DESIGN OF INKJET INK FORMULATION FOR REDUCING VOCS AND ODOURS IN THE CERAMIC TILE MANUFACTURING PROCESS (VITALIS)

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ABSTRACT

The technology change involved in incorporating inkjet printing systems into the ceramic tile sector has led, among other things, to a significant reduction in manufacturing costs and increase in production capacity, as well as to achievement of a greater level of end-product customisation, ultimately prevailing over and, almost

completely, replacing the other decorating techniques (screen printing, flexography, and rotogravure) used till then in this context.

In view of the current, growing need to increase the degree of digitalisation in the ceramic tile manufacturing process (FULL DIGITAL), together with the growing need to produce ever-larger ceramic tiles, it is vital, among others, not only to adapt inkjet technology to these new formats, but also to reformulate and develop new inkjet ink compositions, owing to the demand for deposition of larger amounts and use of different organic solvents that irremediably entail emission of VOCs and generation of odours in the thermal treatment stage of the developed ceramic product.

It is precisely the persistence of certain constraints entailed by the use of water in inkjet ink formulations, owing to the use of piezoelectric printheads, that makes this study particularly important, while at the same time providing it with an innovative character, it being of great interest for the ceramic tile sector.

The VITALIS research project thus seeks to develop new strategies in inkjet ink formulation that, applied to ceramic tile decoration, are able to clearly and satisfactorily enhance manufacturing process sustainability, significantly reducing environmental impact and odour generation in order to meet regulatory limits. The study therefore examines the impact of different solvents on the physical and chemical properties of the formulated inkjet inks (viscosity, particle size, colloidal stability, printability, etc.), as well as on VOC emissions and odours in the firing cycles customarily used in the ceramic tile industry.

1. RESEARCH BACKGROUND AND CONTEXT

The decoration of surfaces of varying chemical nature (plastics, wood, ceramics, glass, cardboard, paper, and metal) by different application techniques (screen printing, flexography, rotogravure, and inkjet printing) entails formulating and developing ink compositions that must adapt both to the type of substrate to be decorated and to the application and technology to be used, in addition to the intended use of the finished surfaces.

Although this entire adaptation process will largely condition the final properties of the developed applications, the role played by the chemical nature of the components making up the prospective ink formulations is of vital importance in meeting European and national regulations in force.

Thus, for example, as set out in The European Printing Ink Association (EUPIA), Swiss Ordinance RS817.023.21, and Nestlé Packaging list, restrictions are in place on the use of certain groups of different types of components of varying chemical nature in decorating and printing materials and surfaces that are going to be in direct contact with food, as these components are deemed highly pollutant and harmful (odours, generation of vapours, etc.) for human beings. Thus, contact of these types of components (plastic, paper, cardboard, metal packaging, etc.) with the foods they contain entails a series of risks that, in most cases, endanger human health and safety.

In the case of ceramic materials, however, there is obviously no such pollutant or harmful contact. Nevertheless, ceramic materials are affected by Directive 2010/75/EU of the European Parliament and the Council, of 24 November 2010, on industrial emissions during the manufacturing process, known as the Industrial Emissions Directive (IED).

The above leads to an obvious question: What emissions occur in the ceramics manufacturing process? There are many such emissions: water, carbon dioxide, carbon monoxide, nitric and nitrous oxide, sulphides, hydrochlorides, fluorides, hydrocarbons, formaldehyde, acetaldehyde, ammonia, etc.). However, in the ceramic industry, the use, mainly, of different raw materials of an organic nature in the compositions of the tile body, engobe, and glaze, as well as in the digital decoration of ceramic tiles, gives rise to emissions of different gas pollutants when the gases are exhausted from the decoration lines and firing kilns. Therefore, the main objective of the present study was to determine the following emissions:

- **Volatile organic compounds** (VOCs) defined, according to Directive 1999/13/EC, as any compound of an organic nature having, at 293.15 K, a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under particular conditions of use.

  From a normative standpoint, VOC emissions are not envisaged in the BREF document for ceramics on best available techniques. VOCs are only mentioned generally, being identified as possible gaseous pollutants generated in the firing stage in the case of ceramic tile manufacture.

  The primary preventive measures proposed for mitigating emission of these pollutants include reducing the precursors (additives, binders, plasticisers, inks, etc.) present in the starting raw materials.

- **Formaldehyde**. This is a volatile organic compound (VOC) that behaves as a colourless gas at ambient temperature. However, its emission in various industrial processes, such the ceramic process, causes mucous membrane and tissue irritation and can lead to carcinogenic diseases.

- **Odoriferous emissions** from the burnout of organic substances during the thermal treatment stage. They exhibit low olfactory thresholds, so that they can lead to olfactory annoyances in the production plant itself or even in nearby towns. In this case, the reference method for odour measurement is based on standard UNE-EN 17325, which enables quantification of odours in European odour units, ouE/m3.

  There is currently no emission limit value for odour emission relating to ceramic materials use in the reference BREF or in the Integrated Environmental Authorisations (IEAs) granted to ceramic tile manufacturing companies in Spain and Italy.

Preliminary considerations are particularly important, as the incorporation of inkjet printing systems in the ceramic tile sector, which has practically prevailed over traditional tile decorating techniques (screen printing, flexography, and rotogravure), has not only contributed significantly to raising process productivity and reducing manufacturing costs, but also to developing new textures, finishes and, in short, to providing the finished ceramic product with new qualities thanks to the current growing need to increase the degree of digitalisation of the ceramic manufacturing process (FULL DIGITAL).

