FEASIBILITY STUDY OF NYNAS SPECIALTY NAPHTHENIC OILS FOR CERAMIC INKJET INKS

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ABSTRACT

A comparison study is done to evaluate the feasibility of naphthenic oils used as liquid vehicle in ceramic inkjet ink formulations. The results reveal that the viscosity of a vehicle is an essential property which impacts the key properties of ceramic inkjet inks. Low viscosity naphthenic oils exhibit excellent performance as well as selected ether and ester in the developed ink formulations in terms of not only the right viscosity, density and dynamic surface tension, but also the colloidal stability and printability before and after accelerated ageing.

1. INTRODUCTION

In the past two decades, inkjet printing technology has developed fast in the ceramic industry, and now is a leading technology in ceramic tile decoration to obtain surfaces with excellent technical and aesthetic properties. The reasons are its great advantages compared to traditional printing technologies such as screen printing, flexography, and rotogravure. The successful implementation of this promising technology in ceramic production is greatly dependent on development of specific devices (printer, printhead) and raw materials. Among them, the development of ceramic inkjet inks with the right chemical and physical properties plays a key role.

Ceramic inkjet inks must satisfy a wide range of requirements, regarding not only their behaviour during the jetting cycle but also their performance before and after the printing stage [1]. Inks must be stable during storage and transportation when sedimentation and agglomeration phenomena should be avoided. The ink should behave in the desired way on the unfired ceramic substrate. The ink should maintain thermal stability at working temperature and exhibit very low evaporation. The ink must pass the small-sized membrane filter easily and cause no clogging of the nozzles.

A solvent-borne ceramic inkjet ink is comprised of solid particles (pigments, frits, etc.), liquid vehicles, and additives [2]. The vehicle, which accounts for around 50% by weight of the ink formulation, plays a critical role in terms of an ink's chemical and physical properties. The rheological behaviour of an ink during drop and dot formation is greatly dependent on vehicle properties such as viscosity, density, and surface tension. The vehicle also has a great impact on inks colloidal stability under working conditions and during storage, chemical compatibility with device components, and performance after ageing.

Ether and ester are the commonly used vehicles in ceramic inkjet inks. However, the specialty naphthenic oil is also recognized as an appropriate vehicle for this application. In order to have a full overview of the performance of naphthenic oil, ether and ester in ceramic inkjet inks, a comparative study was done by Nynas in collaboration with an external institute.

2. EXPERIMENTS

2.1 FORMULATION AND RAW MATERIALS USED

The formulation and raw materials used in this study are shown in Table 1. Two inks (pink and brown) were prepared with each vehicle. Ether and ester are both widely used products in the market.

MH 9, MH 22 and MH 110 are naphthenic mineral oils that are hydrogenated to a degree that optimizes the solvency by the presence of around 10% mono and di-aromatic structures and 42% naphthenic structures (measured by ASTM D2140) on their hydrocarbon molecules. The hydrogenated products meet the requirements (DMSO extractible compounds<3% by IP 346) for non-carcinogenic products.

SH 9 and SH 90 are naphthenic mineral oils that are severely hydrogenated to remove most aromatic structures, leaving about 2% mono and di-aromatic structures measured with ASTM D2140. Even if most aromatic structures are removed, the high naphthenic contents maintain solvency even though they have a lower solvency compared to MH counterparts. These severely hydrotreated products meet the requirements for incidental food contact according to FDA 178.3620 (b) or (c). They have a watery white appearance and are practically de-odorized.

The test methods of several key properties of ether, ester and naphthenic oils differ according to their product datasheet. For the sake of convenient comparison, key properties of these vehicles were tested by the same methods in the lab and are shown in Table 2. Among them, aniline point is a specification linked to polarity and solvency of naphthenic mineral oils. The lower the value of the aniline point, the higher the polarity and the better the solvency of the oil.

