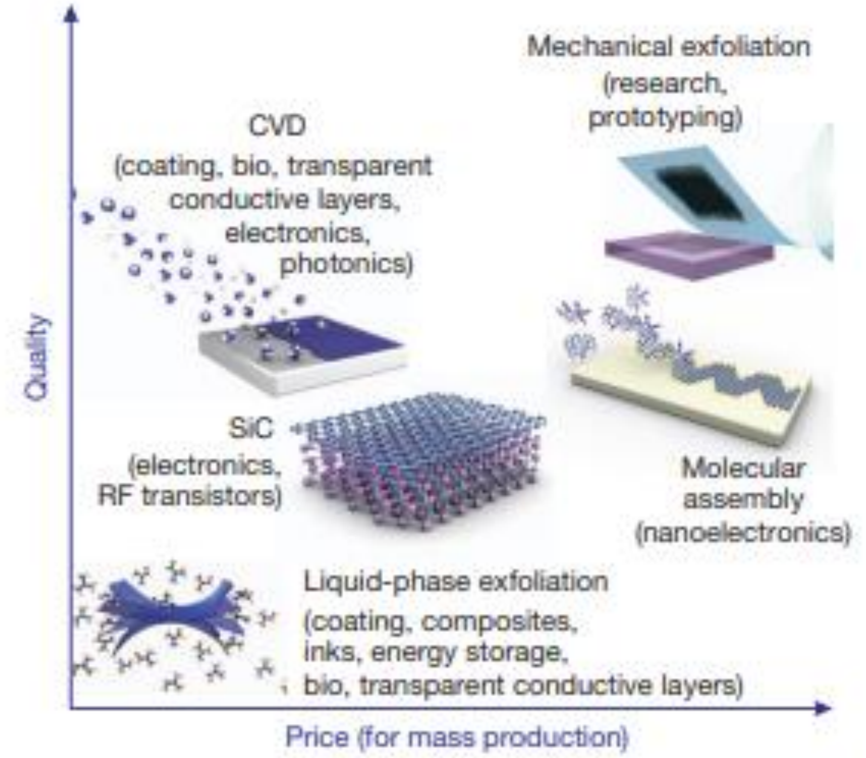


Fig.19 Scheme of quality/price relation for different production techniques for mass production of graphene (25)

On the other side, bottom-up methods produce graphene with a higher quality but they require very high temperatures and possible dangerous toxic and expensive chemical agents, making them very costly, and this is why they are present in the upper part of Fig.19 (high costs).

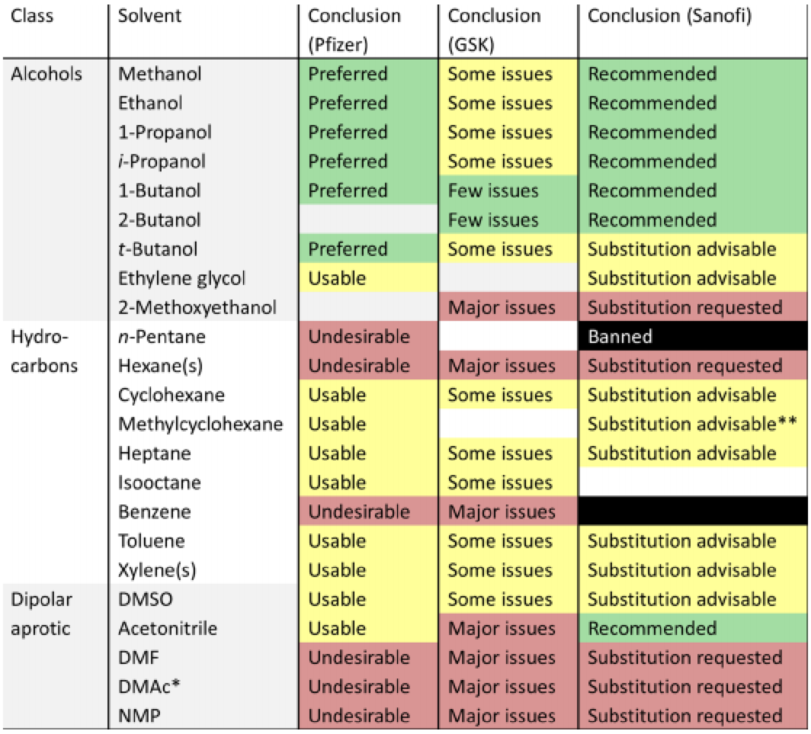
According to what are the features needed for a particular application, it’s possible to choose one process instead of the others.

1.2.3 Graphene-XT production process

Graphene-XT produces graphene by a Liquid Phase Exfoliation (LPE) process which is a mechanical exfoliation in a water suspension without the need of toxic agents or high temperatures, due to the use of an exfoliating agent patented by the company.

This is an enormous advantage over the common LPE processes which use 1-methyl-2-pirrolidone (NMP) or cyclopentanone (CPO) that are toxic and dangerous for workers.

According to United States Environmental Protection Agency (33) there are unreasonable risks for workers for many working conditions and uses of NMP. NMP is also an hazardous solvent and its replacement is strongly recommended by many solvent guides as Pfizer, Sanofi and GSK (34) (Fig.20).



Class	Solvent	Conclusion (Pfizer)	Conclusion (GSK)	Conclusion (Sanofi)
Alcohols	Methanol	Preferred	Some issues	Recommended
	Ethanol	Preferred	Some issues	Recommended
	1-Propanol	Preferred	Some issues	Recommended
	i-Propanol	Preferred	Some issues	Recommended
	1-Butanol	Preferred	Few issues	Recommended
	2-Butanol		Few issues	Recommended
	t-Butanol	Preferred	Some issues	Substitution advisable
	Ethylene glycol	Usable		Substitution advisable
	2-Methoxyethanol		Major issues	Substitution requested
Hydrocarbons	*n*-Pentane	Undesirable		Banned
	Hexane(s)	Undesirable	Major issues	Substitution requested
	Cyclohexane	Usable	Some issues	Substitution advisable
	Methylcyclohexane	Usable		Substitution advisable**
	Heptane	Usable	Some issues	Substitution advisable
	Isooctane	Usable	Some issues	
	Benzene	Undesirable	Major issues	
	Toluene	Usable	Some issues	Substitution advisable
	Xylene(s)	Usable	Some issues	Substitution advisable
Dipolar aprotic	DMSO	Usable	Some issues	Substitution advisable
	Acetonitrile	Usable	Major issues	Recommended
	DMF	Undesirable	Major issues	Substitution requested
	DMAc*	Undesirable	Major issues	Substitution requested
	NMP	Undesirable	Major issues	Substitution requested

Fig.20 Solvent guides (34)

The other common solvent used in LPE is CPO which is a very flammable liquid and can irritate skin and eyes, according with its safety data sheet.

Exfoliation needs the reduction of interfacial tension of the layers and this is commonly done by the intercalation of solvent (NMP or CPO) between the graphite layers. Working in water there is the need of an exfoliating agent which perform this work instead of the solvent and that’s why Graphene-XT patented its own exfoliating agent (Non-Disclosure Agreement) which is not toxic.

Replacing these solvents with water (and exfoliating agent) is a real advantage in terms of workers’ safety and environmental impact, moreover the scale-up perspective is easier than using problematic solvents.

Graphene-XT uses ball mill which produces the shear forces to exfoliate graphene sheets. Graphite, water and exfoliating agent are inserted in the part of the mill in which the balls are present. Balls can perform two different mechanisms: the first is the exfoliation itself while the second is a fragmentation; obviously in this process both are present.

Among all the processes the liquid exfoliation is the best one in terms of production rates and yield (>70% in case of electrochemical exfoliation, 50% for ball milling (35)). Yield can be improved by a centrifuge-based separation process that divides graphene from the remaining graphite, which is recovered and recycled in the process.

In this way two of the most important principles of green chemistry are respected:

- 1° Prevention: “is better to prevent wastes instead of threat them once formed” (recycling graphite);
- 5° Safer solvents and auxiliaries: “the use of auxiliaries and solvents should be made unnecessary wherever possible, and innocuous when used” (replacing NMP/CPO with water).

Every improvement and declaration about “greenesses” of a process have to be supported by data and for that reason some parameters were calculated.

The first was the Atom Economy of the process which refers to the ratio between the molecular weight of the reactants and the molecular weight of the products, in order to understand how many atoms of the reactants are incorporated into the final products.

AE = (MW reactants / MW products) * 100

Graphene can have different number of sheets and different sheets dimensions, and their precise calculation is very difficult. This is why is not easy to calculate a precise molecular weight. For this reason the Atom Economy is assumed to be 100% because what is used as reactant is only carbon (graphite), obtaining only carbon as well (graphene).

The second parameter is the Yield of the process, expressed as percentage, which gives informations about the process itself and not about the reaction. It's the ratio between the mass of obtained product and the mass of theoretical product.

Not only graphene is considered as a product but also the exfoliating agent. This because it, in part, remains in the graphene and it is responsible for the adjusting of graphene properties.

Yield = (mass of obtained product / mass of theoretical product) * 100 = (1431,70g graphene + 724,43g exfoliating agent / 3060,00g graphene + 1299g exfoliating agent) *100 = 49,46 %

This yield is a good value because almost half of the graphite (and exfoliating agent) is transformed into product. Maybe 49,46% could seem not good enough but considering that the unreacted graphite (in addition to exfoliating agent and water) is recycled for the following process, this percentage increase its value.

Another important parameter is the Process Mass Intensity (PMI) which refers to the total mass of materials divided for the mass of isolated product. It is calculated as follow:

PMI = total mass of materials / mass of isolated product = input mass of graphene + exfoliating agent + water / output mass of graphene and exfoliating agent= 3060g graphene + 1299g exfoliating agent + 40000g water / 1431,70g graphene + 724,43g exfoliating agent = 20,6

This value is high to be considered a good value but it does not take into consideration that all the water (which contributes for the almost total of the PMI is recycled at the end of the process).

Finally the E-Factor, the ratio between mass of total waste and mass of isolated product, is another fundamental metric which gives indications about how many wastes are generated for every kilogram of product. It does not consider unreacted reactant (graphite in this case), solvents and recycling. According to that, in this case is related only to the percentage of exfoliating agent which not remain in the product.

Environmental-Factor = mass of wastes / mass of product = 57457g / 2156,13g = 0,27

The E-Factor value is a good value which indicates that only 0,27 kg of wastes are produced every kg of graphene.

Wastes of this process are only exfoliating agent, which remain in the water and water itself (not included in the calculation) while unreacted graphite is not considered as a waste because is easily recyclable. All of them are recycled in the following production (as well as water), meaning that in reality the wastes are zero.

Tab.2 shows all the Green Metrics calculated in this paragraph, giving a clear picture of the process helping to understand how the process works and how low are its wastes.

Atom Economy	100%
Yield	49,46%
Process Mass Intensity	20,6
Environmental Factor (E-Factor)	0,27

Tab.2 Green metrics of Graphene-XT production process

Obviously, further developments are under scrutiny with the aim of improving the production process as much as possible, in particular yield and PMI.

1.2.4 Applications

All the properties described in the previous chapters made graphene really interesting and suitable for a wide variety of applications.

Quality of graphene must be high in order to replace materials that are already in use for many years, and until now graphene is not consolidated in the market yet, but is more in a research phase. However, there are market sector that already use this material.

Most important sectors that have interest in graphene are lubricants, paints, membranes, electronics, energy and composites.

In membranes it can be used due to the impermeability (or selective permeability by creating controlled-defects on the structure) to gases, while the electrical features can be exploited in supercapacitors or batteries for energy industry.

Another application are the composites, in which graphene is added to a matrix to increase the performances of the materials, mainly in sports as for example tennis rackets (Head) or bike helmets (Catlike helmet company).

Lubricant industry is another important sector in which graphene can be used because of its important lubricant activity. It is very effective in decreasing friction forces in both dry and humid situation, differently from graphite, and its effectiveness increases with the number of layers (36).