The inks used in the ceramic sector are thus generally made up of complex mixtures consisting, mainly, of a solids component of inorganic nature comprising (singly or jointly) inorganic pigments, refractory materials, and/or ceramic frits (25–

55(wt)%), solvents of different chemical nature (45–65(wt)%), and different additives: dispersants, stabilisers, and/or visco-depressers (1–10(wt)%). Of all these, as a result of their greater contribution in the formulation, it is precisely the chemical nature of the solvents used in the formulation (and their percentage) that, even though they may display important biodegradability indices and not need hazard pictograms, entail certain environmental problems as their organic nature irremediably gives rise to VOC emissions, as well as to odour generation in the thermal treatment stage. This fact, together with the growing need to produce ever-larger ceramic tiles, requires actions in designing digital inkjet ink and/or product formulations aimed at reducing human vulnerability and environmental impact.

In view of the above, and the absence of studies on the issues in point, Lamberti, S.p.A., and Instituto de Tecnología Cerámica (ITC), understanding and aware of the above considerations, have sought to work together and design, in this research study, new strategies aimed at formulating digital inkjet inks and/or other products that exhibit the required technical and technological characteristics of suspension printability with those of environmental sustainability and human integrity as a result of the use in their compositions of solvents of different organic nature.

2. EXPERIMENTAL METHODOLOGY

2.1. MATERIALS USED

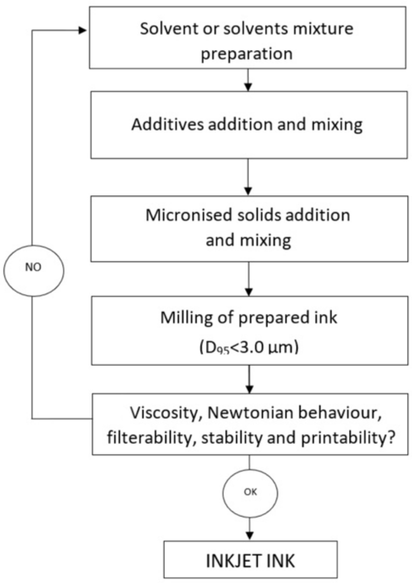
The materials used in the formulation of the test inks are set out in Table 1:

Component	Reference	Functionality	Chemical description
Solvent	Printojet SB-1	Milling and dilution solvent	100% Standard fatty acid ester
	Printojet SB-2	Milling and dilution solvent	100% Modified fatty acid ester
	Printojet SB-3	Milling and dilution solvent	Mineral oil
	Printojet SB-4	Milling and dilution solvent	100% glycol ether
	Printojet WB-5	Milling solvent	Water-based
	Printojet SB-6	Milling and dilution solvent	100% Fractionated fatty acid ester
	Printojet SB-7	Milling and dilution solvent	Glycol ether/non-fatty acid ester B= 55/45
	Printojet SB-8	Milling and dilution solvent	Glycol ether/modified glycol = 10/90
	Printojet SB-9	Milling and dilution solvent	Glycol ether/non-fatty acid ester A= 45/55
Additives	Fluijet SB	Organic system dispersant additive	Synthetic polymer
	Fluijet WB	Aqueous system dispersant additive	Synthetic polymer
Solids	Digital glaze	Refractories and fluxes	Inorganic compound

Table 1. *Components in the VITALIS study.*

2.2. INK PREPARATION FOR INKJET TECHNOLOGY

The stages carried out in preparing, formulating, and milling the inkjet inks being studied are set out below:



Component	Total Carbon (%)
Printojet SB-1	76.80
Printojet SB-2	75.70
Printojet SB-3	84.70
Printojet SB-4	63.10
Printojet SB-5	19.50
Printojet SB-6	80.40
Printojet SB-7	60.30
Printojet SB-8	64.70
Printojet SB-9	65.10
Fluijet SB	73.80
Fluijet WB	26.20
Digital glaze	0.00

Figure 1. *Ink preparation (left) and total carbon (%) of the components by TruSpec-CHNS (right).*

Ink ref.	Milling solvent	Dispersant
INK-1	Printojet SB-1	Fluijet SB
INK-2	Printojet SB-2	Fluijet SB
INK-3	Printojet SB-3	Fluijet SB
INK-4	Printojet SB-4	Fluijet SB
INK-5	Printojet WB-5	Fluijet WB
INK-6	Printojet SB-6	Fluijet SB
INK-7	Printojet SB-7	Fluijet SB
INK-8	Printojet SB-8	Fluijet SB
INK-9	Printojet SB-9	Fluijet SB

Table 2. *Components used in test inkjet ink preparation.*

Ink ref.	SC (wt)%	Solvent (wt)%	Dispersant (wt)%	Theor. total carbon (%) (Calculated from Figure 1, right)
INK-1	44.2	50.0	5.8	42.6
INK-2	44.1	50.2	5.7	42.2
INK-3	44.0	51.6	4.4	46.9
INK-4	44.0	51.6	4.4	35.8
INK-5	44.0	47.2	8.8	17.9
INK-6	44.0	50.7	5.3	44.7
INK-7	44.0	50.7	5.3	34.5
INK-8	44.0	50.7	5.3	36.7
INK-9	44.0	50.7	5.3	36.9

Table 3. *Inkjet ink formulations of inks developed at constant solids content (SC).*

2.3. DETERMINATION OF THE PHYSICAL PROPERTIES OF THE DEVELOPED INKS

The physical characterisations performed to determine the technical feasibility of the developments in the inkjet printhead were as follows:

- Viscosity, density, PSD, colloidal stability, suspension filterability.
- Theoretical and experimental printability with DIMATIX SG 1024 HFL inkjet printhead.