Components	Percentage	Chemicals
Solids	45%	Pink pigments (Ca, Sn, Si)
		Brown pigments (Fe, Cr, Mn)
Liquid vehicles	49.10%	Ether
		Ester
		Naphthenic oil SH 9
		Naphthenic oil MH 9
		Naphthenic oil MH 22
		Naphthenic oil SH 90
		Naphthenic oil MH 110
Dispersant	5.90%	Hyperdispersant

***Table 1**. Formulation and chemicals used in this study*

Liquid Vehicles	Density at 15℃ (g/cm^3)	Viscosity 40℃(cSt)	Aniline point (℃)	Surface tension at 25℃ (mN/m)
Test method	ASTM D4052	ASTM D445	ASTM D611	Modified ASTM D971
Ether	0.973	3.9	≤ -18.3	29.7
Ester	0.971	8.35	≤ -18.3	30.7
SH 9	0.880	8.6	80	29.7
MH 9	0.889	9.0	70	30.0
MH 22	0.901	22.4	77	30.8
SH 90	0.897	84	103	31.4
MH 110	0.916	109	86	31.9

***Table 2.** Key properties of the liquid vehicles*

2.2 INK PREPARATION

The principal operational stages carried out for preparing and milling ceramic inkjet inks are detailed below:

Stage 1. Mixing liquid vehicle, solids and dispersants.

Stage 2. Particle size reduction by a grinding process in a microbead mill reaching a particle size D_{97}<1 µm.

Stage 3. Suitability of the physical properties of the developed ceramic inkjet inks (particle size, viscosity, Newtonian behaviour, density, colloidal stability, filterability and printability).

At the milling stage, the components of mixtures are 55.7% solids, 37.1% vehicle, and 7.2% dispersant. After milling, each of the above prepared concentrates is diluted by its vehicle respectively.

2.3 TESTS

The physical and chemical properties of developed inks are tested to determine their feasibility of ceramic inkjet printing. Details as below:

- Milling process by laboratory microbead mill LABSTAR
- Viscosity by BROOKFIELD DVE VISCOMETER
- Density by a pycnometer (200 g of weight and 100 cc of volume)
- Dynamic surface tension by a bubble pressure tensiometer model BP100 from Kruss
- Particle size distribution by a MALVERN laser diffraction instrument
- Colloidal stability by Turbiscan Lab Expert equipment from the registered trademark Formulaction based on multiple light scattering
- Filterability through a 5 µm filter membrane
- Printability by an INK-TESTER from the registered trademark Personas y Tecnología, equipped with a SEIKO 1536-L industrial printhead
- Accelerated ageing by an INK-TESTER from the registered trademark Personas y Tecnología, equipped with a SEIKO 1536-L industrial printhead after inks were put in an electric oven at 45℃ for 100 days

3. RESULTS AND DISCUSSION

3.1 MILLING PROCESS

Given the same formulation and same milling energy, table 3 shows that the milling time required to achieve the target differs according to different vehicles. It can be seen from figure 1 that the milling time correlates with the viscosity of the vehicles. The lower the vehicle viscosity, the more milling time is required; the higher the vehicle viscosity, the less milling time is required.

Vehicles	Pink ink Time (min)	Brown ink Time (min)	Energy (kWh/kg solid)
Ether	136	110	1.23
Ester	84	104	1.23
SH 9	85	98	1.23
MH 9	78	95	1.23
MH 22	81	80	1.23
SH 90	74	74	1.23
MH 110	67	71	1.23