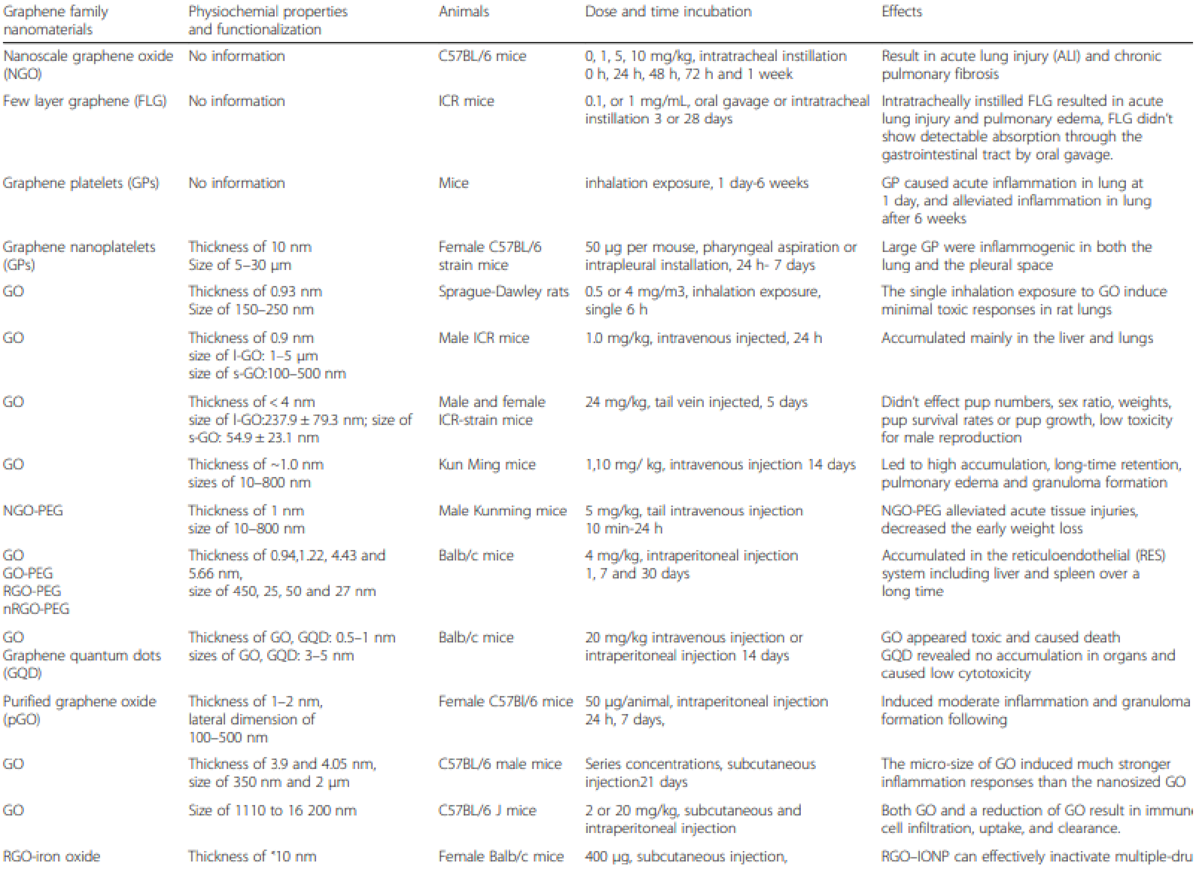
The last important field of application is the paints industry, which is the focus of this thesis work.

1.2.5 Graphene toxicity

Recent big advancements in the field of nanotechnologies and graphene in particular put its safety under investigation, to understand what are the real risks for humans, animals, environment and society.

Graphene and graphene family materials can enter the organism by several different routes, and, in addition to the tissue distribution, concentration, location, can determine the degree of toxicity (37). Graphene toxicity is, at the time, an under-development field in which there are many contrasting papers and discussions, most of the times without enough data to outline a precise conclusion. The review by L.Ou et al shows that most of the results are for GO or reducedGO, with only few studies on FLG or graphene nanoplatelets (Fig.21).

The most relevant exposure route of graphene related materials in animals is the respiratory route and their accumulation occurs mainly in the lungs: for example graphene-oxide (GO) nanosheets can affect the pulmonary surfactants (37).



Graphene family nanomaterials	Physiochemial properties and functionalization	Animals	Dose and time incubation	Effects
Nanoscale graphene oxide (NGO)	No information	C57BL/6 mice	0, 1, 5, 10 mg/kg, intratracheal instillation 0 h, 24 h, 48 h, 72 h and 1 week	Result in acute lung injury (ALI) and chronic pulmonary fibrosis
Few layer graphene (FLG)	No information	ICR mice	0.1, or 1 mg/mL, oral gavage or intratracheal instillation 3 or 28 days	Intratracheally instilled FLG resulted in acute lung injury and pulmonary edema, FLG didn't show detectable absorption through the gastrointestinal tract by oral gavage.
Graphene platelets (GPs)	No information	Mice	inhalation exposure, 1 day-6 weeks	GP caused acute inflammation in lung at 1 day, and alleviated inflammation in lung after 6 weeks
Graphene nanoplatelets (GPs)	Thickness of 10 nm Size of 5–30 μm	Female C57BL/6 strain mice	50 μg per mouse, pharyngeal aspiration or intrapleural installation, 24 h- 7 days	Large GP were inflammogenic in both the lung and the pleural space
GO	Thickness of 0.93 nm Size of 150–250 nm	Sprague-Dawley rats	0.5 or 4 mg/m3, inhalation exposure, single 6 h	The single inhalation exposure to GO induce minimal toxic responses in rat lungs
GO	Thickness of 0.9 nm size of l-GO: 1–5 μm size of s-GO:100–500 nm	Male ICR mice	1.0 mg/kg, intravenous injected, 24 h	Accumulated mainly in the liver and lungs
GO	Thickness of < 4 nm size of l-GO:237.9 ± 79.3 nm; size of s-GO: 54.9 ± 23.1 nm	Male and female ICR-strain mice	24 mg/kg, tail vein injected, 5 days	Didn't effect pup numbers, sex ratio, weights, pup survival rates or pup growth, low toxicity for male reproduction
GO	Thickness of ~1.0 nm sizes of 10–800 nm	Kun Ming mice	1,10 mg/ kg, intravenous injection 14 days	Led to high accumulation, long-time retention, pulmonary edema and granuloma formation
NGO-PEG	Thickness of 1 nm size of 10–800 nm	Male Kunming mice	5 mg/kg, tail intravenous injection 10 min-24 h	NGO-PEG alleviated acute tissue injuries, decreased the early weight loss
GO GO-PEG RGO-PEG nRGO-PEG	Thickness of 0.94,1.22, 4.43 and 5.66 nm, size of 450, 25, 50 and 27 nm	Balb/c mice	4 mg/kg, intraperitoneal injection 1, 7 and 30 days	Accumulated in the reticuloendothelial (RES) system including liver and spleen over a long time
GO Graphene quantum dots (GQD)	Thickness of GO, GQD: 0.5–1 nm sizes of GO, GQD: 3–5 nm	Balb/c mice	20 mg/kg intravenous injection or intraperitoneal injection 14 days	GO appeared toxic and caused death GQD revealed no accumulation in organs and caused low cytotoxicity
Purified graphene oxide (pGO)	Thickness of 1–2 nm, lateral dimension of 100–500 nm	Female C57Bl/6 mice	50 μg/animal, intraperitoneal injection 24 h, 7 days,	Induced moderate inflammation and granuloma formation following
GO	Thickness of 3.9 and 4.05 nm, size of 350 nm and 2 μm	C57BL/6 male mice	Series concentrations, subcutaneous injection21 days	The micro-size of GO induced much stronger inflammation responses than the nanosized GO
GO	Size of 1110 to 16 200 nm	C57BL/6 J mice	2 or 20 mg/kg, subcutaneous and intraperitoneal injection	Both GO and a reduction of GO result in immun cell infiltration, uptake, and clearance.
RGO-iron oxide	Thickness of ˚10 nm	Female Balb/c mice	400 μg, subcutaneous injection,	RGO–IONP can effectively inactivate multiple-dru

Fig.21 Graphene family nanomaterial toxicity studies and results (37)

Finally, it is very hard to have a clear picture of the toxicity problems related to graphene and many focused studies are necessary to define a conclusion.

About GO many studies cited in this review show adverse effects as acute lung injury, pulmonary fibrosis and/or edema, inflammation and granuloma; graphene nanoplatelets shows only low lungs inflammation by inhalation, pulmonary edema by intratracheally instilled entry route, low gastrointestinal adsorption by oral administration.

2. Thesis target

Graphene's properties of thermal and electric conductivity, its hardness, superficial area and the possibility to use it in composite materials makes the interest in this material growing year by year. One of the most active research is done in the paint and coating field, and for that reason the focus of this experimental thesis was graphene use in combination with a paint to create a graphene-paint which at the end can go into the growing paints and coating market.

Graphene addition to a paint can provide different advantages over other protecting paints. Its mechanical properties and conductive nature can be used to bring some new or better features to the original paint. Graphene is also impermeable and the passage of molecular oxygen towards covered surfaces is lower, meaning better anti-corrosive properties avoiding that oxygen molecules oxidate metals forming rust (graphene-coated copper is one hundred times more resistant to corrosion than uncovered copper) (38).

Graphene is becoming one of the most studied material in the world with many companies and universities working on it with many projects. Among them Graphene Flagship Project is one of the biggest examples, an European project of 1 billion euro budget including 171 academic and industrial research groups with 1356 people in 22 member states, all working on graphene and its applications (39).

Graphene-XT, located in Anzola nell 'Emilia (BO), is one of those companies. Its liquid phase exfoliation method and its patented exfoliating agent allow to produce high-quality graphene with a reduced environmental impact (recycling graphite, working in water and at low temperatures).

Many other companies in the world are working on that field, and some of them have already launched their graphene-paint as for example Applied Graphene Materials, in collaboration with Sherwin-Williams Protecting and Marine Coating, who has created a corrosion protective paint to be used in equipment for petrochemical industry, construction and transports, and in particular for ships' hulls to protect them from water corrosion. Another important company, GrapheneStone, developed a conductive paint for internal house walls which increase the thermal properties of the wall making the heat dissipating slower through the wall, meaning less heating needed, and higher mechanical resistance (40).

The internship work is dedicated to the main goal of “improving mechanical and conductive properties of commercial paints by adding graphene”, and three different projects are carried on:

1. Graphene addition to a teflon-base paint to increase mechanical properties;
2. Graphene addition to an acrylic-base paint to create a conductive paint;
3. Graphene addition to an acrylic-base paint to increase mechanical properties.

3. Results and discussion

Addition of graphene was performed on two different types of paints: one acrylic base and one teflon base.

Each one will be discussed explaining what are the formulation, the methods and the instruments used, the analysis performed and the results obtained. A discussion will follow every result.

3.1. Teflon-based paint

The first part of the internship was dedicated to the formulation of a black teflon-based paint for an external company with the aim of improving mechanical properties.

Initially, the base was analyzed in order to find the best deposition method and parameters, then the work of creating new formulations was performed.

The teflon base depositions contains a lot of bubbles which are not agitation-related or thickness-related, and for this reason a multiple (three) passages through the Three Roll Mill (TRM) are necessary to drastically reduce the quantity of bubbles in the deposited paint (Fig.22).

Fig.22 Micrometric knife deposition of teflon base treated with TRM (right) and not treated with TRM (left)

In addition to bubble reduction, the TRM is used to mix in an effective way the different components: teflon base and graphene powder. The consecutive passages press the powder and fragmentate it in smaller particles, increasing the superficial area that interact with the solvent, making it more dense.

The deposition was performed in two consecutive spreads of 80microns by a micrometric knife followed by hot gun heating for 15’ at <100°C and 40’ at 280°C in the oven.

Teflon + graphene A

An initial formulation n°1 is created adding 2%w of graphene (A type) in powder (Table 3).