2.4. DETERMINATION OF THE CHEMICAL PROPERTIES OF THE COMPONENTS AND FORMULATED INKJET INKS

The chemical characterisations performed are detailed below:

- Chemical analysis of the solids component used.
- Identification of the thermogravimetric curves of the test solvents.
- Total carbon content of the solids component, solvents, and additives used, and the formulated and deposited inkjet inks on the test ceramic body at constant 25 g/m^2 laydown using a LECO TruSpec (CHNS) laboratory analyser.
- Total VOC (TVOC) and formaldehyde in a laboratory electric muffle kiln and pilot plant gas kiln. Inkjet ink laydown at 25 g/m^2. In the former case, a flame ionisation detection (FID) measurement apparatus was used according to standard UNE EN 12619:2013, whereas, in the latter, the FTIR technique based technical specifications CEN/TS 1737:2019 and Technical Guidance Note M22 of the UK Environmental Agency was used.
- Odoriferous emissions in pilot plant gas kilns of solvents used in the developed inkjet inks deposited by inkjet processes on test substrates at 25 g/m^2, through the dynamic olfactometry technique based on standard UNE-EN 13725/03 and UNI-EN 13725/04.

3. RESULTS

3.1. FORMULATION AND DEVELOPMENT OF INKJET INKS AT SC=44(WT)%

Table 4 sets out the milling conditions used in reducing the particle size of the formulated inks, modifying the dispersant content.

Ink ref.	Time (min)	KWh/kg solids
INK-1	65	1.08
INK-2	68	1.08
INK-3	73	1.08
INK-4	68	1.08
INK-5	68	1.08
INK-6	72	1.08
INK-7	71	1.08
INK-8	72	1.08
INK-9	80	1.08

Table 4. *Developed ink milling conditions at constant solids content (SC) (44(wt)%).*

3.2. DETERMINATION OF THE PHYSICAL PROPERTIES OF THE DEVELOPED INKS

Table 5 details the physical properties of each developed ink. Furthermore, the following figures display the behaviour during printing of the developed inks.

Ink ref.	Density at 25ºC (g/cm³)	D97 (µm)	Viscosity at 45ºC (mPa·s)	Sedimentation 50ºC (%) (MLS)	Agglomeration 50ºC (%) (MLS)	Re	We	Oh	Z
INK-1	1.300	2.120	16.53	3.20	0.20	34.3	141.6	0.35	2.9
INK-2	1.300	2.000	15.48	5.50	0.10	36.0	139.4	0.33	3.0
INK-3	1.210	1.800	9.81	3.10	0.10	49.2	137.7	0.24	4.2
INK-4	1.370	2.310	11.70	7.00	0.15	44.2	148.6	0.28	3.6
INK-5	1.550	1.420	17.58 (at 35ºC)	7.80	0.20	36.4	114.3	0.29	3.4
INK-6	1.293	2.170	22.47	6.80	0.18	24.2	137.8	0.49	2.1
INK-7	1.406	1.960	24.60	2.80	0.15	23.8	146.6	0.51	2.0
INK-8	1.388	2.210	27.09	2.90	0.15	21.5	145.7	0.56	1.8
INK-9	1.366	1.960	23.49	3.00	0.15	24.4	143.1	0.49	2.0
Typical theoretical values of DOD dimensionless moduli according to the literature [2]						2-50	50-150	0.1-1	1-10

Table 5. *Physical properties of the inkjet inks prepared at SC=44(wt)%. Filtration at 5 µm.*