Table 3. *Milling conditions of the developed inks*

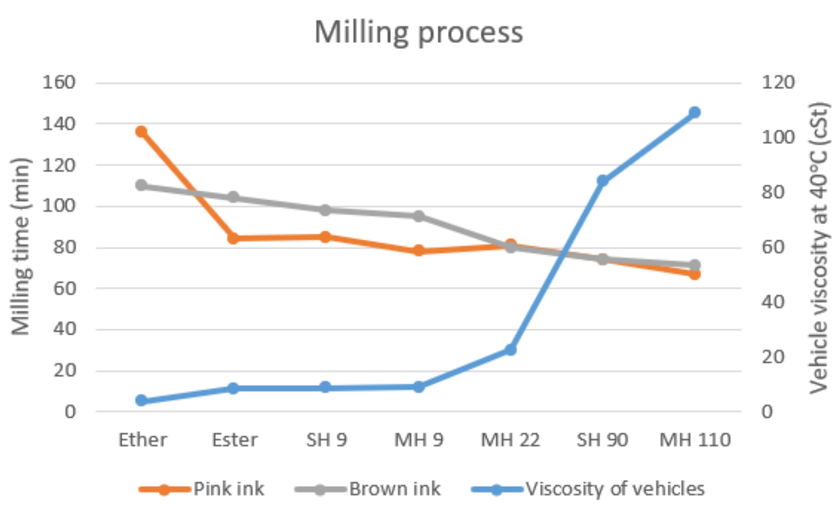

Figure 1. *Correlation between milling time and vehicle viscosities*

3.2 VISCOSITY, DENSITY AND DYNAMIC SURFACE TENSION

Because the viscosities of SH 90 and MH 110 are recognized as too high, the inks prepared by these are not included in the rest of tests. The viscosity, density and dynamic surface tension of the inks prepared by ether, ester, SH 9, MH 9 and MH 22 are listed in table 4.

	Vehicle	Ink viscosity at 45℃ (mPa·s)		Density at 25℃ (g/cm³)	Dynamic surface tension at 45℃ (mN/m)
		12 rpm	20 rpm		
Pink ink	Ether	11.90	10.56	1.421	31.49
	Ester	22.70	21.78	1.414	33.98
	SH 9	22.70	21.30	1.313	34.55
	MH 9	23.35	21.75	1.323	33.38
	MH 22	43.70	*	1.286	38.05
Brown ink	Ether	10.35	9.06	1.433	31.39
	Ester	19.00	18.03	1.413	33.91
	SH 9	21.95	17.25	1.323	33.86
	MH 9	19.40	17.61	1.336	33.72
	MH 22	37.00	*	1.352	37.00

***Table 4**. Viscosity, density and dynamic surface tension of the prepared inks*

As the industry prefers ink viscosity between 10 to 25 mPa·s at 45℃ [2], the inks prepared with SH 9 and MH 9, ether and ester are in the range. The viscosity of the ink prepared with MH 22 exceeds the preferred range when it is used alone as ink vehicle. Figure 2 exhibits the strong correlation between the viscosities of the vehicle and the prepared inks.

With regard to the density, all the inks with Nynas naphthenic oils were in the target range (1.2 to 1.4 g/cm^3) [2]. However, the densities of the inks with ether and ester are higher than 1.4 g/cm^3 due to the relatively higher density of ether and ester. Given the same formulation, the density of ink directly correlates with the density of the vehicle as figure 3 shows.

In terms of dynamic surface tension of ceramic inkjet ink, the industry prefers the value at 25~35 mN/m at 45℃ [2]. The inks prepared with SH 9 and MH 9, ether and ester are in the target range. The dynamic surface tension of the ink prepared with MH 22 exceeds the preferred range slightly when it is used alone as ink vehicle. It was also found that the dynamic surface tension of developed inks correlated closely with the viscosity of vehicles, as figure 4 demonstrates, rather than the surface tension of vehicles.