Formulation n°	Graphene (g)	Teflon-paint (g)	Teflon-paint solids (g)	Graphene weight %
1	0,5	99,73	24,38	2,0

Tab.3 Composition of the formulation n°1

The formulation was treated with the TRM with a yield of 73,74%, losing 26,24% of the product due to the three passages in the machine and the recovery through the containers.

Fig.23 shows that both the deposition were not homogeneous: the left one has parts with different thickness while the right one has bubbles and accumulation parts. This inhomogeneity could be related to bad deposition procedure (human error) or micrometric knife defect (machine error), and for that reason another deposition method was investigated, the Mayer bar.

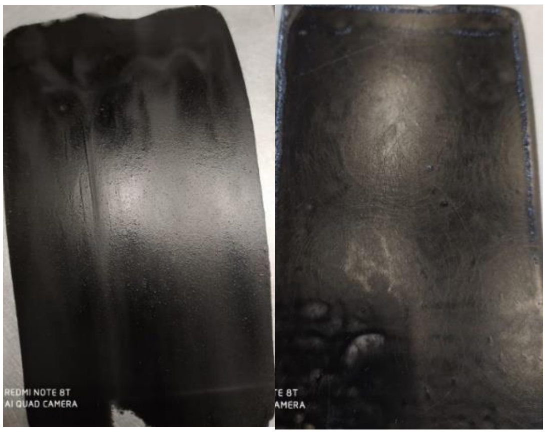


Fig.23 Micrometric knife deposition of teflon base (left) and formulation n°1 (right)

The best deposition sequence for this type of product is: agitation – disareation through vacuum pump – 80micron Mayer bar deposition.

Mayer bar deposition is a method which consists in a deposition of the paint on a plate and a linear translation of the Mayer bar from the initial deposition point to the end of the plate.

Fig.24 below shows the deposition of teflon base and formulation n°1 (with graphene) by the use of Mayer bar, demonstrating that this method gives a better results in terms of homogeneity. For that reason this is the deposition method and procedure used for the following tests.

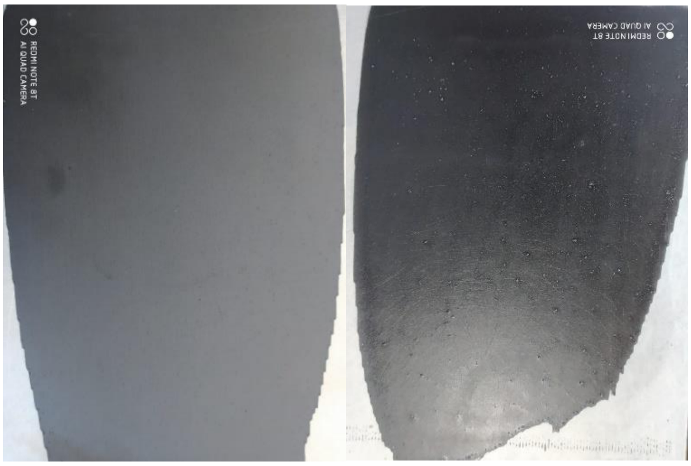


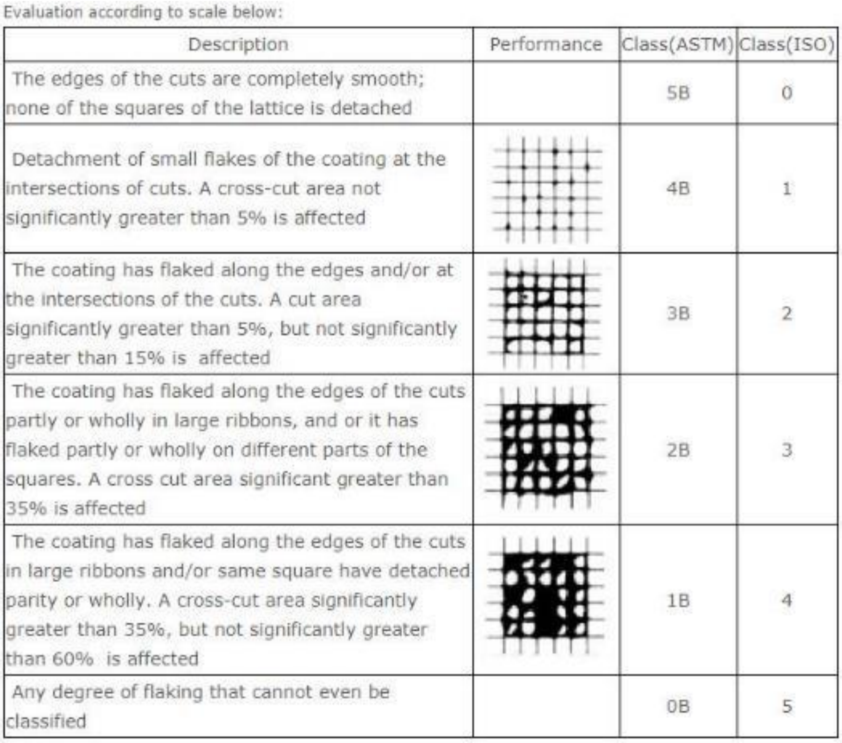
Fig.24 Mayer bar deposition of teflon base (left) and formulation n°1 (right)

If the density of the formulation is too high, waves are created on the deposition's surface and to remove them a dilution is necessary (in this case 5%w, 10%w, 15%w and 20%w dilution tests were performed and 20%w is the optimal percentage).

The 20%w diluted depositions were used to measure the effect of graphene addition to the teflon base, through cross-cut test and scratch test.

Cross-Cut Test:

It is an adhesion test, it is regulated by ASTM D3359 legislation and is performed by an appropriate instrument called cross-cut tester (Fig.25).



Evaluation according to scale below:

Description	Performance	Class(ASTM)	Class(ISO)
The edges of the cuts are completely smooth; none of the squares of the lattice is detached		5B	0
Detachment of small flakes of the coating at the intersections of cuts. A cross-cut area not significantly greater than 5% is affected		4B	1
The coating has flaked along the edges and/or at the intersections of the cuts. A cut area significantly greater than 5%, but not significantly greater than 15% is affected		3B	2
The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and or it has flaked partly or wholly on different parts of the squares. A cross cut area significant greater than 35% is affected		2B	3
The coating has flaked along the edges of the cuts in large ribbons and/or same square have detached parity or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 60% is affected		1B	4
Any degree of flaking that cannot even be classified		0B	5

Fig.25 Cross cut test result scale

In Fig.26 are reported the results obtained by cross cut test for the teflon base and formulation n°1: both have an optimal adhesion to the substrate (ISO 0). This results show that 2%w graphene A addition does not decrease the adhesion of the virgin teflon base, but it is difficult to understand if its addition has an improving effect on the already-optimal adhesion of the base.

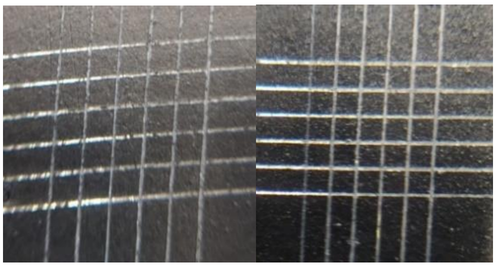
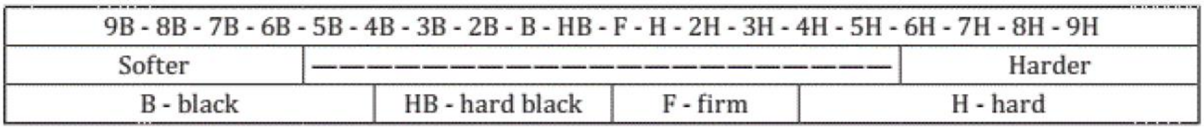


Fig.26 Cross cut test of teflon base (left) and formulation n°1 (right)

Scratch Test:

Scratch test is related to the hardness of a coating, measuring its resistance to pencil scratch and is regulated by ASTM D3363-20 legislation. Also in this case an appropriate instrument is used (scratch tester or pencil hardness tester) in which a pencil is fixed at a certain angle (45°) and used to scratch the surface, using all the different hardness-scale pencils (Fig.27).



9B - 8B - 7B - 6B - 5B - 4B - 3B - 2B - B - HB - F - H - 2H - 3H - 4H - 5H - 6H - 7H - 8H - 9H			
Softer	————————————————————		Harder
B - black	HB - hard black	F - firm	H - hard

Fig.27 Hardness pencil scale used for scratch test

Adhesion results performed on the samples are optimal for both, making impossible to understand if graphene addition has a positive impact (Table 4). Scratch test indicate that teflon base is harder than formulation n°1.

Formulation	Cross-cut test (ASTM)	Scratch test
Teflon base	5B	4H
N°1 (teflon base + graphene A 2%)	5B	3H

Tab.4 Cross cut test and scratch test results of teflon base and formulation n°1

Combining these results the addition of graphene does not improve the hardness and/or the adhesion of that coating and for these reason other formulations are created.

Teflon base + graphene B 2%w

In order to improve the performances, a first approach was to change the type of graphene, using the B type, without changing the concentration (2%) (Table 5).

Formulation n°	Graphene (g)	Teflon-paint (g)	Teflon-paint solids (g)	Graphene % weight
2	1,00	199,39	48,85	2,0

Tab.5 Composition of the formulation n°2

Also in this case the formulation was passed in the TRM with a yield of 81,62%, losing 18,38% of the product.

Teflon base and formulation n°2 were deposited by Mayer bar and then same tests were performed (cross-cut test and scratch test). Changing graphene type means changing a bit the properties and in this case there is a change in density, for that reason the optimal dilution percentage was 10% instead of 20% for the previous formulation.

Cross-cut test

Cross-cut test was performed as in the previous part and the result is the same as the previous formulation: optimal adhesion for both with and without graphene.

Scratch test

Scratch test was performed showing that the formulation n°2 has the same hardness of the teflon base (Table 6).

Formulation	Cross-cut test (ASTM)	Scratch test
Teflon base	5B	4H
N°2 (teflon base + graphene B 2%)	5B	4H

Tab.6 Cross-cut test and scratch test results for teflon base and formulation n°2

According to these results, the following formulation was prepared increasing the graphene percentage up to 10%w.

Teflon base + graphene B 10%w

That was the last formulation and is prepared by adding 10%w of graphene to the teflon base and passing it in the TRM with a yield of 76,90%. It was diluted at 20%w (Table 7).

Formulation n°	Graphene (g)	Teflon-paint (g)	Teflon-paint solids (g)	Graphene Weight %
3	2,72	98,41	23.84	10,14

Tab.7 Composition of the formulation n°3

Cross-cut test

The results are the same as the previous formulations for both with and without graphene, ASTM 5B, which is the best adhesion possible.

Scratch test

Also in this case the hardness is a value lower than teflon base, as seen for the previous formulation (Table 8).

Formulation	Cross-cut test (ASTM)	Scratch test
Teflon base	5B	4H
N°3 (teflon base + graphene B 10%)	5B	3H

Tab.8 Cross-cut test and scratch test results of teflon base and formulation n°3

All the tests performed and every result obtained shows that addition of graphene (at 2%w and at 10%w) on a teflon base does not improve neither hardness and adhesion.

3.2. Antistatic acrylic-based paint

The goal of the work is to create an antistatic (conductive) paint combining an acrylic base and graphene.

The initial formulations were the n°1-2-3-4 and contain the same percentage of components: 70% of graphene (and 30% of acrylic) in the dry solid residue of the paint.

What changes among these four formulation is the presence (or combination) of acetone and adhesion promoter. The first has neither of them, the second has only adhesion promoter, the third has only acetone and the fourth has both. Then, two already-existing formulations are tested, called A and B.

Moreover, two other formulations are prepared and tested. These two has gradually reduced graphene percentage and are named n° 5 and 6. Finally, these last two formulations are created again but using another graphene using the same percentages, they are named n° 5N and 6N. All the formulations with their relative compositions are showed in the Tab.9 below.