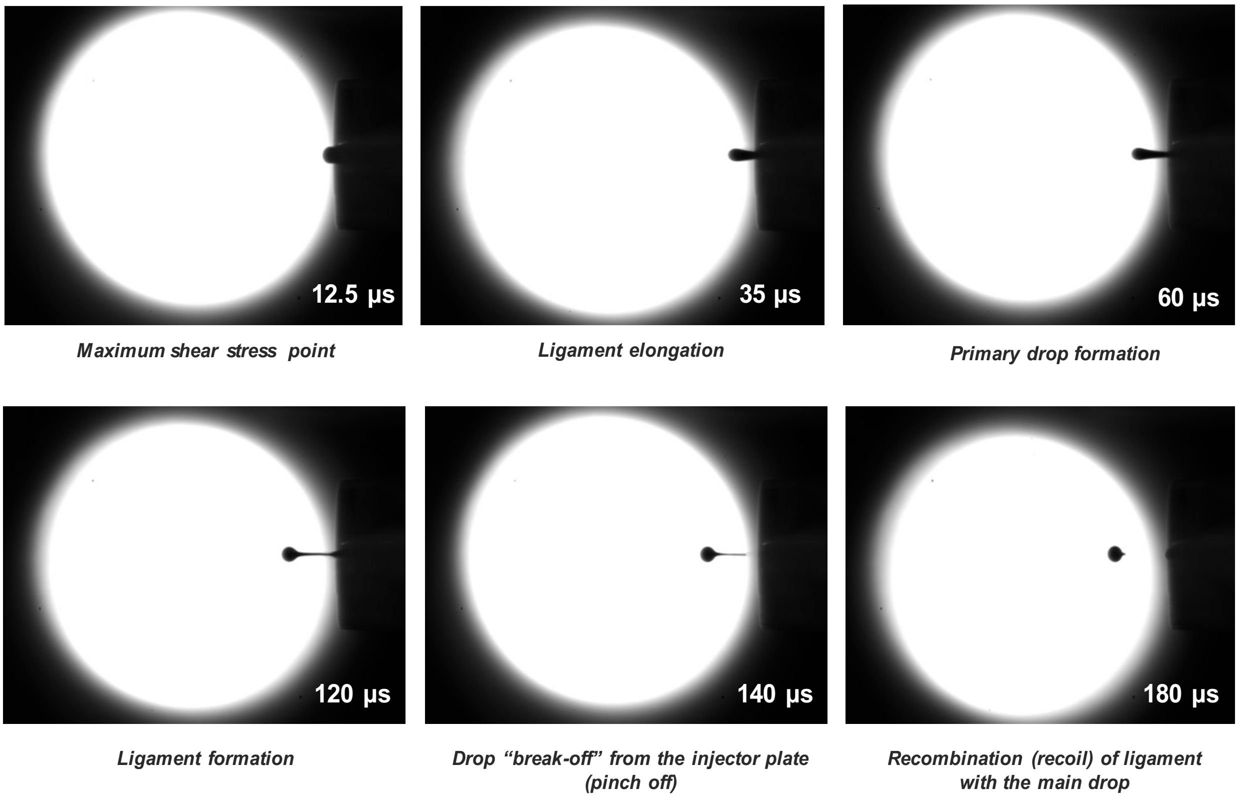


Figure 2. *Inkjet ink behaviour during jetting using a Dimatix SG 1024 HFL DOD printhead. Stroboscopic analysis.*

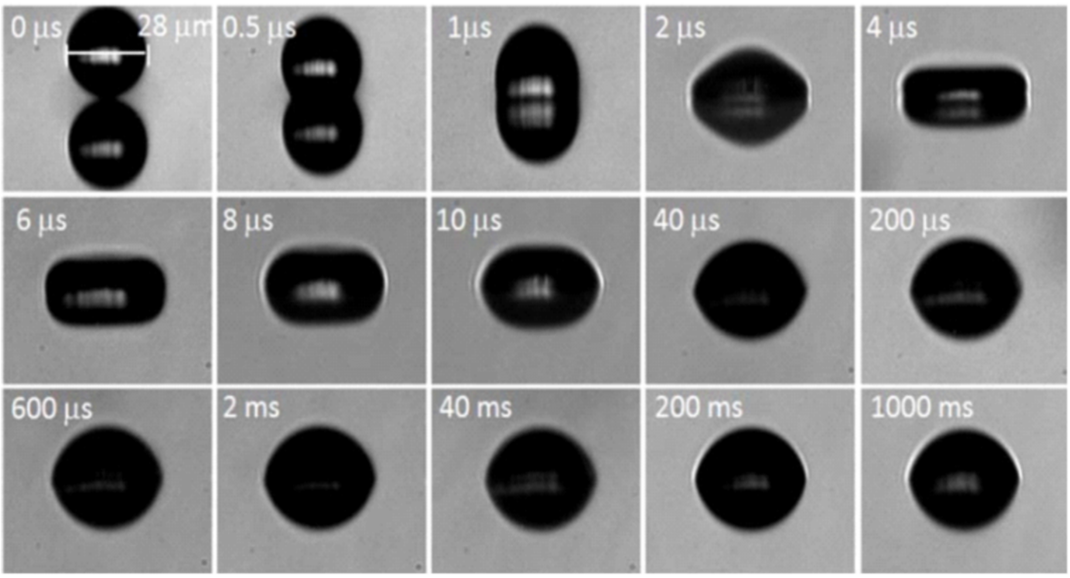


Figure 3*. Ink drop behaviour during impact on a solid substrate using inkjet technology. High speed camera analysis (Fiducial camera).*

The suitability of the developed inks for use in the proposed technology was verified by the above results.

3.3. DETERMINATION OF THE CHEMICAL PROPERTIES OF THE DEVELOPED INKS

3.3.1. CHEMICAL ANALYSIS OF THE SOLIDS COMPONENT AND THERMOGRAVIMETRIC ANALYSIS (TGA) OF THE TEST SOLVENTS

The chemical analysis of the solids component used, as well as the thermogravimetric curves of the test solvents, is detailed below.