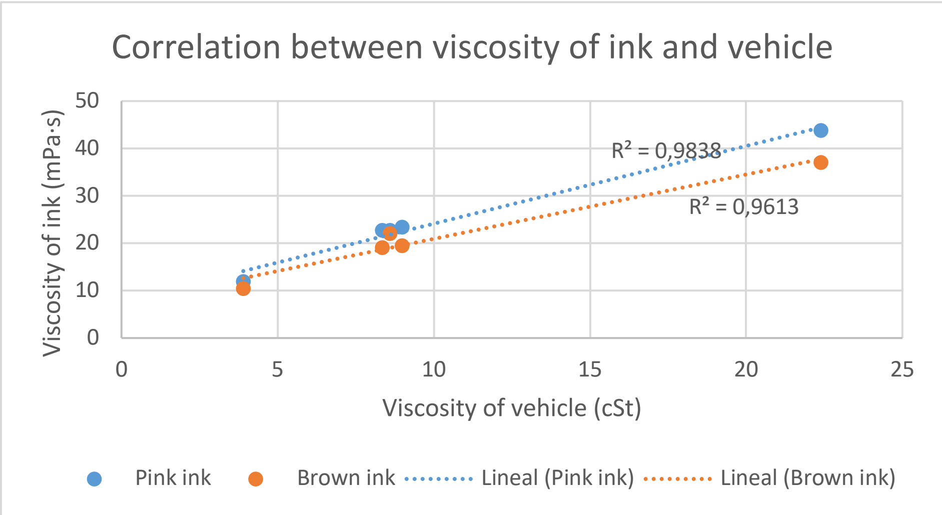

***Figure 2.** Correlation between vehicle and ink viscosities*

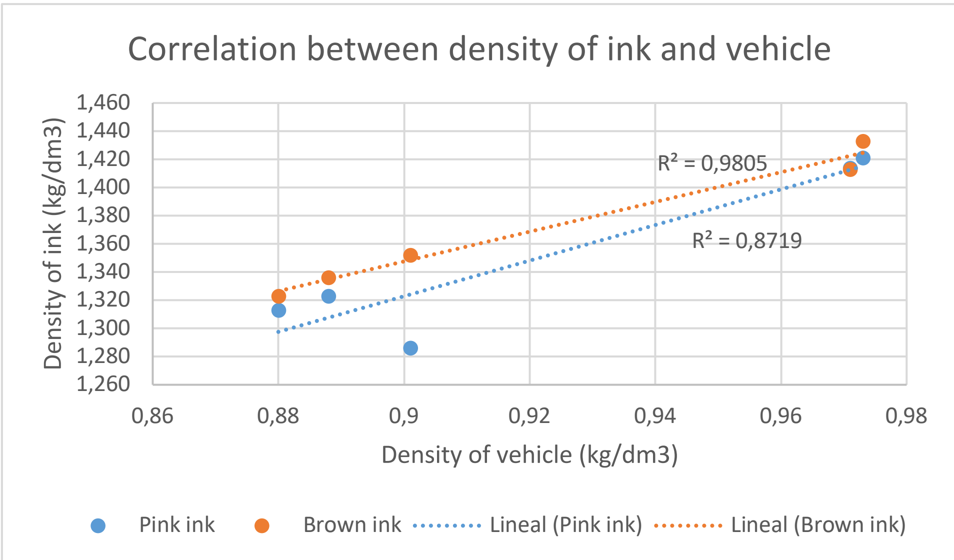

***Figure 3.** Correlation between vehicle and ink densities*

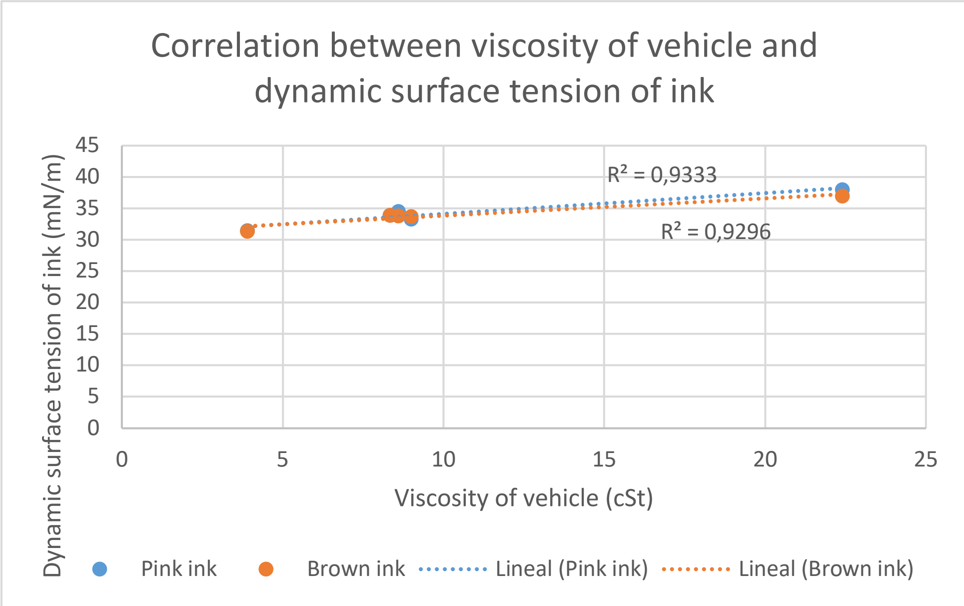

Figure 4. *Correlation between vehicle viscosity and dynamic surface tension of the ink*

3.3 PARTICLE SIZE DISTRIBUTION

The final particle size and characteristic diameters of the developed inks are shown in table 5. All the inks meet the target. However, no clear correlation can be found between the properties of the vehicles and particle size distribution in this study.

