BEYOND COLOUR DECORATION BY INKJET TECHNOLOGY

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1. INTRODUCTION

Inkjet technology is being called upon to take up a privileged place in the technological evolution of the ceramic sector. The most difficult aspect to gauge at present is the final magnitude of the technology leap, motivated mainly by the potential applications of this technology beyond colour decoration. The first indications of those possibilities have already materialised in the latest related innovations, recently presented in the sector. These have specifically taken place in applications of engobes, glazes, and other decorative finishes that go far beyond chromatic decorations.

The Instituto de Tecnología Cerámica (ITC) has conducted an in-depth study, through the Technology Observatory, of the applications generally performed by inkjet technologies worldwide which could be potentially transferred to the ceramic sector.

The definitive implementation of this technology as a decorating system *par excellence* has coincided with a very critical moment, involving the deepest international crisis to date, which has been particularly intense in the Spanish national context and especially in the Spanish building sector, the major ceramic floor and wall tile customer.

In view of this scenario, the only way of improving sales is through the internationalisation of ceramic sector companies, which requires addressing strong international competition and rival substitute materials in order to be able to gain market share. It is in this context that inkjet technology could raise the ceramic sector's prestige and enhance its legend, by becoming a work tool that goes far beyond current colour decoration.

2. INKJET PRINTING TECHNOLOGY

Inkjet printing consists of the deposition of a material on a substrate, characterised by the absence of contact between the substrate and the part of the technology that does the printing. Two types of technology may be distinguished in terms of the physical mechanism used in the deposition process: continuous inkjet and drop-on-demand inkjet printing.

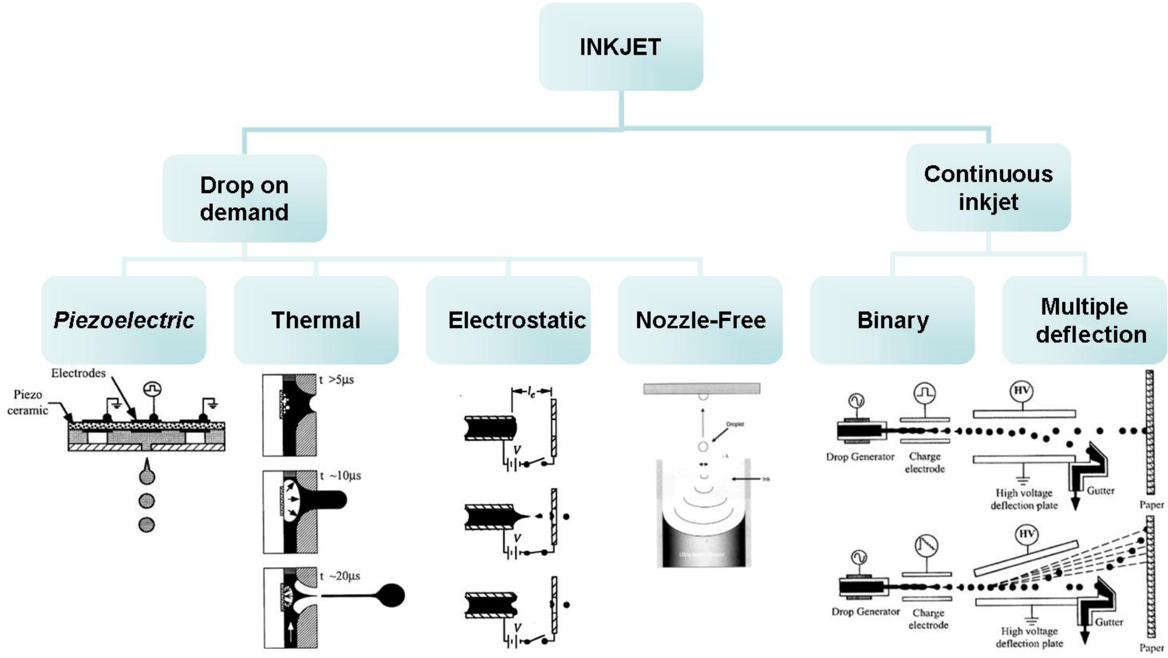

Figure 1. Classification of inkjet printing technologies
Source: LE H.P, 1998; Hohemberger, 2002; Hosokawa, 2007)

The materials used are generally suspensions or solutions with colouring agents and a series of substances that provide an appropriate medium in order to avoid precipitation and facilitate transport and fixing on the substrate, among other features. The composition of this medium varies as a function of the field of application, which may be water, oil (long-chain glycols and/or hydrocarbons), or other solvents such as alcohol, glycols, or lactates.