SiO_2	63,0	%
Al_2O_3	7,9	%
B_2O_3	1,96	%
Fe_2O_3	0,13	%
CaO	13,6	%
MgO	1,28	%
Na_2O	0,87	%
K_2O	3,54	%
TiO_2	0,05	%
ZrO_2	0,19	%
BaO	0,31	%
Li_2O	<0,01	%
PbO	0,64	%
ZnO	6,4	%
HfO_2	<0,01	%
P_2O_5	0,03	%
SrO	0,10	%
MnO	0,01	%

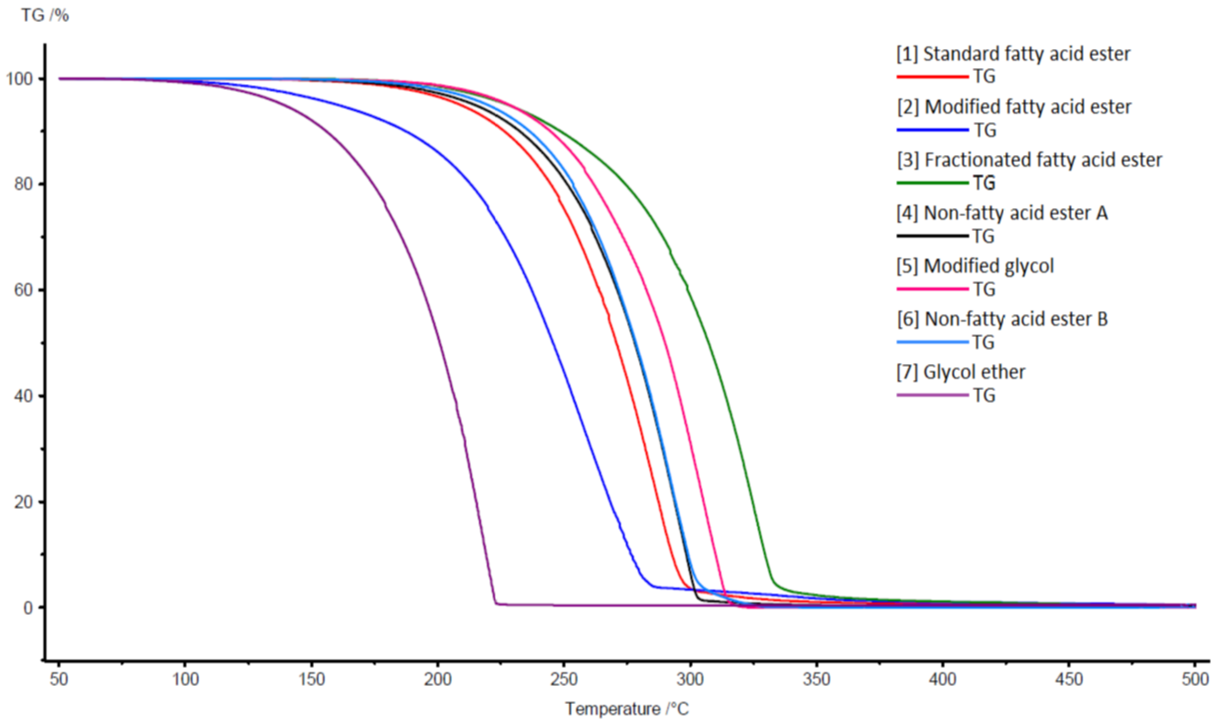


Figure 4. *Thermogravimetric curves of the test solvents.*

3.3.2. DETERMINATION OF TOTAL CARBON BY THE LABORATORY ANALYSER (CHNS)

Table 6 details ink total carbon (expressed in ppm) and applied at 25 g/m^2 on porcelain tile bodies by inkjet technology.

Ink ref.	Total carbon (ppm)	% decrease (relative to INK-3)
INK-1	2500	3.85
INK-2	2500	3.85
INK-3	2600	0.00
INK-4	1700	34.62
INK-5	900	65.38
INK-6	2500	3.85
INK-7	1800	30.77
INK-8	2100	19.23
INK-9	2400	7.69

Table 6. *Total carbon (ppm) by the laboratory analyser of the developed inks at 44(wt)%.*

3.3.3. DETERMINATION OF TVOC AND FORMALDEHYDE EMISSION BY FID AND FTIR, RESPECTIVELY, USING A LABORATORY ELECTRIC MUFFLE KILN AND A PILOT PLANT GAS KILN

Table 7 shows the maximum static and dynamic emission values (average values) obtained in a laboratory electric muffle kiln and a pilot plant gas kiln of the total volatile organic component and formaldehyde.

Ink ref.	Laboratory electric muffle kiln		Pilot plant gas kiln	
	TVOC (mg/Nm^3)	CHOH (mg/Nm^3)	COVT (mg/Nm^3)	CHOH (mg/Nm^3)
INK-1	562	-	14	4
INK-2	498	-	-	-
INK-3	829	-	-	-
INK-4	558	-	-	-
INK-5	214	-	-	-
INK-6	462	95	11	3
INK-7	720	116	13	3
INK-8	527	157	-	-
INK-9	677	136	-	-

Table 7. *TVOC and formaldehyde (CHOH) values of the inkjet inks formulated at 44(wt)%.*

3.3.4. DETERMINATION OF ODOUR EMISSION FROM THE SOLVENTS USED

Table 8 details the odour levels of the solvents used in the test inkjet ink compositions.

