# Thermal behavior of vehicles and digital inks for inkjet decoration of ceramic tiles

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## ABSTRACT

Nowadays, after a sudden development in the last 2–3 years, inkjet decoration of ceramic tiles is the major decoration technique, but scientific studies on characteristics and behaviors of digital inks are quite rare.

A set of common vehicles and digital inks for ceramic decoration have been studied by FTIR spectrometry to characterize their organic components and TG-DTA to understand their thermal behavior. This characterization is necessary to evaluate how inks react entering in the firing kilns and how they can influence emissions at chimneys.

We were able to identify 6 classes of inks, depending on the nature of their vehicles.

First thermal data show that the major part of inks start to evaporate, between 170 and 285 °C, then volatile compounds decompose with exothermic reactions, between 200 and 315 °C, depending on the nature of vehicles and heating rate. Differences in the intensity of phenomena are clearly visible between slow and fast heating rates, suggesting a predominance of combustion over evaporation at fast heating rates. Further studies are necessary to clarify the competition between evaporation and combustion phenomena.

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## 1. Introduction

Inkjet technology is well-known because of its application to several technological fields, from desktop printers to production of microchips [1,2].

Since 2001, inkjet printing technology has been applied also to the decoration of ceramic tiles before their firing and today it is the most widespread method in this field [3].

Inkjet decoration of ceramic tiles is based on the drop-on-demand (DOD) technique, which entails the deposition of inks on a substrate, drop by drop, and only when required by a control software [1].

Digital ceramic inks are composed of a solid coloring phase and of a liquid phase.

The coloring phase is a finely ground crystalline pigment, usually based on metal aluminates, oxides or silicates.

The liquid phase can be obtained by the mix of two main components. The first one is the vehicle, often called "solvent" i.e. an organic compound or mix with specific technological properties (low viscosity, high boiling point, etc.) that has to keep pigment particles in suspension. The second one is composed by different additives: "hyperdispersants", usually block co-polymers or polymeric anionic surfactants that prevent pigment agglomeration, defoamers, antibacterials, etc.

Inkjet decoration has become the most chosen decoration method thanks to its many pros: easier storage of materials (decoration models are now completely digital), unlimited possibilities of decorations, expanded and non-flat surfaces (not obtained in a traditional rotary serigraphy and Rotocolor® systems), etc. Moreover, inkjet printing is a non-contact decoration technique that reduces hazards of mechanical stress on unfired tiles.

Inkjet decoration has also some cons. For instance, inks must have specific rheological properties to be jettable (e.g., diameter of pigment particles below 1 μm, surface tension between 20 and 45 mN/m, etc.) [4]. Granulometry of pigments has to guarantee specific chromatic performances, but it has to be low enough to be jettable, with consequent problems of sedimentation: even if the density of pigments for digital inks is similar to the traditional pigments one, the granulometric distribution is lower and common methods, like stirring, are no more sufficient to overcome sedimentation. Moreover, polluting emissions from firing of these inks are not well studied yet.

**Table 1**
Sampled vehicles.

| Vehicles | Sample name |
|---|---|
| Isoparaffin oil | PRF1 |
| n-Paraffin oil | PRF2 |
| Tripropylene glycol n-butyl ether | TPnB |
| 2-ethylhexyl stearate | 2-EHS |
| Ethylhexyl cocoate | EHC |
| Caprylic/capric triglyceride | CCT |
| 2-ethylhexyl laurate | 2-EHL |
| 2,2'-Ethylenedioxydiethyl bis(2-ethylhexanoate) | Gl_Est_1 |
| Tripropylene glycol monomethyl ether | TPM |

Most of these cons depend on the composition of the vehicle and this stage of inks preparation still requires huge support from scientific research.

Because the application of inkjet technology to ceramic tiles is a quite recent innovation, scientific studies and characterizations cover just few points of this technique and they are focused mostly on the connection between the nature of vehicles and the rheological properties of inks [5,6].

Scientific literature does not provide the chemical characterization of ceramic inks. Gazulla et al. [7] carried on one of the first chemical study of digital inks by FT-IR, WD-XRF and elemental analysis, to identify the major compounds of the organic fraction.

The present study focuses on the characterization of a wide range of inks now in commerce, to understand their thermal behavior, chemical composition, polluting emissions during firing and rheological properties, to improve scientific knowledge on digital ceramic inks.

In this paper, we present the results of the chemical characterization and first results of thermal analyses on a set of commercial inks and vehicles.

The knowledge of thermal behavior is necessary to understand which kind of phenomena occur to the inks during firing of ceramic tiles, especially because of the particular design of ceramic kilns, which operate in counter-current of hot air, with the main exhaust chimney installed at the inlet of the kiln. This leads the tiles entering in the kiln to have a strong thermal shock, from about $50\,^{\circ}C$ to $450\,^{\circ}$–$500\,^{\circ}C$. Thermal effects in this step of firing process are the major responsible of inks contribution to VOC emissions at chimneys.