For example, the inks used traditionally in the graphic arts sector have a wide range of colours, with an exceptional intensity and gloss. However, when they are exposed to sunlight, they quickly degrade, leading to colour fading and an important loss of colour quality compared with the initial work. In contrast, in the ceramic sector, the use of inorganic suspensions (pigmented inks) allows firing at high temperatures, thus generating a maximum colour yield that then remains unvaried independently of exposure to sunlight.

Printers are widely used in the home at present, always for reproducing images and documents. The same occurs in their industrial use, both in the ceramic sector and in most other sectors.

3. OBJECTIVE AND REASON FOR THE STUDY

However, inkjet printing exhibits a series of singularities that make it unique. It is an electronically-run system that works digitally without any contact with the substrate on which the ink is deposited. Nor is any physical support (screens, rollers, etc.) needed to transfer a particular image, which allows decorated pieces with innumerable combinations and designs to be made even to the point of not having two identical items.

In view of the above, it may be deemed just a matter of time before inkjet technology applications will be extending far beyond current colour decoration. Examples are, for instance, the latest novelties presented at the recent CEVISAMA trade fair (2011) by different ceramic companies. In particular, ceramic prototypes were to be seen that had been glazed (engobe and glaze) by inkjet techniques. Inkjet printing finishes were also displayed that were designed to provide the piece with particular, enhanced mechanical properties, among other effects.

The radical advances in electronics (greater speeds, improved printheads, etc.), together with the intense quest for innovations that characterises the Spanish ceramic sector, suggest that innovations such as those remarked in the foregoing paragraph are going to become a constant feature in the market and will lead to a great number of hitherto unimaginable, innovative applications on ceramics.

Also to be taken into account are the advances that have taken place in Nanotechnology in recent years. These advances have made it possible to work with a great number of materials that it had previously been impossible to deposit by this technique.

The ceramic sector companies directly involved in all these developments have been, in the first place, the ceramic machinery companies, though the advances were also enabled by the raw material companies as potential suppliers of the consumables, in addition to the ceramic floor and wall tile manufacturing companies as the principal beneficiaries and sufferers of the technology and its inks.

The first study on ceramic decoration using inkjet technology by ITC (published in 2010) and the multiple innovations and advances by the companies (in both technology and materials) clearly highlight the leading global role of the Spanish industry in the development of this technology.

With a view to supporting and strengthening that leadership, it was considered of great interest to investigate what additional (actual and potential) possibilities, in addition to decoration, might be developed with the help of this technology and the appropriate consumables or inks.

The present paper seeks, simply, to help and stimulate companies in this sector in their search for such new solutions, and in creatively intuiting solutions that go beyond what has been expressed in writing here.

4. FUNCTIONAL PRINTING

In this study, the information search has focused in general on the use of inkjet technology for applications other than decorative uses, and especially on functional printing, this being understood as the deposition of any material with a view to providing the substrate on which it is deposited with a new functionality or to enhancing its properties in an important way, so that it can be used for a new purpose or functionality.

More specifically, this paper examines both the deposition of materials that have an own functionality (known as functional printing) and the deposition of one or more materials to generate an electronic component (known as printed electronics)

Printed electronics is one of the most promising branches as it is replacing traditional electronics and, more importantly, greatly extending the number of applications in this field. The significant advantages of printed electronics are their low cost, the possibility of being applied on to flexible surfaces, the ability to work on large substrates, ease of application, etc.

At present, multiple applications are already to be found in the market. Owing to their young commercial life, the economic numbers are not yet very high but the predictions for the medium term are spectacular. Business volume is expected to grow in just a decade (2009–2019) by about 2000% in applications such as OLEDs, photovoltaics, sensors, etc.

In printed electronics, electronic devices based on organic materials have aroused the greatest interest in the scientific community. This has led to many applications that are already beginning to be marketed. The following figure presents a Roadmap, drawn up by the Organic Electronics Association, showing a forecast of future applications (in the short, medium, and long term) for a series of fields or sectors.