Formulation n°	Graphene ink (PR-N-5-30)	Acrylic base	Adhesion promoter (%w on the total)	Acetone	Graphene %w on total dry solid	Acrylic %w on total dry solid
1	59,26 g	0,74 g	0	No	70,47	29,53
2	59,25 g	0,75 g	4,03	No	70,19	29,81
3	39,54 g	0,50 g	0	14,99 g	70,21	29,79
4	39, 52 g	0,49 g	4,05	15,71 g	70,62	29,38
5	39,11 g	1,05 g	4,04	No	52,61	47,39
6	38,08 g	2,00 g	4,05	No	36,20	63,80
5N	30,01 g N	0,75 g	4,06	No	46,81	45,61
6N	29,99 g N	1,59 g	4,10	No	29,20	64,02
A	1,25%w PRMAC 3-45	98,75%	4	27,3%		
B	1,25%w PRMAC 3-45	98,75%	4	no		

Tab.9 Antistatic formulations: names and compositions

Once formulated, all of that show a deposition of the acrylic part on the bottom of the container/flask and this is why a vigorous agitation is needed before every deposition.

These formulations were deposited in two different methods: micrometric knife and spray deposition. The procedure was agitation-deposition-heating at 165°C for 30 minutes for both the deposition methods.

Initially, for the n°1-2-3-4-A-B, the deposition was performed in ten consecutive spreads, one over the other, to reach an appropriate thickness (Fig.28). Then, for the n°5-6-5N-6N, according to the fact that is commercially impossible to sell a ten-spreads paint, other parameters were set: two micrometric knife spreads or spray deposition.

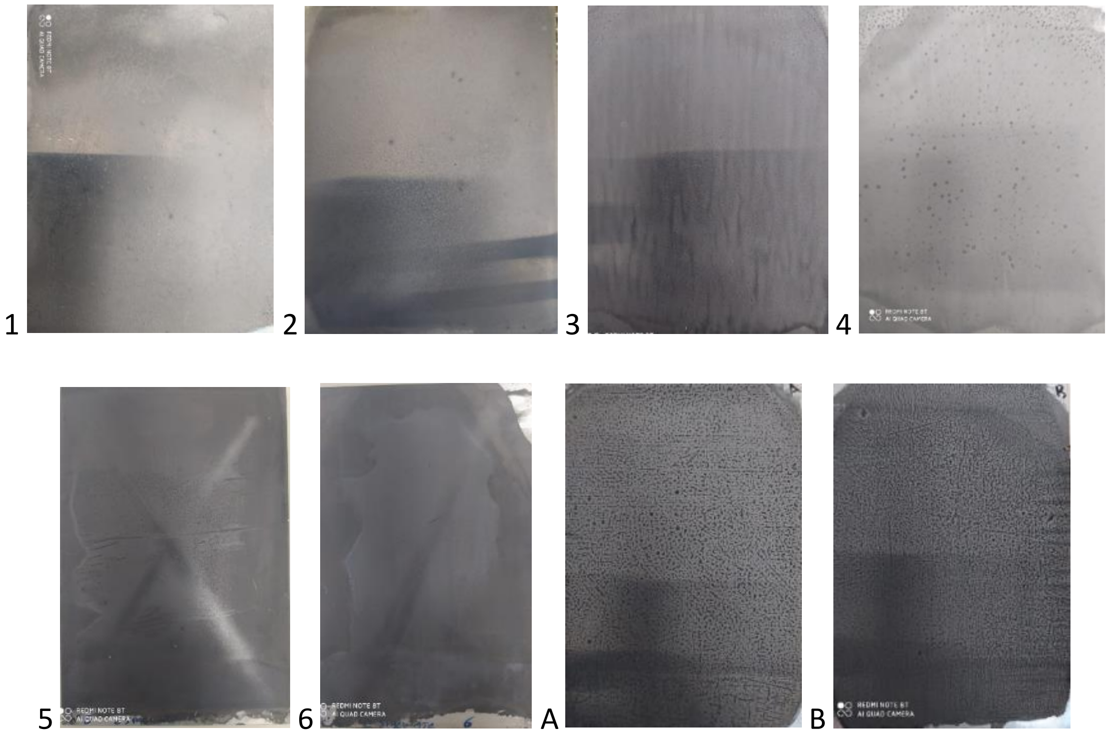


Fig.28 Deposition of formulation n°1-2-3-4-5-6-A-B

Many tests are executed on these depositions in order to assess every single aspect of these products, and precisely:

- cross-cut test (adhesion)
- scratch test (hardness)
- conductivity test
- gloss measurement

- dirtiness
- aging by water immersion

Cross-cut test

Cross-cut test was performed as showed in the previous chapter, according to ASTM D3359 (Fig.29).

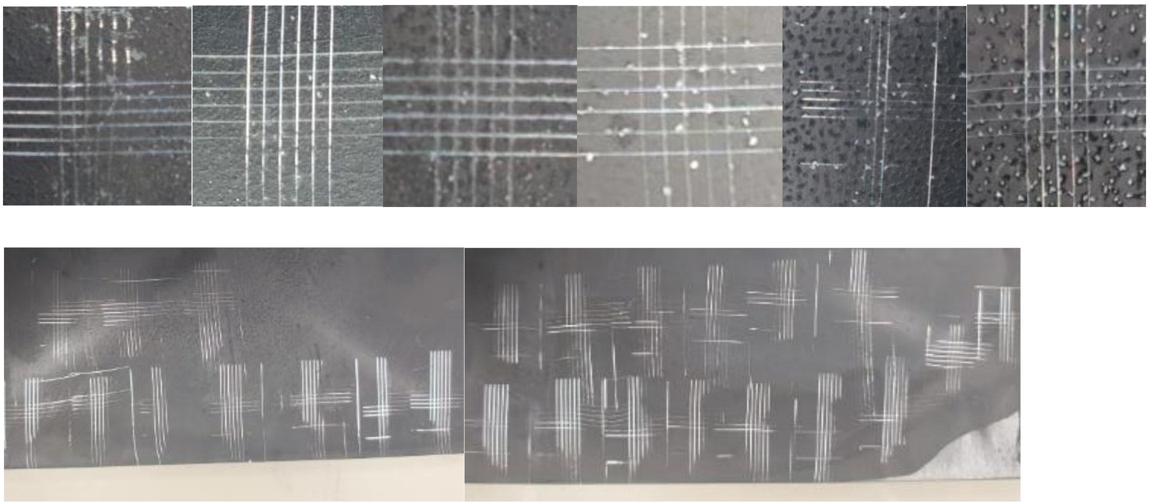


Fig.29 Cross-cut test of formulation n°1-2-3-4-A-B (top part, from left to right) and n°5-6 (bottom part, from left to right)

Scratch test

Scratch test was performed as showed in the previous chapter, according to ASTM D3363-20.

Conductivity test

Conductivity test was performed by an appropriate conducimeter to measure the sheet resistance (ohm) of the coating. The goal of this part of the thesis was to exploit the conductivity of graphene to create an antistatic coating, making the conductivity test one of the most important test for that coating. The relevant results are reported in Table 10.

Formulation n°	Cross-cut (ISO)	Sheet resistance (ohm)	Scratch test
1	1-2	20-40	No scratch
2	0	30-50	No scratch
3	1	20-35	No scratch
4	1	70-130	No scratch
A	1-2	130-210	No scratch
B	2	80-140	No scratch
5	0	160-290	No scratch
6	0	600-1300	No scratch

Tab.10 Cross-cut test, scratch test, conductivity test results for formulation n°1-2-3-4-5-6-A-B

These results show a very good adhesion for all the formulation, and in particular the n°2, 5 and 6 have the best adhesion possible. Scratch test indicates that the coating was not scratched by any of the pencil used (all the scale), meaning an high hardness.

Sheet resistance results are good for all the formulations (also the n°5 and 6, which have higher sheet resistance, have a good value).

Gloss test

Brightness was measured by gloss test using a BYK-Gardner colorimeter after a precise calibration procedure using light trap, black and white standards, green check (Table 11).

Formulation n°	1	2	3	4	5	6
Gloss value	5,5	2,9	1,7	2	7,2	8,8

Tab.11 Gloss value of formulation n°1-2-3-4-5-6

Dirtiness

Dirtiness is an important parameter because the coating should not release dirty when it is touched or rubbed, for that reason an analysis on that was performed.

A white paper was fixed on the round bottom part of a glass with a constant mass of 70g on it. At this point, the glass was moved horizontally over the plate for ten times and compared with the scale below (Fig.30 and Table 12).

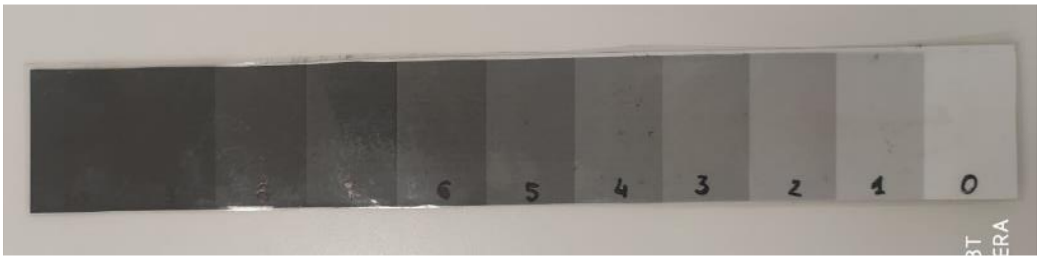


Fig.30 Dirtiness scale (0-10)

Formulation n°	1	2	3	4	A	B	5	6
Deposition method	knife	knife	knife	knife	knife	knife	knife	knife
Dirtiness value	8	3-4	5-6	2	8	2	1,5	0,5

Tab.12 Dirtiness values for micrometric knife-deposited formulation n°1-2-3-4-5-6-A-B

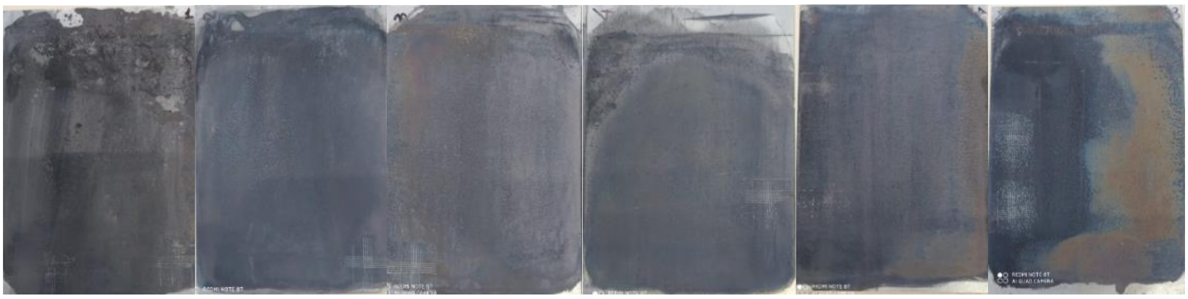
According to these data the best formulations in terms of dirtiness are the n°5 and n°6 and this makes them more attractive than the n°1-2 which, from the cross-cut and sheet resistance tests, seemed to be the best two. This because is better to have lower conductivity and less dirtiness than the contrary.

For that reason the next deposition method (spray) was done only for formulation n°5-6, which in addition were also formulated using another graphene (5N-6N).

Water immersion aging

The depositions were immersed in water for one week to understand what is the impact of the water on the coating. After the week cross-cut test and conductivity test were performed again to see the difference between before and after water immersion.

This test was executed only for formulation n°1-2-3-4-A-B because the others (5-6-5N-6N) were formulated after this test. The relevant results are reported in Figure 31 and Table 13.