## 2. Materials and methods

### 2.1. Samples

We collected 39 inks and 9 common vehicles (re-named as in Table 1), from inks suppliers in the ceramic district of Sassuolo (Italy). For the most part of inks, no information was given about their composition.

Each sample was first characterized by infrared spectroscopy, in order to understand at least the class of the main organic compounds. Then, each sample was analyzed by TG-DTA to study its thermal behavior, to compare inks with common vehicles and to try to hypothesize which phenomena occur during firing.

### 2.2. Infrared spectroscopy

Infrared spectroscopy analysis was carried out by FTIR Spectrometer Jasco FT/IR 4700, in the $4000$–$400\,cm^{-1}$ range, with a spectral resolution of $2\,cm^{-1}$, at room temperature. Both inks and vehicles were analyzed by loading liquid samples directly between two NaCl disks.
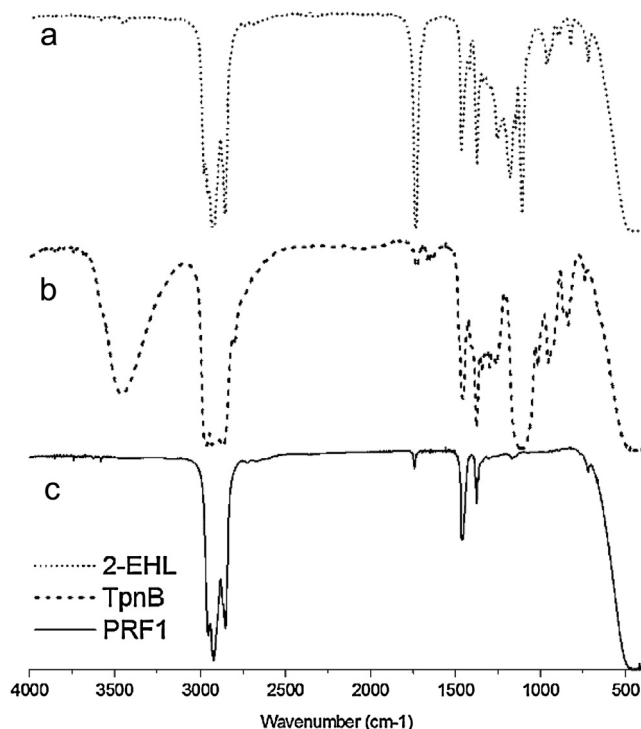


**Fig. 1.** FTIR spectra of a) 2-EHL b) TPnB c) PRF1.

### 2.3. TG-DTA analysis

Simultaneous TG-DTA analysis was performed by Netzsch STA 409 thermal analyzer, with a sensitivity of 0.025 mg for TG and of $0.01\,\mu V$ for DTA.

During the experiment, 10 mg of sample were loaded in an open platinum crucible and heated up from $20\,^{\circ}$ to $700\,^{\circ}C$. Two measurements were carried out for each sample, at two different heating rates: $5\,^{\circ}C/min$ and $50\,^{\circ}C/min$, in static laboratory air.

The slow heating rate was chosen to have a better separation of thermal processes, the fast one to simulate the heating rate of kilns in the ceramic industry.

Because of the good thermal conductivity of our samples and because of the low quantities of samples, an empty open platinum crucible was used as reference.

## 3. Results and discussion

### 3.1. Infrared spectroscopy

Regarding vehicles, esters (2-EHS, EHC, CCT, 2-EHL) (Fig. 1a) are characterized by C=O stretching between 1737 and $1740\,cm^{-1}$, $C(O)$—O—R vibrations between 1150 and $1170\,cm^{-1}$ and O—C—C vibrations between 1100 and $1120\,cm^{-1}$. Also symmetrical and asymmetrical stretchings of saturated C—H ($2960$–$2855\,cm^{-1}$), asymmetrical deformations of $CH_3$ and deformations of $CH_2$ ($1464$–$1463\,cm^{-1}$) and symmetrical deformation of $CH_3$ are visible.

IR spectra of TPM and TPnB (Fig. 1b) show typical signals of —OH vibrations ($3475$–$3460\,cm^{-1}$) and C—O—C vibrations of ethers ($1113$, $1010\,cm^{-1}$), together with vibrations of saturated —$CH_3$ and —$CH_2$.

IR spectra of PRF1 (Fig. 1c) and PRF2 show just —$CH_3$ and —$CH_2$ vibrations ($2953$-$2853$, 1460, 1376, $720\,cm^{-1}$), as expected [8,9].

Poor differences were recognizable between IR spectra of compounds of the same classes (e.g., the 4 esters).