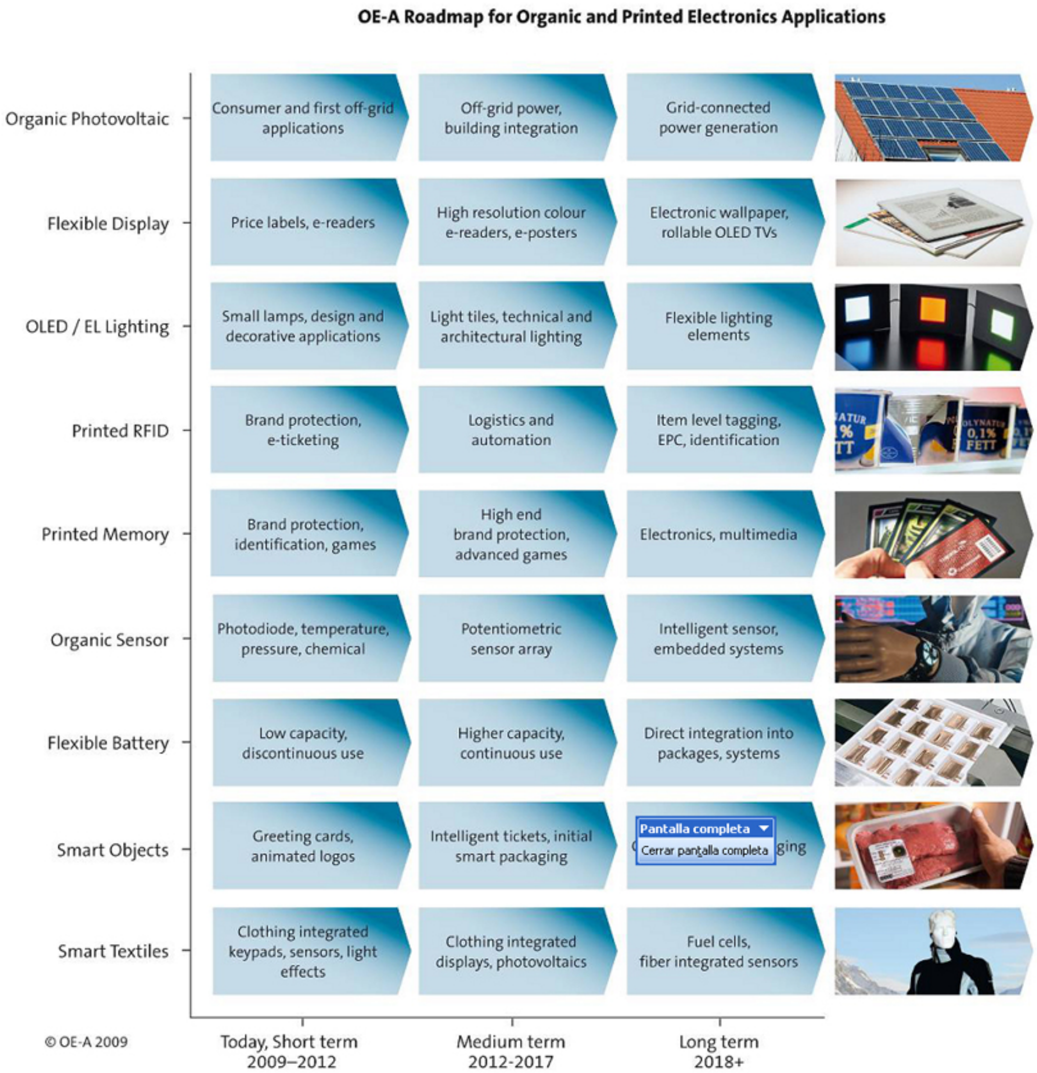

Figure 2. Roadmap for organic and printed electronics applications
Source: Organic Electronics Association

Although printed electronics has to date been more closely related to the use of organic materials, inorganic materials are being increasingly studied and used in the quest for enhanced properties or for performance features that cannot be obtained with organic materials. Such is the case of the use of metallic nanoparticles in conductivity issues, zinc oxide-based semiconductors (greater stability and duration), and many other applications that are discussed below.

In addition to all the above applications, as indicated at the beginning of this section, this study also takes into account a further group of materials that have a functionality of their own. The advantage of applying them by inkjet technology stems from the benefits provided by the process, such as selective customized application, very low consumption, possible application on profiled surfaces, etc.