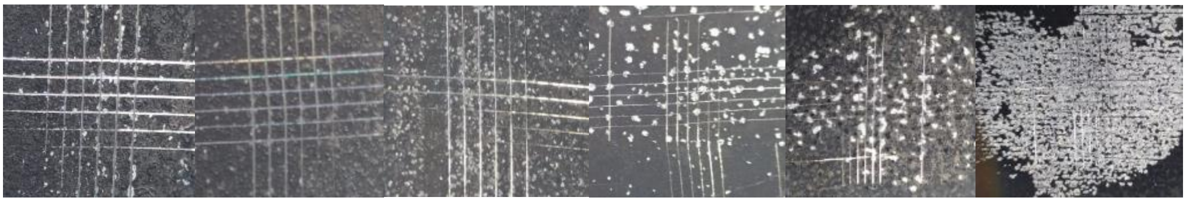


Fig.31 External aspect (top photos, in order from left to right) and cross-cut test (bottom photos, in order from left to right) of formulation n°1-2-3-4-A-B after water immersion aging

The comparison between pre and post water immersion shows that n°1-2 seem to be the more resistant ones and this behaviour can be attributed to the absence of acetone in the formulation, which can decrease its resistance to water changing too much the adhesion properties (and sheet resistance).

Formulation n°	Δ cross cut (ISO)	Δ sheet resistance (ohm/sq)
1	0	0/0
2	0-1	+10/+15
3	2-3	+20/+115
4	2	-10/0
A	1	-70/-70
B	3	+120/+160

Tab.13 Cross-cut and sheet resistance difference after water immersion for formulation n°1-2-3-4-A-B respect to virgin one

That consideration, in addition to the fact that a dirtiness reduction is needed, was the reason why the formulations 5 and 6 were created, avoiding acetone and using less graphene.

At this point the formulation 5 and 6 seem the most interesting because they have good adhesion, good sheet resistance and good dirtiness. Then, these two were deposited via spray deposition on the same substrate (metal plates, FeZn) using a Dexter air gun (max 8bars, max flow of 200 litres/min, stainless stell nozzle with 1,5mm opening, 14 spreads). After the deposition, heating at 165°C for 30 minutes as for the deposition by micrometric knife.

In addition, these two formulation were created (with the same percentages) using another graphene material, called N, conferring to them the name 5N and 6N. They were deposited by spray deposition and analyzed together with the 5 and 6. The relevant results obtained are reported in Fig.32.

Fig.32 Spray deposition of formulation n°5-5N-6-6N respectively (left to right)

Cross-cut test, scratch test, conductivity test, thickness analysis and dirtiness test were performed in these depositions as in the previous, resulting in the data showed in Table.14

Formulation n°	Cross cut (ISO)	Scratch test	Sheet resistance (ohm)	Thickness (micron)	Dirtiness
5	0	No scratch	500-1000	4,5	3,5
5N	0	No scratch	8000-13000	5	3
6	0	B	1300-2200	4	4
6N	0	HB	2000-5000	5	3,5

Table.14 Cross-cut test, scratch test, conductivity test, thickness analysis and dirtiness test results for the formulation n°5-5N-6-6N deposited by spray deposition.

Thickness is too low for a coating which usually is around 10-20 microns. For that reasons, spray deposition tests are in progress in order to find the optimal parameter to reach that thickness. Adhesion was the best possible for all the formulations, while the hardness was better for n°5 and 5N.

Although sheet resistance is higher than micrometric knife deposition, it is a good value, and in particular it is lower for n°5, meaning a higher conductivity respect to the others.

Dirtiness, which is fundamental for a commercial coating, is higher for spray-deposited coating respect to micrometric knife-deposited ones, and the formulation with the “N” graphene is a bit lower than its counterpart. Considering the fact that this type of coating will ideally be commercialized, spray deposition is for sure the way to go because it is lower time consuming deposition method, less product become waste, it is faster and more tuneable by changing the spray conditions or the gun. For all that reasons, spray depositions are weighted more than the other results for dirtiness and sheet resistance.

It is possible to conclude that, according to the results of cross-cut test, scratch test, conductivity test, dirtiness test, two different methods for deposition and changes in deposition parameters, the formulation n°5 seems to be the best one, combining together good adhesion, hardness, conductivity and dirtiness.

Obviously, many other tests are necessary to ensure its real effectiveness, marketability in the future and other possible applications and scenarios.

3.3. Hard acrylic-based paint

The last part of the thesis was a paint which exploits the addition of graphene to increase its mechanical properties, in particular hardness, without compromising the other features as adhesion, resistance to solvents/light/water. The concept was the same as the first project but changing the base from a teflon to an acrylic base.

Initially the formulations X-Y-Y2-Y3 with an increasing graphene concentration (from 0,25%w to 2,5%w) were prepared, and then, when an increased hardness was observed for 2,5%w, others formulations (Y3.1-Y3.2-Y3.3) with fixed graphene percentage and changing adhesion promoter were examined.

All the formulations with relative names and compositions are described in the Table.15.

Formulation name	Acrylic base (g)	Water (g)	Adhesion promoter (g)	Adhesion promoter %w	Graphene ink (PR-N-5-30)	Graphene %w on dry solid
X	22,31	2,00	0,81	4,31	No	no
Y	22,30	2,00	0,82	4,36	1,86g	0,25
Y2	22,30	2,00	0,81	4,31	9,53g	1,26
Y3	22,30	2,00	0,79	4,21	19,72g	2,57
Y3.1	11,00	no	0,97	9,86	9,03g	2,39
Y3.2	11,00	no	1,48	14,30	9,04g	2,39
Y3.3	9,77	no	0,62	7,29	7,99g	2,38

Tab.15 Acrylic-based formulations: names and compositions

These formulations were deposited on metal substrate (FeZn) by the two already described methods: micrometric knife deposition and spray deposition. Applications consists in two consecutive spreads with a time distance of one day.

To have a clear picture of the influence of some parameters they are changed during the experiments, in particular:

- Adhesion promoter (AP) addition time (just before the deposition or three days before addition);
- Substrate preparation (pre-treatment with sandpaper + cleaning or only cleaning);

- Formulation order (graphene + acrylic + adhesion promoter or acrylic + adhesion promoter + graphene).

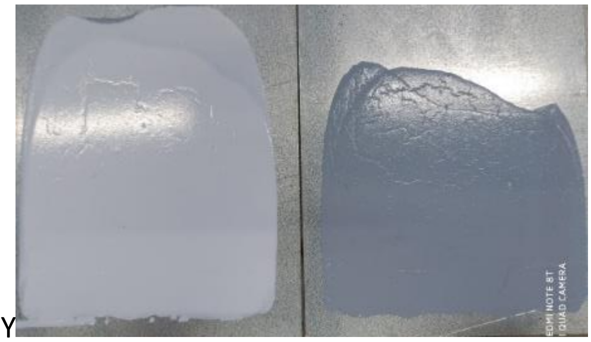
According with the increasing concentration from the X to the Y3, the colour is changing from the acrylic's white to the grey for the formulations with 2,5%w of graphene (Fig.33).

Fig.33 Formulation n° X-Y-Y2-Y3-Y3.1-Y3.2-Y3.3

This study includes many more tests than the previous projects, and in particular the following tests were executed:

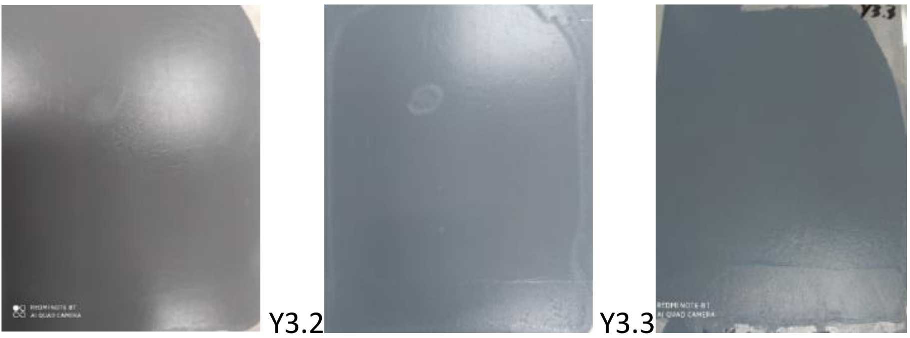
- Cross-cut test
- Scratch test
- Conductivity
- Dry solid residue
- Yellow Index (pre and post water immersion / humidity effect / sunlight effect)
- Gloss (pre and post water immersion / humidity effect / sunlight effect)
- IR (pre and post water immersion / humidity effect / sunlight effect)
- Resistance to common chemicals
- Thickness

Initially, the formulations were deposited on only cleaned substrate and adding the adhesion promoter just before the deposition. These depositions were called "A" and shown in Fig.34.

XY


Y2


Y3

Y3.1 Y3.2 Y3.3

Fig.34 "A" depositions

Then the same formulations were deposited on substrate treated with sandpaper and AP added three days before the formulation. These depositions are called "B" and shown in Fig.35.

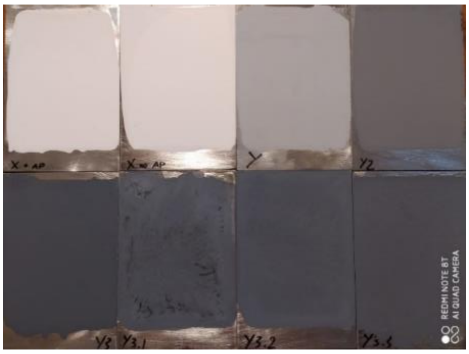


Fig.35 "B" depositions

Again, they have been deposited on substrate treated with sandpaper and adding adhesion promoter just before the deposition. These depositions were called "C" (Fig.36).

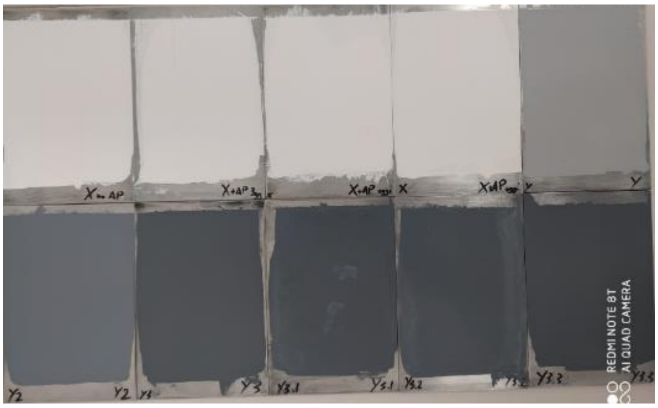


Fig.36 "C" depositions

Moreover, also a deposition on plexiglass (called "P") was performed, but only for virgin base and formulation Y3.1, Fig 37.

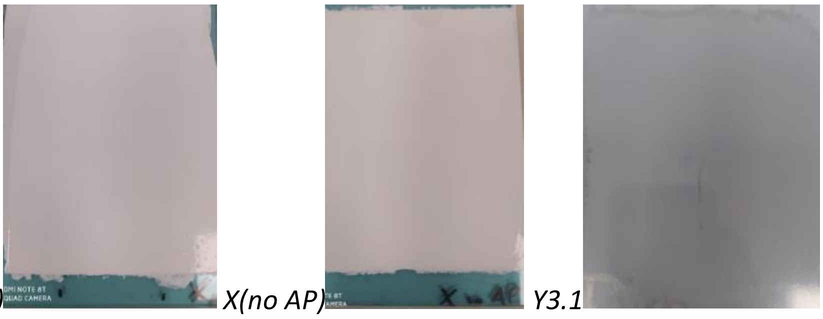

X (+AP) X(no AP) Y3.1

Fig.37 P deposition on plexiglass of X (with and without AP) and Y3.1

Finally, formulations X-Y-Y3-Y3.1-Y3.2-Y3.3 were deposited by micrometric knife and spray deposition. These were called deposition D and Dspray (Fig.38).