Component	Reference	ou_E/m^3
Solvent	Printojet SB-1	2100
	Printojet SB-2	2450
	Printojet SB-3	2800
	Printojet SB-4	1600
	Printojet WB-5	450
	Printojet SB-6	1380

Table 8. *Odour emission values of the test solvents.*

4. INTERPRETATION OF RESULTS

4.1. EFFECT OF DISPERSANT ADDITION ON TOTAL CARBON DETERMINED BY THE LABORATORY ANALYSER (CHNS)

To ascertain whether the dispersant addition to the inkjet suspensions contributed to the total carbon concentration in the laboratory analyser (CHNS), different inks were prepared at 44(wt)% modifying the dispersant addition and analysing emitted total carbon. (Values compared with those detailed in Table 3).

Ink ref.	SC (wt)%	Solvent (wt)%	Dispersant (wt)%	Theoretical total carbon (%)
INK-1	44.2	50.0	5.8	42.6
	44.2	47.0	8.8	42.6
INK-2	44.1	50.2	5.7	42.2
	44.1	47.2	8.7	42.2
INK-3	44.0	51.6	4.4	46.9
	44.0	48.6	7.4	46.6
INK-4	44.0	51.6	4.4	35.8
	44.0	48.6	7.4	36.1
INK-5	44.0	47.2	8.8	17.9
	44.0	44.2	11.8	34.3
INK-6	44.0	50.7	5.3	44.7
	44.0	47.7	8.3	44.5
INK-7	44.0	50.7	5.3	34.5
	44.0	47.7	8.3	34.9
INK-8	44.0	50.7	5.3	36.7
	44.0	47.7	8.3	37.0
INK-9	44.0	50.7	5.3	36.9
	44.0	47.7	8.3	37.2

Table 9. *Inks developed modifying the dispersant addition in the ink formulation.*

Table 10 details the influence of the amount of dispersant added to each developed ink on the total carbon content obtained in the inks deposited at 25 g/m^2 on the test substrate after quantitative analysis. (Values compared with those detailed in Table 6).

Ink ref.	Dispersant (wt)%	Total carbon (ppm)
INK-1	5.8	2500
	8.8	2500
INK-2	5.7	2500
	8.7	2500
INK-3	4.4	2600
	7.4	2600
INK-4	4.4	1700
	7.4	1700
INK-5	8.8	900
	11.8	900
INK-6	5.3	2500
	8.3	2500
INK-7	5.3	1800
	8.3	1800
INK-8	5.3	2100
	8.3	2100
INK-9	5.3	2400
	8.3	2400

Table 10. *Effect of the dispersant addition to the inkjet inks on total carbon content (ppm).*

As may be observed in the above results, the low dispersant additions in the developed inkjet ink formulations did not alter the total carbon results obtained in the test samples.

4.2. RELATIONSHIP BETWEEN FORMULATED INK THEORETICAL TOTAL CARBON CONTENT AND TOTAL CARBON DETERMINED BY THE LABORATORY ANALYSER (CHNS)

On plotting the theoretical total carbon values set out in Table 3 and the concentrations obtained by the laboratory analyser (CHNS) of the formulated inkjet inks (Table 6), a linear relationship was found between these parameters, as shown in Figure 5.

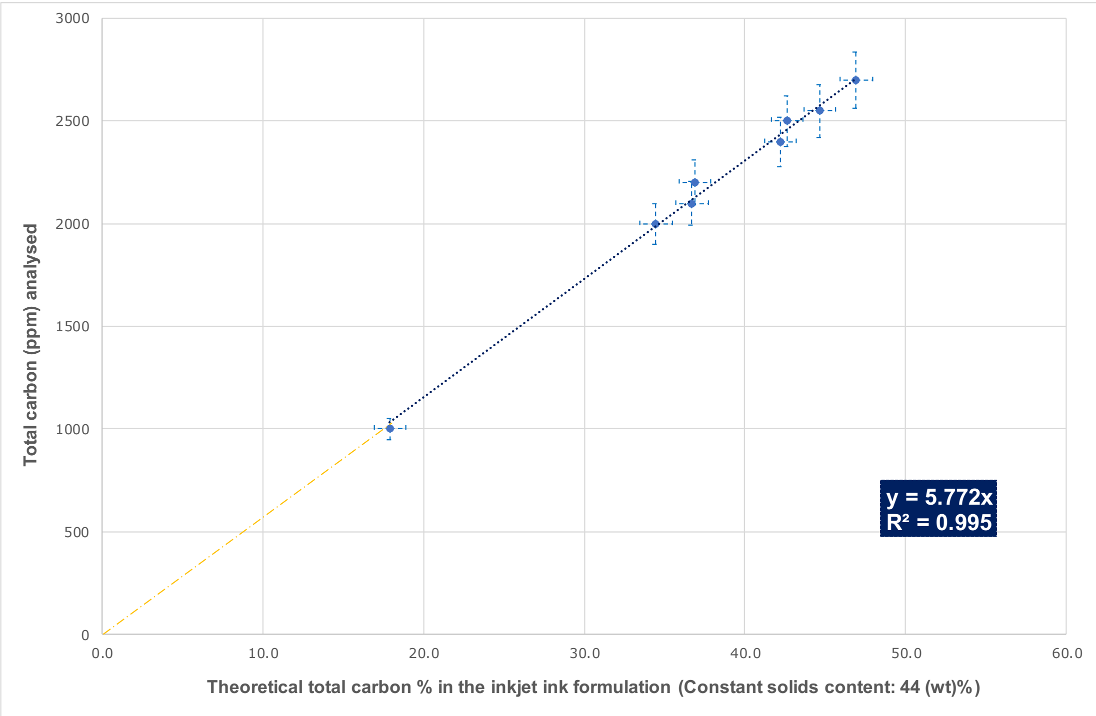


Figure 5. *Linear relationship of theoretical total carbon content and analysed total carbon concentration (ppm) of the inkjet inks developed at constant solids content (44(wt)%).*