5. DIFFERENT MATERIALS AND APPLICATIONS FOR FUNCTIONAL PRINTING

This section describes a series of materials considered of interest because of their different functional applications and their possible application by inkjet technology.

5.1. Metallic inks

This is the group of materials that have led to the greatest number of studies in the literature, owing to the numerous people engaged in investigating their multiple possibilities. At present, the best known and most widely used inks in printed electronics are nano-silver inks. The reason is their very high conductivity, in addition to the possibility of being applied by inkjet technology.

In addition to displaying excellent conductivity, silver is a very stable material with regard to oxidation, its oxide also exhibiting very acceptable conductivity, oxidation affecting the conductive properties of the material to a lesser extent over time, unlike what occurs with other more economic metals like copper or aluminium. Expensive inks are involved, though this drawback is minimised because of the small volume of material that is deposited, thanks to the application by inkjet technology.

Companies that have developed conductive inks for processing printed circuits or other devices, though not necessarily for inkjet printing, are, for example, DuPont Microcircuit Materials[1] and Xerox (*Silver Bullet* ink)[2]. In 2009, Xerox launched a type of conductive silver capable of integrating printed circuits in a simple way on fabrics and articles of clothing owing to its low melting temperature (140 ºC). In 2010, DuPont launched its new inks DuPont 7723 and 9169, a further development of its series of conductive inks 5033, which the company had launched in 2005.

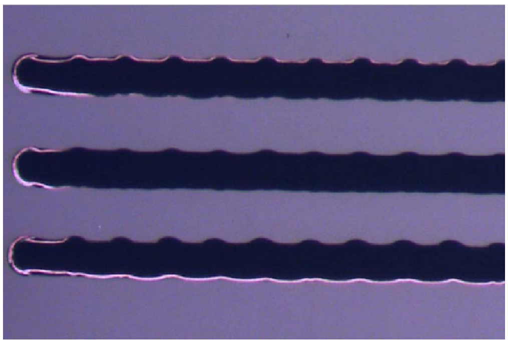

Figure 3. Silver ink. Cima Nanotech
Source: Microfab

It is currently already possible to buy commercial inks of nano-silver, gold, and other metals (Advanced Nano Products Co., UT Dots, Inc.), while there are a great number of research groups pursuing the development and synthesis of silver

1 http://www.gruponeva.es/blog/noticia/3790/dupont-7723-y-9169-nuevas-tintas-conductoras-de-plata-para-pantallas-tactiles-y-dispositivos-oled.html

2 http://www.xerox.com/innovation/news-stories/silverbullet/enus.html

nanoparticles for the manufacture of inkjet inks, such as Kosmala and her research group at the University of Cranfield (UK), whose study *Synthesis of silver nano particles and fabrication of aqueous Ag inks for inkjet printing* was recently published in the *Materials Chemistry and Physics* journal (June 2011).

With regard to their functional applications, these are mainly focused on printed electronics with a great number of specific applications (OLEDs, RFIDs, screens, etc.), in the case of silver its proven bactericidal properties also being used[3].

However, silver and gold are not the only metals used in fabricating conductive inks. As an alternative to these high-cost materials, companies in this field have already developed and are offering conductive nano-aluminium, copper, and nickel inks. An example is Applied Nanotech Inc., whose copper ink (Cu-iJ70) was recognised as one of the 100 most significant innovations of 2010 by *R&D Magazine*.

5.2. Carbon nanotube inks

Nanotubes are tubular structures with a diameter of just a few nanometres and a length of up to a millimetre. There are nanotubes of many materials, although the best known and most widely used are carbon nanotubes.

Their main property is their excellent conductivity, which makes them recommendable materials for a very broad spectrum of applications, ranging from the manufacture of new RFIDs[4] to solar cells or light-emitting systems[5], among many others.

The following figure illustrates the potential market and degree of maturity or development of the technologies in different sectors.

