INVESTIGATION ON VOC CONTENT FROM CAR INTERIOR FINISHING SYSTEMS AND ITS INFLUENCE ON LEATHER PERFORMANCES

R. Pasquale[1b], D. Cisco[1], T. Pellegrini[1a]

1 GSC GROUP SPA via dell'Industria 5 Montebello Vicentino (VI) 36054 ITAL

corresponding author: a) tomasopellegrini@gscspa.it, b) riccardopasquale@gscspa.it

Abstract. Car industry is highly demanding for low emission parameters and despite remarkable results have been achieved since the last decade, the requests are day by day more sophisticated. The focus on emission is a severe task and requires the investigation on emissions on a full-range perspective and involves the expertise of multi and inter disciplinal competences. This investigation demonstrated that silicon-based compounds were the most important part of the car-interior emissions, which were also responsible for remarkable leather physical performances. However, these compounds contribute to less sustainable emissions, due to the intrinsic hazardless (SVHC substances) and volatility. In this context, this research has focused on the study of novel finishing formulation aiming to overcome the impact of the high emission contribution from the silicon-based compounds and to maintain/improve the leather performances.

Keywords: automotive industry, air quality, VOC, leather performances, sustainability.

1 Introduction

The 2019 Car Industry is currently looking at of the most explosive change and developments in this area: automated driving, sharing economy/transportation, artificial intelligence, industry 4.0, connectivity, electric vehicles are some of the hot topics that this industrial sector is facing, and which are bringing innovation and new technological developments. In addition, the meaning of transportation is also changing, thus urging the re-evaluation of the construction/design of the vehicles: such amendments will pose attention on safety, seating and interior functionality and in a general way to all the vehicle architecture. Sustainability will then be taken as a principle for the architecture of the new vehicles. The new car-industry will also focus on environmental impact of the design, construction and development of the vehicle; which mean that all the materials involved in these actions must meet the same concerns/requirements (ADIENT, 2018).

The leather industry is a clear key ring for car interior suppliers and it is also focusing on more sustainable processes and reducing the emission of pollutants to the environment, prompting the commitment of leather suppliers, tanneries, and chemical auxiliaries' producers. From our perspective, in fact, one of the major problems that car interior producers are currently facing is the production of low-emitting leather, which requires special chemical auxiliaries to be achieved. At a glance, the concept of emission must be applied to any discharged substance from one to another environment: each substance has a vapour tension which tells how difficult is its release from the source to the external environment. The car-industry considers the emissions due to combustion engine (i.e. CO_2, NO_x etc), or other power sources, but also the emissions derived from the manufacture of the vehicle and all the material which are part of it. Thus, leather is definitely included as a source and contribution (Drive Sustainability, Responsible Minerals Initiative, The Dragonfly Initiative, 2018).

In this context, our research has focused on the study of volatile organic compounds VOC substances from car interiors, in particular on finishing systems, aiming at their reduction without losing the original performances of the finished leather articles. It is important to underline that the quality and quantity of such emissions influence the quality of the environment, especially if the emission is made of pollutants, or hazardless substances.

Previous study from Feduruk and Kergent showed that the pattern and magnitude of the emissions is influenced by temperature and air turnover, thus suggesting that the static determinations were higher in volatile content than the dynamic analyses (Fedoruk & Brent, 2013).VOCs are organic chemicals that have a high vapor pressure at ordinary room temperature, which include large numbers of molecules that evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air. VOC classification is therefore based on the boiling point of the substances, which are summarised in **Table 1**.

Table 1. VOC classification with respect to boiling point of the substances.

Boiling Point (Bp, °C)	Name	Example
< 50	VVOC Very Volatile Organic Compounds	Formaldehyde, Acetaldehyde
50 < Bp < 260	VOC Volitile Organic Compounds	BTEX (Toluene, xylene etc)
> 260	SVOC Semi-Volatile Organic Compounds	Phthalates
> 400	Particulate Organic Matter	PCB (Polychlorinated biphenyl)

Table 2. methods developed for VOC and FOG analyses.

Method	Name	Principle	Unit of Measure
ISO 17071	Fogging Test	Evaporation followed by condensation on cooled surface (R o G)	mg or %
VDA 275	Aldehydes/ketones Emission	Evaporation followed by water absorption; colorimetric analysis of water	mg/kg
ISO 17226-1	Chemical determination of formaldehyde content from leather	Evaporation followed by water absorption; HPLC analysis	mg/kg
VDA 276	BMW Summer test (GS 97014—3), Toyota Test	Active air sampling of specimen from thermostatic chamber	ug/m^3 or ug/m^3 per m^2
VDA 277	VOC Determination	Static headspace analysis	mg/kg
VDA 278	VOC FOG Determination	Dynamic headspace analysis	mg/kg
ISO 16000	Blue Angel	Active air sampling of specimen from thermostatic chamber	ug/m^3
ISO 12219	Interior air of road vehicles	Active air sampling of specimen from thermostatic chamber	ug/m^3