4.3. EFFECT OF INK DENSITY ON TOTAL CARBON CONCENTRATION DETERMINED BY THE LABORATORY ANALYSER (CHNS)

4.3.1. INKJET INK FORMULATION AT CONSTANT DENSITY (1.300 g/cm^3)

In this study, the inkjet inks were formulated and developed, operating under conditions of constant solids content (44(wt)%), to enable the effect of the chemical nature of the different solvents used on the physico-chemical properties of the suspensions, as well as on the emissions generated during the thermal treatment stage, to be verified. However, during industrial inkjet ink manufacturing processes, it is often possible to operate under working conditions of constant density, so that it was necessary to perform a meticulous study of the influence of ink density on the resulting total carbon concentration by a carbon analyser.

To do so, new ink compositions were prepared such that a final density of 1.300 g/cm^3 was obtained. (The suitability of the newly developed compositions was verified for their use in the proposed printing technology).

Ink ref.	SC (wt)%	Solvent (wt)%	Dispersant (wt)%	Theoretical total carbon (%)
INK-1	44.2	50.0	5.8	42.645
INK-2	44.1	50.2	5.7	42.228
INK-3	49.5	44.5	6.0	42.046
INK-4	38.9	56.4	4.7	39.057
INK-5	23.3	73.9	2.8	31.905
INK-6	45.4	49.1	5.5	43.542
INK-7	36.7	58.9	4.4	38.764
INK-8	38.0	57.5	4.5	40.597
INK-9	36.6	59.0	4.4	41.591

Table 11. *Compositions at constant density modifying the solvent proportioned in the ink formulations.*

Ink ref.	D97 (µm)	Viscosity at 45ºC (mPa·s)	Sedimentation 50ºC (%) (MLS)	Agglomeration 50ºC (%) (MLS)	Re	We	Oh	Z
INK-1	2.120	16.53	3.20	0.20	34.3	141.6	0.35	2.9
INK-2	2.000	15.48	5.50	0.10	36.0	139.4	0.33	3.1
INK-3	2.300	12.39	2.90	0.10	47.8	147.9	0.25	3.9
INK-4	2.060	10.02	2.50	0.20	56.3	140.9	0.21	4.7
INK-5	1.460	25.55 (at 35ºC)	3.70	0.40	21.0	134.2	0.55	1.8
INK-6	1.970	18.36	2.90	0.40	31.2	143.3	0.38	2.6
INK-7	2.200	17.22	3.40	0.35	31.2	134.2	0.37	2.7
INK-8	2.330	18.84	3.60	0.20	30.5	143.4	0.39	2.5
INK-9	2.000	10.02	2.90	0.15	53.4	133.8	0.22	4.6
Typical theoretical values of DOD dimensionless moduli according to the literature [2]					2-50	50-150	0.1-1	1-10

Table 12. *Physical properties of the inkjet inks prepared at 1.300 g/cm^3. Filtration 5 µm.*

The above results confirmed the suitability of the developed inks, operating at constant density (1.300 g/cm3), for use in inkjet printheads.

4.3.2. INK TOTAL CARBON CONTENT AT 1.300 G/CM^3 USING THE LABORATORY ANALYSER (CHNS)

Once the technical feasibility of the inks developed at constant density had been verified, total carbon content was determined by the laboratory analyser (CHNS).

Ink ref.	SC (wt)%	Total carbon (ppm)
INK-1	44.4	2500
INK-2	44.3	2500
INK-3	49.5	2300
INK-4	38.9	1900
INK-5	23.3	1600
INK-6	45.4	2400
INK-7	36.7	2000
INK-8	38.0	2300
INK-9	36.6	2700

** Note that the formulated compositions INK-1 and INK-2 at 44(wt)% already exhibited a final density of 1.300 g/cm^3.*

Table 13. *Total carbon (ppm) determined by the laboratory analyser of the inks developed at 1.300 g/cm^3.*

Using the above values, performing a linear plot of the results corresponding to the analysed total carbon (Table 13) and the theoretical total carbon of the inkjet ink compositions developed at constant density (Table 11), yielded the following figure.