	Vehicle	Characteristic Diameters (μm)				
		D_{10}	D_{50}	D_{90}	D_{95}	D_{100}
Pink ink	Ether	0.281	0.435	0.662	0.730	0.873
	Ester	0.300	0.465	0.725	0.803	0.990
	SH 9	0.299	0.463	0.722	0.798	0.990
	MH 9	0.289	0.443	0.666	0.732	0.873
	MH 22	0.316	0.473	0.702	0.762	0.989
Brown ink	Ether	0.300	0.477	0.745	0.824	0.993
	Ester	0.253	0.404	0.659	0.742	0.990
	SH 9	0.260	0.417	0.677	0.760	0.990
	MH 9	0.264	0.420	0.665	0.740	0.989
	MH 22	0.300	0.477	0.746	0.826	0.998

Table 5. *Final particle size and ink characteristic diameters*

3.4 COLLOIDAL STABILITY

The colloidal stability is evaluated by measuring how many particles settle and agglomerate. The less settling and agglomeration, the better the colloidal stability of the ink. The results are shown in figure 5 which indicate that the inks prepared with SH 9 and MH 9 exhibit less or equivalent settling compared to the ether or the ester. The agglomeration of all the inks is very low and at the same level.

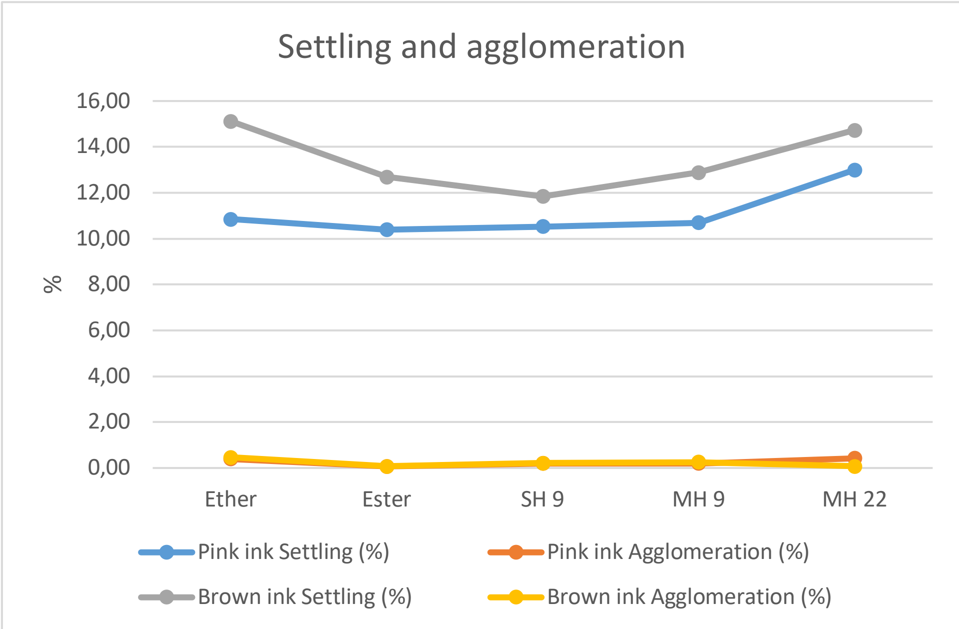

Figure 5. *Settling and agglomeration of the prepared inks*

3.5 FILTERABILITY AND PRINTABILITY

The inks formulated with SH 9, MH 9, ether and ester exhibit excellent filterability through a 5 µm filter membrane, and also excellent printability. The actual printing images can be seen in figure 6 and 7. However, the inks prepared with MH 22 exhibit problems of filtering through the 5 µm filter membrane due to the higher viscosity values obtained, therefore not exhibiting good printability.