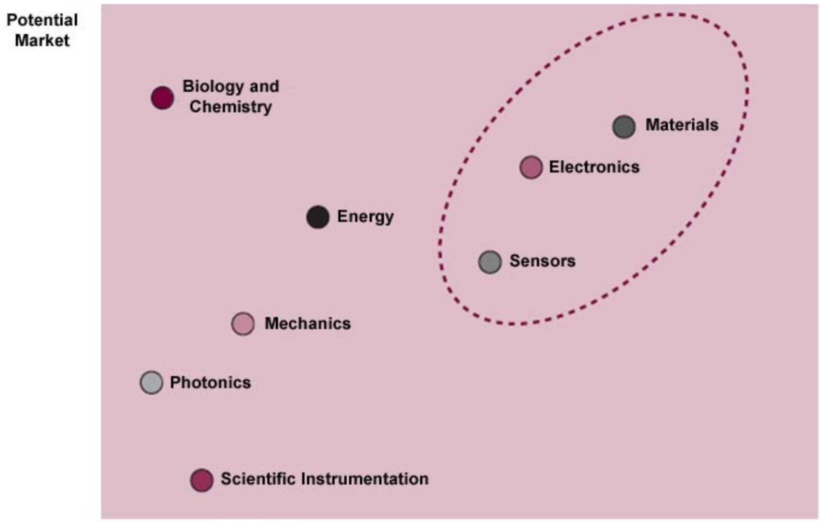

Figure 4. Potential market and development of the technologies in the different sectors
Source: Informe de VT de Madri+d

3 http://www.inktec.com/english/pdf/electronic/7.pdf
4 http://www.technologyreview.es/read_article.aspx?id=36191
5 http://www.sciencedaily.com/releases/2011/07/110706094339.htm

Carbon nanotube inks are already available for deposition by inkjet technology. An example is Bayer Materialscience, which offers water-based carbon nanotube inks under the trade name BayInk TP CNT[6].

5.3. Photovoltaic inks

Printed electronics also plays a very important role in the development of renewable energies, particularly in solar energy-related technology.

Thin films or thin-film modules are photovoltaic systems that consist of thin layers of semi-conducting material (thickness ranging from nanometres to several microns), which are used for producing photovoltaic cells. These thin-film modules are constructed by depositing photosensitive materials on low-cost substrates such as glass, stainless steel, or plastic.

Thin-sheet technology has developed very quickly and become one of the most interesting options for the future, also because of the ensuing reduction in manufacturing costs. The recent introduction of thin-film technology in the photovoltaic market is fostering research into and development of new printable materials, whether inorganic (gallium arsenide, cadmium telluride, or copper indium diselenide) or organic.

In this line, University of Oregon engineers recently managed to obtain flexible solar cells based on CIGS inks, applied by inkjet technology, for the first time. The results of this investigation have been patented and published in *Solar Energy Materials and Solar Cells*[7] and they augur a promising future for the technology in the field of solar energy.

A great number of photosensitive inks for photovoltaic cells have already been put on the market since 2007. On an industrial level, particularly to be noted are the companies Konaka (U.S.A.), G24i (Wales), Eight19 (Cambridge, United Kingdom), and 3GSolar (Israel), which develop and market third-generation organic solar cells[8].

Figure 5. Printed flexible sheet and applied layer sequence
Source: Konarka

6 http://www.fundacionquimica.org/noticia_foro.php?tipo=0&id=1011&vlv=boletin_quimica_sociedad.php
7 http://www.eurekalert.org/pub_releases/2011-06/osu-ipc062811.php
8 http://www.konarka.com/index.php/technology/our-evolution/

In this particular case, the production process takes place by means of roll-to-roll printing or screen printing; however, in 2008[9] Konarka demonstrated the possibility of printing these materials by inkjet technology (modifying a conventional printer).

There have also been advances in the field of silicon wafers. The company Innovalight (California), recently taken over by the multinational DuPont (July 2011), markets a silicon ink. The company specialises in improving crystalline silicon solar cell efficiency. It proposes using this ink, applied by inkjet printing, as an additional step in the current manufacturing process of these cells in order notably to enhance cell efficiency.