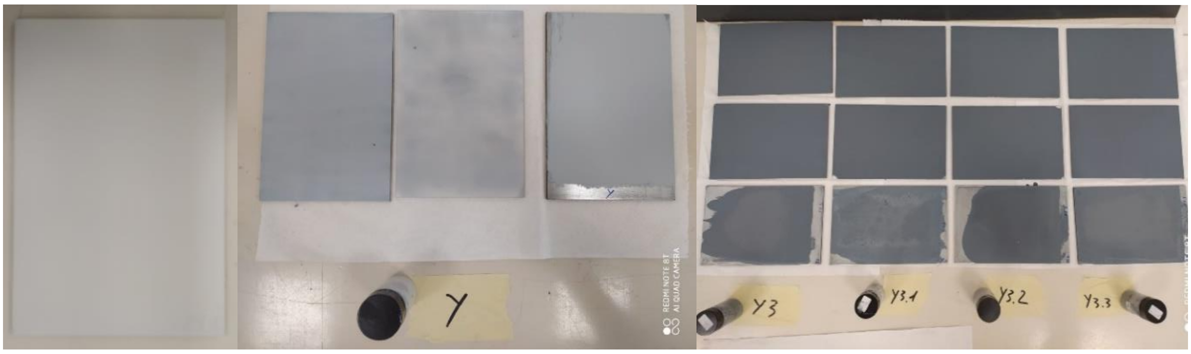


Fig.38 X-Y-Y3-Y3.2-Y3.2-Y3.3 D and Dspray deposition

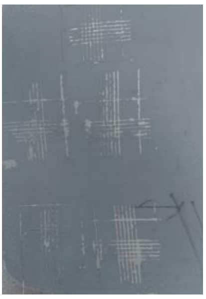
The samples are been tested by all following methods to compare the differences in addition time of adhesion promoter and substrate treatment.

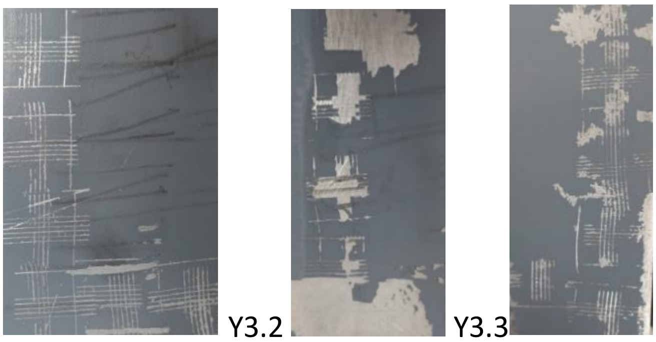
Cross-cut test and scratch test

Cross-cut test and scratch test were performed according with the ASTM D3359 and ASTM D3363. In Fig. 39-40-41-42-43 it is possible to see the results of these tests.

X

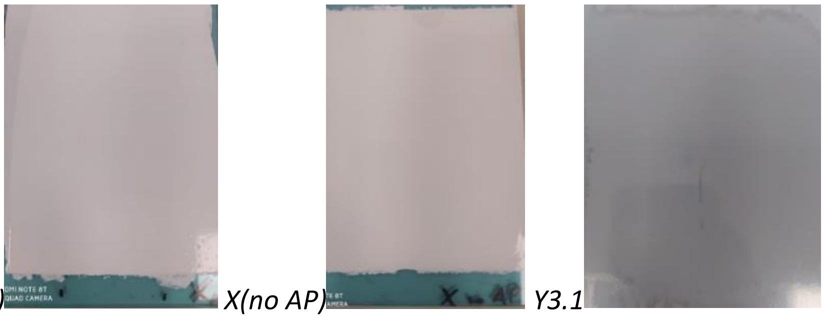
Y

Y2

Y3

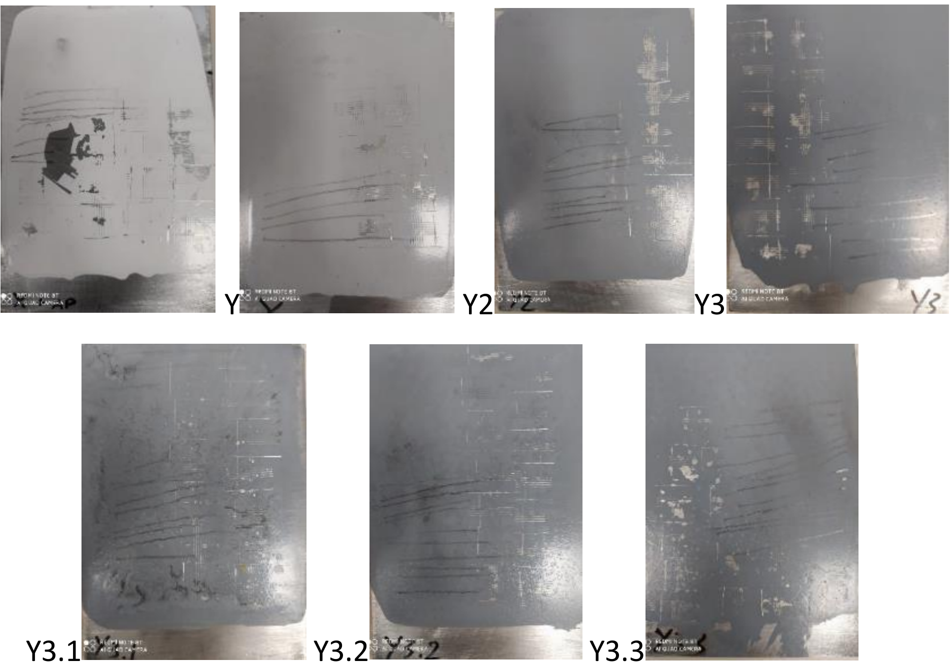
Y3.1 Y3.2 Y3.3

Fig.39 “A” cross-cut test and scratch test results



X (+AP) *X(no AP)* *Y3.1*

Fig.40 “P” deposition on plexiglass



X+AP Y Y2 Y3

Y3.1 Y3.2 Y3.3

Fig.41 “B” cross-cut test and scratch test results

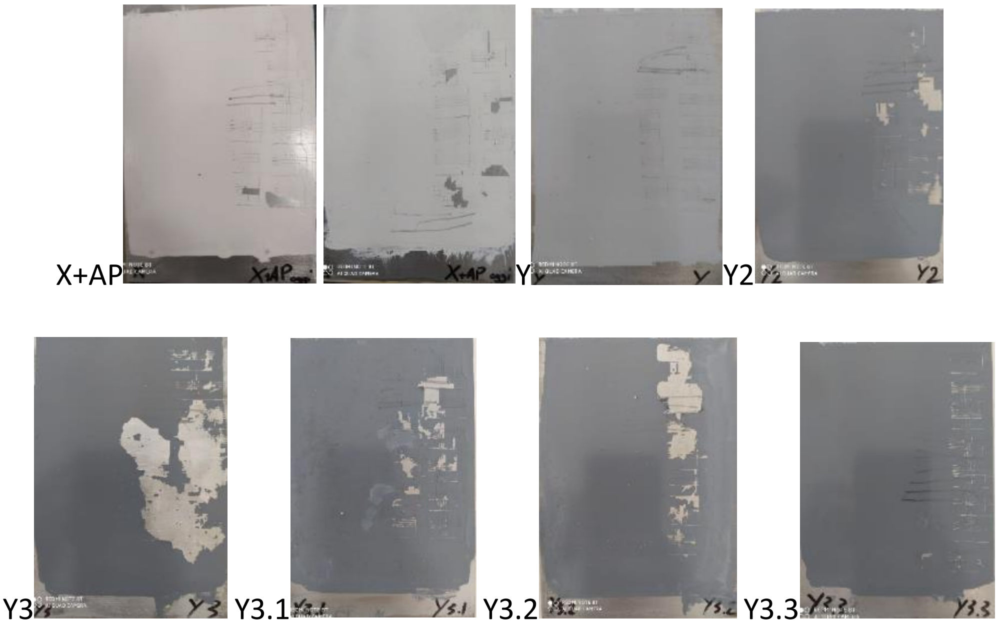


Fig.42 "B" cross-cut test and scratch test results

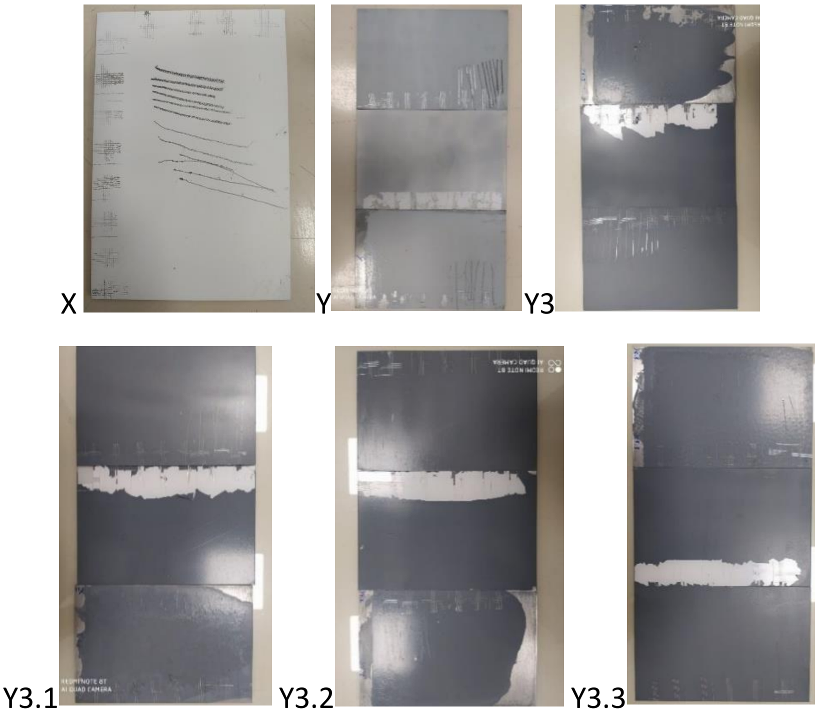


Fig.43 D and D spray deposition

All the results of cross-cut tests and scratch tests were summarized in Tab.16.

Substrate	Deposition method	Graphene %	Formulation	Cross Cut test (ISO)	Scratch test
FeZn not sandpaper (AP just before)	**A**	0	**X**	**0,3**	**5B**
FeZn not sandpaper (AP just before)	A	0,25	Y	0,5	4B
FeZn not sandpaper (AP just before)	A	1,26	Y2	2,2	4B
FeZn not sandpaper (AP just before)	A	2,57	Y3	2,2	B
FeZn not sandpaper (AP just before)	A	2,39	Y3.3	2,2	2B
FeZn not sandpaper (AP just before)	**A**	2,39	**Y3.1**	**1.5**	**B**
FeZn not sandpaper (AP just before)	A	2,38	Y3.2	5	5B
Plexiglass	P	0	X con AP	0	4B
Plexiglass	P	0	X no AP	0	5B
Plexiglass	P	2,39	Y3.1	3,2	B
FeZn sandpaper (AP 3 days)	**B**	0	**X**	**1,9**	**5B**
FeZn sandpaper (AP 3 days)	B	0,25	Y	2,4	3B
FeZn sandpaper (AP 3 days)	B	1,26	Y2	2,5	3B
FeZn sandpaper (AP 3 days)	B	2,57	Y3	2,1	B
FeZn sandpaper (AP 3 days)	B	2,39	Y3.3	2,5	B
FeZn sandpaper (AP 3 days)	**B**	2,39	**Y3.1**	**1**	**B**
FeZn sandpaper (AP 3 days)	B	2,38	Y3.2	1,1	B
FeZn sandpaper (AP just before)	**C**	0	**X**	**1,4**	**5B**
FeZn sandpaper (AP just before)	C	0,25	Y	0,9	5B
FeZn sandpaper (AP just before)	C	1,26	Y2	2,5	5B
FeZn sandpaper (AP just before)	C	2,57	Y3	4,6	3B