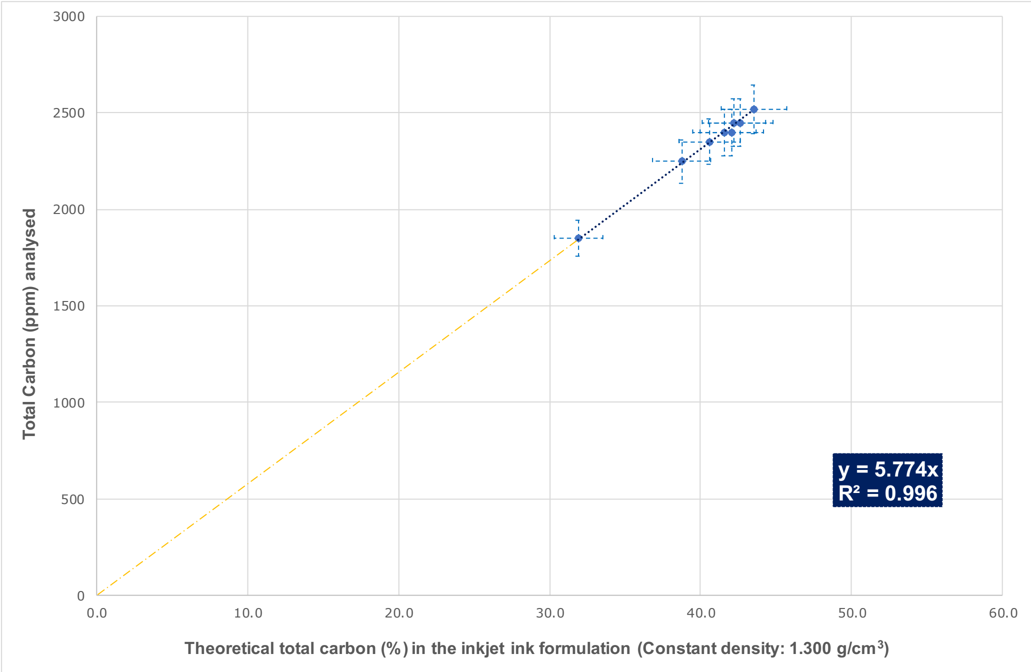


Figure 6. *Linear relationship between the theoretical total carbon content and analysed total carbon concentration (ppm) of the inkjet inks developed at a constant density of 1.300 g/cm3.*

The results obtained show, once again, that the behaviour of the analysed total carbon concentration and of the theoretical carbon content in the inks at constant density was linear and that its slope was similar to that depicted in Figure 5.

5. CONCLUSIONS

The results obtained in the present study allow the following conclusions to be drawn:

- The materials and components used in this study enabled development of suitable inkjet inks for use in inkjet printing systems.
- The addition of larger additions of dispersants did not significantly alter the physical and chemical properties of the developed inkjet inks, no variations being observed in printability and total carbon emissions determined by a laboratory analyser.
- The solids component used did not add to the carbon contribution in the formulated ink compositions.
- Of all the solvents used in this study, those that exhibited a higher decomposition temperature may be expected to yield lower TVOC and formaldehyde emission values in the kiln; this was confirmed by the results obtained for INK-6 (in the pilot plant kiln).
- Thermogravimetric analysis (TGA) allowed performance of an initial validation of the suitability of the test solvents for use in inkjet ink formulations, pending verification of the results obtained for the TVOC and formaldehyde emissions on a pilot plant scale.
- A direct relationship was obtained between carbon content in the theoretical formulation of the formulated inks and carbon concentration (expressed in ppm) obtained by a laboratory analyser. This relationship, represented by a linear equation without ordinate at the origin, allowed satisfactory reproduction of a wide range of carbon contents in the developed inks and, hence, use of solvents of different chemical nature. These results were applicable to formulation methodologies both at constant solids content and at constant density.
- Of the determinations on total carbon content using a laboratory analyser, the inks formulated from vehicles based on glycol ether and those that contained water in their composition exhibited the lowest total carbon levels. In turn, the inks formulated from paraffin and ester exhibited the highest values. This was confirmed by the carbon content in the solvents used in preparing the test inks.
- The technique proposed for determining total carbon in the developed inks by a laboratory analyser (CHNS) satisfactorily enabled identification of the formulation solvent that exhibited the lowest carbon content from a laboratory-level work methodology perspective, without needing to perform preparations or trials at an industrial level and pilot plant scale. Similarly, if their contribution in the formulation and carbon input is important, these

results can be transferred to the other components included in the formulations (solids, additives, etc.).

- The tests conducted in a laboratory electric muffle kiln and pilot plant gas kiln on TVOC emissions indicated that the aqueous solvent and fractionated fatty acid ester were the most promising alternatives for inkjet ink formulation, in relation to standard ink Ink-1.
- The methodology adopted for determining TVOC and formaldehyde emissions in a laboratory electric muffle kiln and pilot plant gas kiln allowed differences and comparisons in emissions between the different developed inkjet ink formulations to be established.
- It was not possible to establish a direct relationship between carbon content determined by a CHNS laboratory analyser (linear relationship with theoretical carbon present in the formulated inks) and the TVOCs emitted in a laboratory electric muffle kiln and pilot plant gas kiln, as the former determined carbon released with temperature in the form of CO_2, whereas the latter corresponded to the emitted amount of carbon not deemed CO_2.
- It was not possible to establish a direct relationship between the results of the emissions in a laboratory electric muffle kiln and in a pilot plant gas kiln, as the former were performed by a static procedure, whereas the latter were conducted in a dynamic sampling process.
- In the odoriferous determinations carried out in the pilot plant gas kiln of the solvents used, differences were established among these, the vehicles containing water in their composition and the fractionated fatty acid ester exhibiting the lowest emissions, while the mineral oils, glycol ether and those based on functional ester groups (standard and modified fatty acid, and non-fatty acid) displayed the highest values.
- To design inkjet ink formulations that emit lower TCOVs, formaldehyde (CHOH), and odours, it is necessary to use vehicles of an aqueous nature and fractionated fatty acid ester.

6. REFERENCES

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