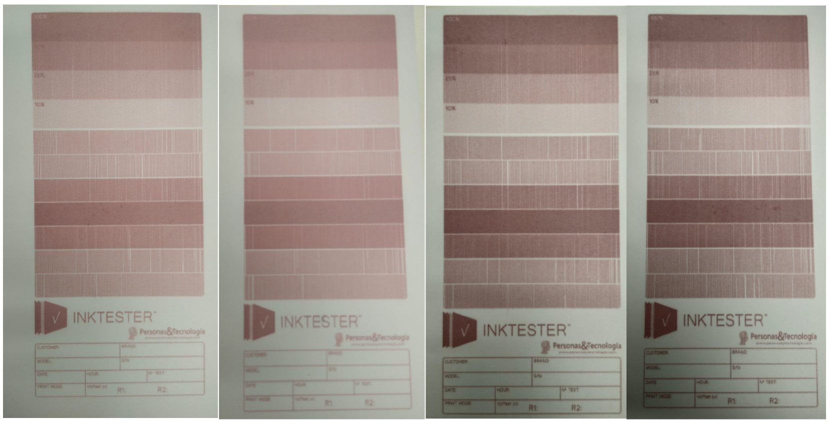

***Figure 6**. Printing images of pink inks formulated with SH 9, MH 9, ether and ester (from left to right)*

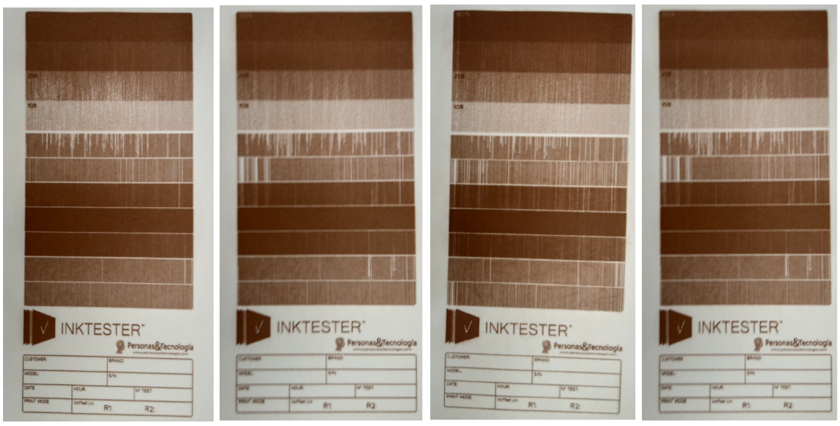

***Figure 7**. Printing images of brown inks formulated with SH 9, MH 9, ether and ester (from left to right)*

3.6 ACCELERATED AGEING

In order to know the suitability of the inks for inkjet technology, an accelerated ageing process of the developed inks is performed, maintaining them inside an electric laboratory oven at 45℃ for 100 days. Printability and reliability tests are run before and after ageing.

	Vehicle	T (℃)	Pressure (bar)	Meniscus (bar)	Voltage (mV)	Drop Volume (pI)	Laydown (g/m^2)
Pink ink- before ageing	Ether	43.6	6.0	-13.1	24.0	109.2	31.2
	Ester	44.2	6.1	-13.2	24.0	110.5	31.4
	SH 9	45.2	5.7	-13.4	24.0	121.0	31.9
	MH 9	44.5	6.0	-13.5	24.0	115.6	30.7
Brown ink- before ageing	Ether	44.3	6.0	-14.2	24.0	105.9	30.5
	Ester	45.1	5.9	-13.9	24.0	106.3	30.2
	SH 9	45.1	5.9	-13.7	24.0	118.7	31.5
	MH 9	44.6	6.1	-14.0	24.0	111.6	29.9
Pink ink- after ageing	Ether	44.8	6.0	-13.1	24.0	111.4	31.4
	Ester	44.7	6.1	-13.2	24.0	109.9	31.2
	SH 9	45.0	5.8	-13.5	24.0	120.0	31.8
	MH 9	45.1	6.0	-13.5	24.0	116.6	30.9
Brown ink- after ageing	Ether	44.6	6.0	-14.2	24.0	115.1	31.5
	Ester	44.8	5.9	-13.9	24.0	109.7	30.8
	SH 9	44.7	5.9	-13.7	24.0	115.4	31.1
	MH 9	45.1	6.1	-14.0	24.0	113.1	30.4

Table 6. *Printing conditions of the inks using the INK-TESTER (5 m/min line speed) before and after ageing*

Table 6 demonstrates the printing conditions of the inks before and after ageing. No obvious variation is observed comparing the printability before and after ageing for all the inks prepared with SH 9, MH 9, ether and ester which means naphthenic oils- SH 9 and MH 9 show equivalent stability to ether and ester in the developed formulation. The actual printing images after ageing can be seen in figure 8 and 9.