FeZn sandpaper (AP just before)	C	2,39	Y3.3	1,4	B
FeZn sandpaper (AP just before)	**C**	2,39	**Y3.1**	**2,6**	**3B**
FeZn sandpaper (AP just before)	C	2,38	Y3.2	3,8	4B
FeZn sandpaper (AP just before, opposite sequence)			**Y3.1**	**2,0**	**2B**
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D	0,25	Y	2,5	B
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D	2,57	Y3	2,4	B
FeZn sandpaper (acrylic + graphene, one week, AP adding)	**D**	**2,39**	**Y3.1**	**0,4**	**H**
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D	2,39	Y3.2	0,3	B
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D	2,38	Y3.3	0,3	HB
FeZn sandpaper (acrylic + AP)	D spray	0	X	1,2	H
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D spray	0,25	Y	0	H
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D spray	2,57	Y3	0	H
FeZn sandpaper (acrylic + graphene, one week, AP adding)	**D spray**	2,39	**Y3.1**	**0**	**2H**
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D spray	2,39	Y3.2	0	H
FeZn sandpaper (acrylic + graphene, one week, AP adding)	D spray	2,38	Y3.3	0	H
Plexiglass (acrylic + graphene, one week, AP adding)	D spray	0,25	Y	5	H
Plexiglass (acrylic + graphene, one week, AP adding)	D spray	2,57	Y3	5	H

Plexiglass (acrylic + graphene, one week, AP adding)	**D spray**	**2,39**	**Y3.1**	**5**	**2H**
Plexiglass (acrylic + graphene, one week, AP adding)	D spray	2,38	Y3.2	5	H
Plexiglass (acrylic + graphene, one week, AP adding)	D spray	2,39	Y3.3	5	H

Tab.16 Cross cut test and scratch test results for all the depositions of formulations X-Y-Y2-Y3-Y3.1-Y3.2-Y3.3

The best formulation in terms of adhesion and hardness was the n° Y3.1 which was harder than the acrylic base for every deposition (A-B-C-D-Dspray) and had a similar (or not decreased adhesion). It was also possible to assess the best deposition method: among the micrometric knife deposition the D sequence shows better results respect to the deposition A-B-C, but in general the spray deposition (Dspray) was the best, reaching an adhesion value better than the base and maintaining the same behaviour of increased hardness.

Combined hardness and adhesion improvements make these formulation and deposition method very attractive, with the need of further tests to consolidate them.

“D” deposition sequence was the way to go because in commercial paints is common to sell a paint and the AP separately, meaning that the paint (in this case acrylic base + graphene was already formulated and stable for long time) must be stable and the promoter must be added just before the deposition. “D” shows the same behaviour as the others for hardness and good adhesion values.

Moreover, comparing the different parameters (AP addition time and substrate preparation) it was possible to assess their influence.

Comparing depositions “A” and “C” it was quite clear that the pre-treatment with sandpaper on the substrate decrease the adhesion and the hardness, while comparing “B” and “C” gives the result that the anticipated AP addition (three days) does not improve adhesion and decrease a little bit the hardness.

Plexiglass was not the right substrate for these formulations as shown in the table. Adhesion was ISO 3.2 for the Y3.1 but it was also calculated for deposition “D spray” on plexiglass, resulting in an ISO 5 for all of them.

Conductivity

Conductivity test was performed by an appropriate instrument but these formulations were not conductive.

Dry solid residue percentage

For every formulation the dry solid residue percentage was calculated through drying at 105°C for three hours (Table 17).

Formulation	X	Y	Y2	Y3	Y3.1	Y3.2	Y3.3
Dry solid residue %	50,00	44,05	34,93	27,83	30,19	29,88	30,19

Tab.17 Dry solid residue for all the formulation

Yellow Index and Gloss (sunlight exposure)

Yellow index is a value which derives from spectrophotometric data and describes the change in colour (towards the yellow) of a sample. Measurements were done by BYK-Gardner colorimeter calibrated as described before with gloss trap, white standard, black standard and green check standard, as showed in Fig.44.

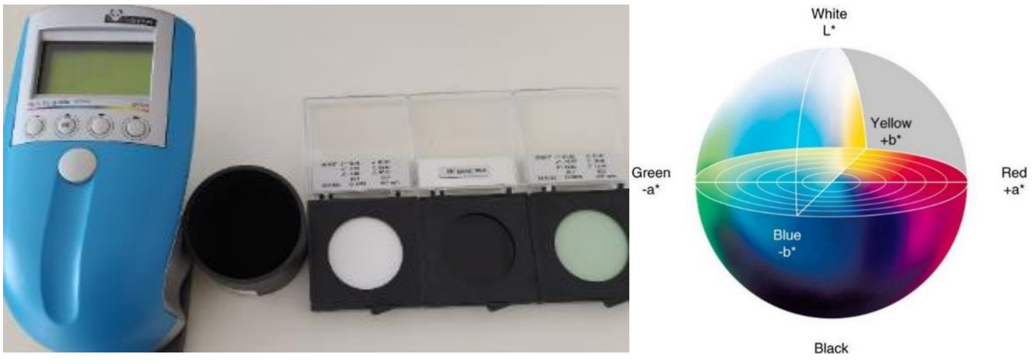


Fig.44 BYK-Gardner colorimeter (left) and Yellow Index scale (right).

Yellow Index and gloss (ISO2813) values were measured before and after sunlight exposure (one month) with the aim of understanding if sunlight induces colour/brightness change. The results are reported in Fig.45 and Table 18.

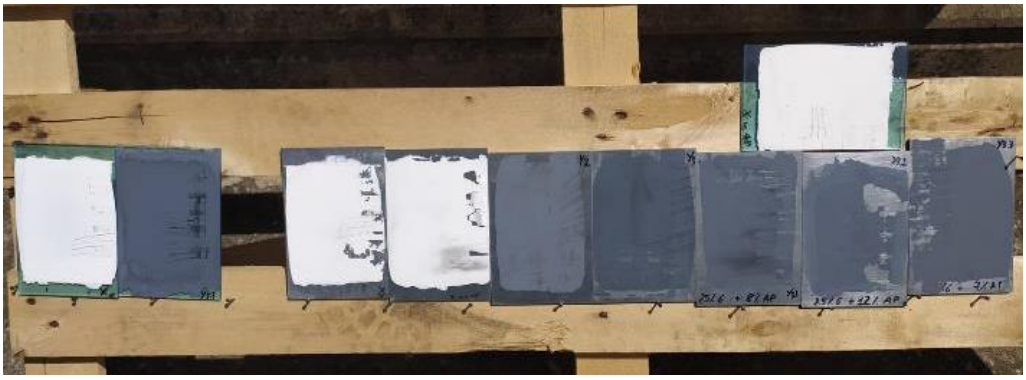


Fig.45 Sunlight exposure of the depositions

Substrate	Formulation	Yellow Index pre	Yellow Index post	Δ yellow index	Cross cut pre	Cross cut post	Δ cross cut	Gloss pre	Gloss post	Δ gloss
FeZn	**X**	**1,66**	**2,00**	**+0,34**	**4,6**	**5**	**+0,4**	**39,14**	**65,90**	**26,76**
FeZn	X no AP	2,08	3,91	+1,83	5	5	0	69,96	66,74	3,22
FeZn	Y	-6,98	-7,17	-0,19	0,5		0	55,22	57,67	2,45
FeZn	Y2	-15,38	-15,23	+0,15	2,2	5	+2,8	45,90	52,90	7,00
FeZn	Y3	-17,69	-17,97	-0,28	2,2	5	+2,8	34,28	38,32	4,04
FeZn	Y3.3	-17,80	-18,03	-0,33	2,2	3	+0,8	42,92	44,34	1,42
FeZn	**Y3.1**	**-18,25**	**-18,27**	**-0,02**	**1,5**	**1,5**	**0**	**43,94**	**44,24**	**0,30**
FeZn	Y3.2	-19,70	-19,80	-0,10	5	3,7	-1,3	38,26	40,02	1,76
Plexiglass	X con AP	-2,37	-1,41	+0,96	0	0,8	+0,8	68,48	62,98	-5,50
Plexiglass	X no AP	3,24	3,63	+0,39	0	0,5	+0,5	72,44	69,14	-3,30
Plexiglass	Y3.1	-18,01	-18,10	-0,09	3,2	2,0	-0,8	62,86	59,92	-2,94

Tab.18 Difference of cross-cut, gloss value and Yellow Index for all the formulation after sunlight exposure

Tab.18 shows the difference in cross-cut, gloss and Yellow Index after sunlight exposure with very interesting results:

- Yellow Index change is very low for all the formulations but in particular for n° Y3.1 which has the minimum variation;
- Cross-cut variation is difficult to evaluate because of the already high value (bad adhesion) for acrylic base and other formulations. The change is not reliable for all of them but because of these problems, though the Y3.1 (the best one until now) shows

an optimal result which can be not taken in consideration, but could give only an indication;

- Gloss variation is low for every formulation but also in this case the best result is obtained for n° Y3.1.

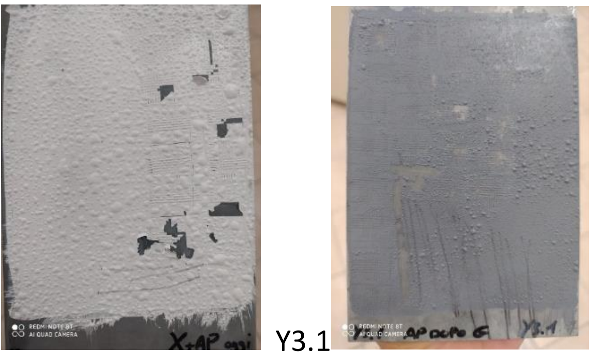
In summary, Y3.1 seems to be the formulation subjected to the minimum variation of gloss and Yellow Index associated to the sunlight.

Water immersion

This experiment was set to examinate the behaviour of the “best” formulation (Y3.1) and the base in water for one week. The results match the value of gloss and yellow index before and after the immersion (Table 19 and Fig.46).

Formulation	**Gloss pre immersion**	**Gloss post immersion**	**Δ gloss**	**Yellow index pre immersion**	**Yellow index post immersion**	**Δ yellow index**
X+AP	65	2,47	-62,53	2,61	3,44	+0,83
Y3.1	41,84	3,82	-38,02	-18,97	-16,66	+2,31

Tab.19 Yellow Index and gloss variation after humidity chamber test.



X+AP Y3.1

Fig.46 Deposition X+AP (acrylic base) and Y3.1 after water immersion test

Yellow Index change for the Y3.1 was bigger than in the acrylic base while the change in brightness was the opposite. These results have not the same behaviour but could be useful to understand that the effects of water immersion (one week) was bigger than the effect of sunlight (one month) for both the parameters examined.

As seen in the photos the coating surface degradation was intense in water, and in particular bigger for the acrylic base. Water and gas diffusion play a relevant role in degrading the coating and graphene, due to its water impermeability and gas barrier properties (41), seems to decrease degradation effect.

This result can be confirmed by the thickness analysis which shows a bigger change in thickness for acrylic base (X + AP) respect to the Y3.1, as show in Tab.20.

Formulation	Thickness pre water immersion (micron)	Thickness post water immersion (micron)	Δ thickness
X + AP	18,50	69,75	51,25
Y3.1	14,25	35,50	21,25

Tab.20 Thickness variation after water immersion

FT-IR tests were performed on both deposition (acrylic base and Y3.1) pre and post water immersion. The spectra are reported in Fig.47-48.