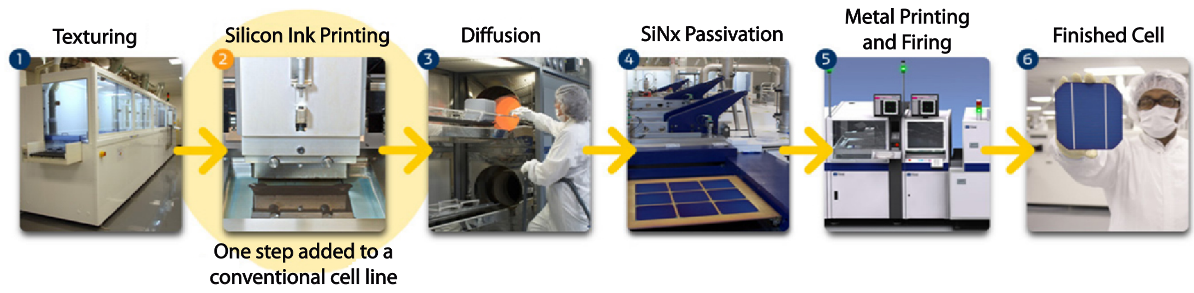

Figure 6. Improved Si solar cell manufacturing process
Source: http://www.innovalight.com

Other silicon inks have also been patented whose compositions contain silicon, either by itself (US 2011120537, CN 101814555) or together with other elements (US 2011109688).

5.4. Electroluminescent materials

Electroluminescence is defined, in a very general way, as the emission of light produced by certain materials when they are subjected to the action of an electric field.

The application of a voltage difference generates a state of excitation in the material, from which deactivation occurs with light emission. Electroluminescent devices have an electroluminescent material arranged between two electrodes (at least one electrode must be transparent to appreciate the effect, customarily ITO).

Their implementation has been particularly successful in the case of TV screens, cell phones, and computer screens. All are commercially available under the so-called OLED technology.

OLEDs (organic light-emitting diodes) are light emitters in which the luminescent selection layer consists of a film of organic components, which generates and emits light by itself when subjected to electric stimulation. The OLED technology is

9 http://www.konarka.com/index.php/site/pressreleasedetail/konarka_announces_first_ever_demonstration_of_inkjet_printed_solar_cells

not new, nor is its inkjet application, which has been studied since the end of the 1990s. Indeed, there are many different OLED technologies: as many as the great diversity of structures (and materials) that it has been possible to devise (and to implement) for holding and maintaining the electroluminescent layer, also based on the type of organic components used.

In 2010 Samsung presented a prototype of a 19'' OLED device obtained by inkjet printing technology at the FPD 2010 international conference.

5.5. Thermochromic inks and other functional effects

Thermochromic inks are characterised by changing colour when the temperature varies in their environment. This type of material is mainly being used in the manufacture of smart labels or packaging for their optical characteristics.

Examples of this type of ink are the inks that incorporate a time–temperature indicator (TTI). One such ink is that of the company BASF (OnVu). This ink is irradiated with a UV light source and has a dark blue colour. The colour then begins to lighten as a function of time and temperature. Other examples are the TTSensor TM (Avery Dennison) or CheckPoint (Vitsab).

Another example of a functional ink (though not thermochromic) is RipeSense®. This consists of a sensor that changes colour by reacting with the aroma emitted by the fruit as it ripens.

Further to be noted here is the European project Sustainpack[10], which ended in 2008, whose partners included the well-known inkjet printhead company Xaar Jet AB. The purpose of one of the subprojects was to develop humidity sensors by inkjet printing.

In the same line, a series of additional functional effects are remarked in the report, whose inkjet application has already been verified, which can provide the end ceramic product with an added value. Effects are described, for example, such as photocatalytic effects and acid or abrasion barrier properties.

6. OTHER SECTIONS OF THE STUDY

This study also contains a series of further sections, in addition to those mentioned in this paper, which for the sake of brevity have not been included. In particular, the study provides a bibliographic analysis in which the major players involved in the area at issue are noted, and the most influential countries, universities, research centres, and companies are detailed.

An extensive list of technology offers and demands is also included, which allows the state of the art to be intuited, while also presenting an excellent opportunity for collaborating with centres and companies already working in these

10 http://www.sustainpack.com

types of applications. The European projects of greatest interest in the Sixth and Seventh Framework Programmes are also identified.

Finally, conclusions are drawn in which a series of reflections are made on the possibilities that might exist for ceramics on applying these materials by inkjet technologies, as well as the role that ceramics might have in other uses through the application of these functional materials.

ACKNOWLEDGEMENTS

This study was supported by the European Union in the Strategic Development Programme through the European Fund for Regional Development (EFRD) and by IMPIVA (Autonomous Government of Valencian). Ref: IMDEEB/2011/19.

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