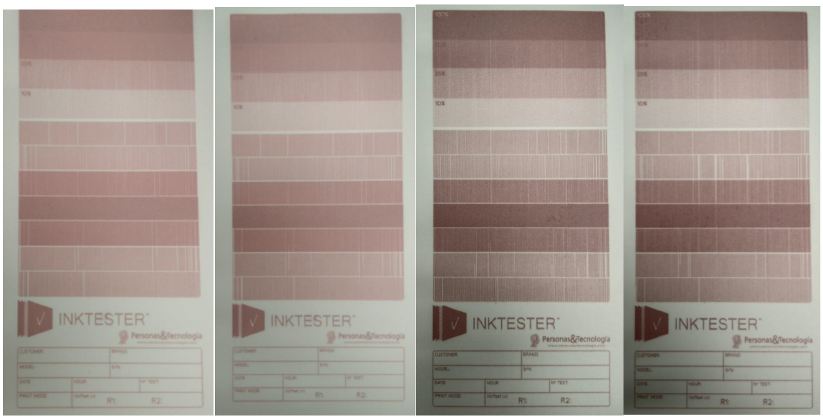

Figure 8. *Printing images of pink inks formulated with SH 9, MH 9, ether and ester (from left to right) after ageing*

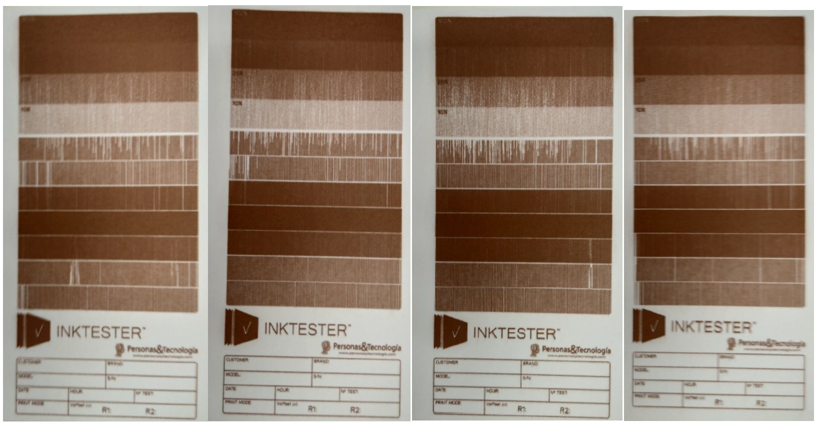

Figure 9. *Printing images of brown inks formulated with SH 9, MH 9, ether and ester (from left to right) after ageing*

4. CONCLUSIONS

- Low viscosity naphthenic oils- SH 9 and MH 9 show excellent performance as well as the selected ether and ester in the developed ceramic inkjet ink formulation in terms of not only the right viscosity, density and dynamic surface tension, but also the colloidal stability and printability before and after accelerated ageing.
- MH 22 doesn't exhibit as good feasibility as above-mentioned 4 vehicles when it is used alone as the vehicle mainly because of its relatively higher viscosity. However, considering the mixability of naphthenic oil and ether or ester, MH 22 could be used by mixing with other vehicles to balance the physical properties.
- The viscosity of a vehicle is an essential property which impacts the properties of inks greatly, such as ink's viscosity, dynamic surface tension, filterability and printability.
- A relatively higher viscosity of milling vehicle tends to reduce the milling time.

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[2] [2] Dr. Vicente Sanz Solana. INKJET PRINTING TECHNOLOGY FOR CERAMIC TILE DECORATION. Instituto de Tecnología Cerámica, Spain. Qualicer 2014.