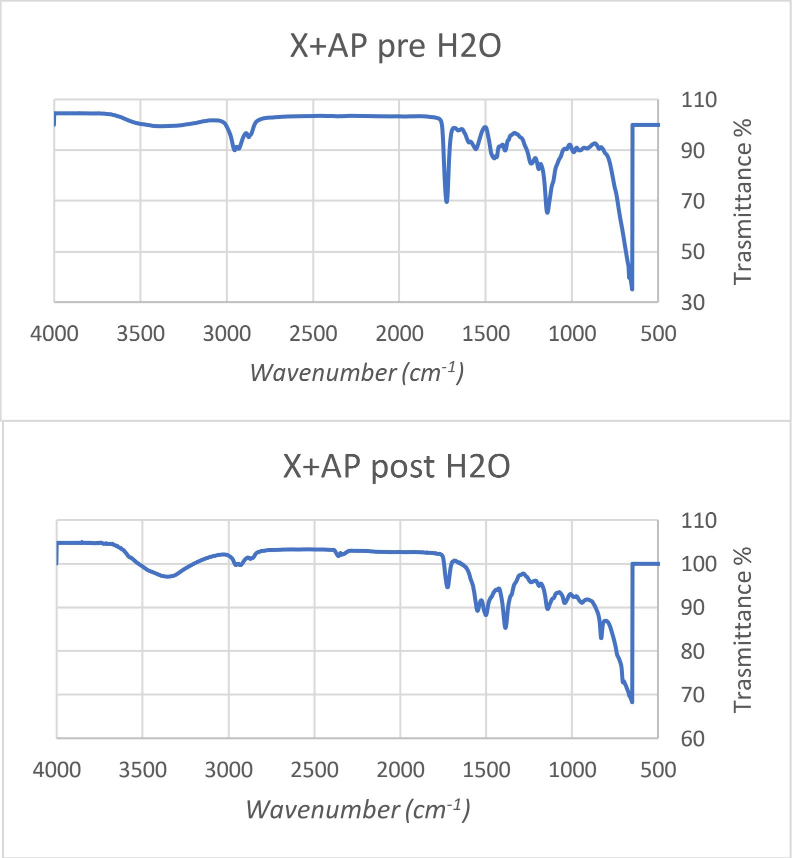


Fig.47 FT-IR spectra of acrylic base X+AP pre and post water immersion

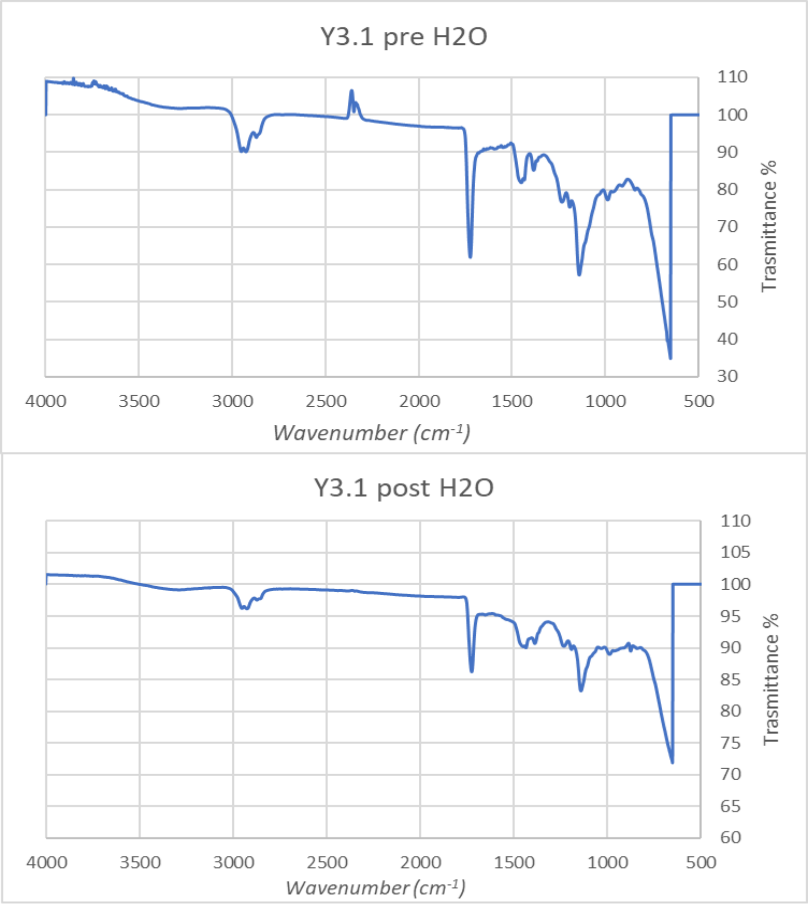


Fig.48 FT-IR spectra of formulation Y3.1 pre and post water immersion

The two spectra were very similar and analysing them qualitatively it was possible to recognize the following peaks:

- Large peak at 3500-3200 cm^{-1} attributed to O-H stretching;
- Peak at 2954 cm^{-1} attributed to acrylic matrix C-H stretching;
- Peak at 1724 cm^{-1} attributed to acrylic matrix C=O stretching;
- Peak at 1141 cm^{-1} attributed to acrylic matrix C-O stretching;

All the recognized peaks were attributed to the acrylic base because graphene cannot be seen in the IR analysis. The conclusion which can be extracted from these spectra is that the graphene addition does not have influence on the acrylic base spectra neither in positive or negative.

Humidity chamber test

The principle was the same of the previous test without immerging the plates in the water but positioning them into a closed chamber with 90% humidity with the aim of evaluating humidity effect on the "best" formulation (Y3.1) and the base. The duration of the test was one week as for the previous immersion test. The results in Tab.21 and the FT-IR spectra in Fig.49-50 show the difference between before and after humidity chamber for both deposition (acrylic base and Y3.1).

Formulation	**Gloss pre humidity**	**Gloss post humidity**	**Δ gloss**	**Yellow index pre humidity**	**Yellow index post humidity**	**Δ Yellow Index**
X+AP	65,44	63,8	-1,64	0,19	0,38	0,19
Y3.1	53,24	53,01	0,23	-19,45	-20,95	-1,50

Tab.21 Yellow Index and gloss variation after humidity chamber test

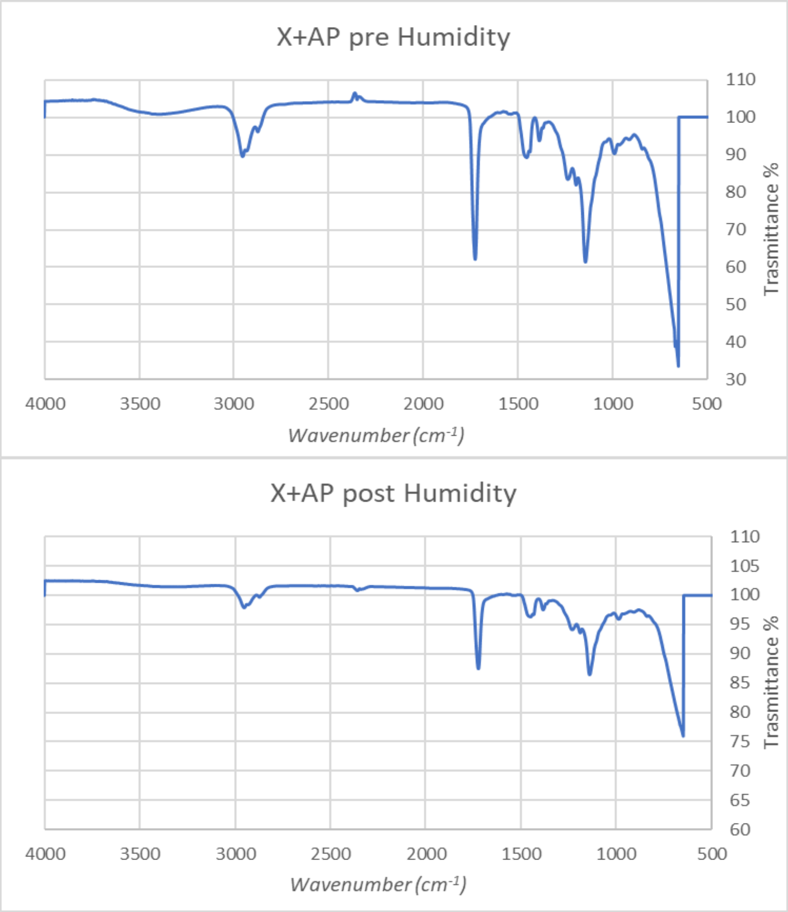


Fig.49 FT-IR spectra of acrylic base (X+AP) pre and post humidity chamber

Fig.50 FT-IR spectra of Y3.1 pre and post humidity chamber

The spectra have the same behaviour as the water immersion test meaning that the two tests have a comparable effect.

Resistance to common household chemicals

The resistance to common chemicals test was performed in two different methods:

- Drop by drop deposition of the chemical onto the surface of the coating and waiting one day before examination;
- Rubbing ten times with a paper impregnated with the chemical of interest.

The results, which are showed in the Tab.22, were evaluated according to a self-created scale of four values:

- Optimal, if the coating surface is not affected;

- Good, if the coating surface is only low ruined;
- Medium, if the coating surface is ruined;
- Bad, If the coating surface is totally ruined.

Resistance to	**Test type**	**X+AP**	**Y3.1**
Acetone	Drop by drop	Optimal	Optimal
Ethyl alcohol	Drop by drop	Optimal	Optimal
Bleach	Drop by drop	Medium	Medium
Turpentine	Drop by drop	Optimal	Optimal
Paint thinner	Drop by drop	Optimal	Optimal
Acetone	Rubbing	Good	Good
Ethyl alcohol	Rubbing	Good	Good
Bleach	Rubbing	Good	Good
Turpentine	Rubbing	Good	Good
Paint thinner	Rubbing	Good	Good

Tab.22 Results of the resistance to common household chemicals test

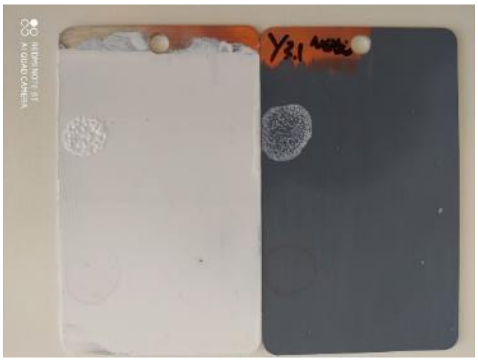


Fig.51 Acrylic base (left) and Y3.1 (right) after drop by drop resistance test

Both the formulations were very resistant to all the common household chemical used in this test, among which only bleach have a stronger effect (only in drop by drop application).

4. Conclusions

Graphene-XT production process used does not involve dangerous/toxic/difficult-handling chemical agents, being a very safe process. Moreover, a complete recycling of unreacted reagents (graphite), exfoliating agent and water is executed every time, avoiding waste production and management, making the process clean and very close to green chemistry principles.

Many and more accurate tests and calculations should be done to check the green metrics improvements over time, but the direction is already optimal.

This work was not a conclusive study but only part of the continuous improvement and testing work which is in progress at Graphene-XT, and for this reason all the obtained results are only partial, and in the future will be examined more in details.

After that, different conclusion can be drawn from this thesis, one for every different projects carried out:

- In the first project graphene addition to a teflon base does not improve mechanical properties neither at 2% or at 10%. Moreover, different graphenes give the same results, proving that.

  For this project many other tests are going on at the third-part company facility and results will be available soon.
- The second project shows that it is possible to exploit graphene conductivity in a paint creating a conductive coating which maintain the optimal properties of the base as adhesion to the substrate and hardness, also showing low dirtiness.

  On this project other tests and improvements must be done: first, trying to deposit by spray deposition a coating thickness of at least 20 micron which is the common thickness for a coating; in addition, tests with other graphenes could give an indication on how the difference in graphenes influences the properties of this product.
- The last project includes many more tests and informations on both properties and deposition methods of the paint. These results show that 2.5% of graphene can increase the hardness (and in the case of spray deposition also the adhesion) of an acrylic base coating.

This hardness behaviour is clear, showing the same increase for all the deposition type and method. The best solution for this product is the spray deposition which combine the optimal results for hardness and adhesion (both increased) with the already good properties of resistance to common household chemicals / sunlight / water immersion /humidity attributed to the base.

To conclude, graphene has very interesting properties which give it so much attention and its application in paints is one of the more active fields. This thesis shows that graphene addition has a better effect on acrylic base respect to a teflon base, showing that it is possible to exploit its properties, in this specific case conductivity and hardness, to enhance the properties of other materials creating an updated product respect to the base. In particular the last two projects show interesting results which put the basis for next studies that surely will be carried out in the next times.

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