Faber (Faber, Brodzik, Gołda-Kopek, & Łomankiewicz, 2013) *et al.* identified VOCs from car-interior into three main group of compounds (aliphatic, aromatic, and cycloalkanes), along with other compounds which belonged to hydrocarbons family. Their investigation also showed that the observed differences in VOC content could directly be related to the equipment and the materials used to finish the interior. Since 2013, our R&D collected a series of analytical data with respect to the evaluation of the leather emissions: different methodologies were used, although most of them were based using heating to pull out form the sample the emitted substances, and gas chromatography as the analytical technique for the analysis of the emission. It is therefore necessary to underline that different substances can be extracted at different temperatures with the respect to the same sample (temperature and time), to produce different results in terms of

emission; for this reason, the methods developed in order to analyse the emissions from such samples took into account of the heating conditions, the vessel where the thermal conditioning was carried out and sampling of the volatiles (see **Table 2**). An outline of these results showed that four classes of substances contributed to these emissions: organic solvents, silane-based substances, small molecular weight substances (MW < 150) and fatty substances (see **Table 3**). The silicon based compounds were the most effective in terms of magnitude with respect to the emitted VOC, and their contribution was remarkable. In addition, the same silicon-based compounds were responsible for the finishing effect; thus, it was necessary to investigate on their role and impact on the emission and finishing performance since their application could affect the final leather properties. **Table 4** summarises the most representative results for the VOC determination from finished and intermediate leather with adaptation of ISO 12219-4; the tests were performed on car-interior leather.

Our investigation focused on full grain finished leathers, evaluating the contribution to the VOC emission from crust leather to the finished articles.

Table 3. List of most recurrent substances found from emission analysis throughout previous investigation.

SUBSTANCE	CAS NO	DESCRIPTION	NOTES
Acetaldehyde	75-07-0	Aldehyde/Ketone	
Acetone	67-67-1	Aldehyde/Ketone	
DIBK	108-83-8	Aldehyde/Ketone	
Formaldehyde	50-00-0	Aldehyde/Ketone	
Heptanal	111-71-7	Aldehyde/Ketone	
Hexanal	66-25-1	Aldehyde/Ketone	
Nonanal	124-19-6	Aldehyde/Ketone	Side product generated upon heating the leather.
NEP	2684-91-4	Distending agent/leveller	
NMP	872-50-4	Distending agent/leveller	
Butyl Digol		Glycol	
DPGME	34590-94-8	Glycol	Residue as solvent for PU dispersion; highly impacting towards the emission
PGMEA	108-65-6	Glycol	
Propyleneglycol Monomethyl Ether		Glycol	
C18-OMe Ester	84988-79-4	Hydrocarbon	
Decane	124-18-5	Hydrocarbon	
Dodecane-1-phenyl	120-01-3	Hydrocarbon	
Undecane	1120-21-4	Hydrocarbon	
CS2	75-10-0	N.D.	
Triethylamine	121-44-8	Organic Amine	Neutralising agent for PU dispersion.
2-Hexyl-1-Octanol	19780-79-1	Raw Material	Used in fatliquoring
Ethylhexanol	104-76-7	Raw Material	Used in fatliquoring
Bis(trimethylsilyl) Oxide	107-46-0	Silane Derivative	
D4-Silane		Silane Derivative	

D6-Silane		Silane Derivative	
Siloxane		Silane Derivative	
Trimethylsilanol	1066-40-6	Silane Derivative	1-5% of the emission, 200-500 ppm as a constant with respect to the sample
Isobutanol	78-83-1	Solvent	
Propylene Carbonate	108-32-7	Solvent	Residue and part of finishing auxiliaries.
Pyridine	110-86-1	Solvent	Side product generated upon heating the leather.
Ethyl Benzene	100-41-4	Solvent BTEX	
Toluene	108-88-3	Solvent BTEX	
Xylene	1330-20-7	Solvent BTEX	
Ethylhexyl Acetate	103-09-3	Solvent for finishing auxiliaries	

Table 4. Most relevant examples for VOC determination via adaptation of ISO 12219-4.

ENTRY	FORM-ALDEHYDE (ug/m3)	ACET-ALDEHYDE (ug/m3)	VOC (ug/m3)	BTEX	SILYL-ETHERS	SOL-VENTS	UN-KNOWN
Finished leather-01	N.D.	1.18	947.00	N	Y	Y	Y
Finished leather-02	N.D.	3.40	2960.00	N	Y	Y	Y
Finished leather-03	N.D.	4.83	25508.00	N	Y	Y	Y
Finished leather-04	0.78	22.06	7711.00	N	Y	Y	Y
Finished leather-05	N.D.	12.32	106791.00	Y	Y	Y	N
Finished leather-06	4.22	0.95	153319.00	N	Y	Y	Y
Finished leather-07	2.20	11.15	2887.00	N	Y	Y	Y
Finished leather-08	2.21	34.60					
Finished leather-09	1.91	38.75					
Intermediate-01	N.D.	N.D.	7.95	Y	Y	Y	Y
Intermediate-02	N.D.	23.29	14.76	Y	Y	Y	Y

2 Materials and Methods

Commercially available chemicals were purchased from *Aldrich*, *Fluka*, *Acros* and *Alfa Aesar* and used as received, unless stated.

Liquid chromatography was used for quantification of aldehydes and ketones if required prior derivatisation with dinitrophenyl hydrazine (DNPH) and was carried out on a *Perkin Elmer ALTUS A-*

10, equipped with a *C18 COLUMN 5* (150 x 4.6 mm) from *Perkin Elmer* and using diode-array detector (DAD). Eventually, the quantification was carried out prior chemical desorption with acetonitrile from special designed cartridges *DNPH TUBE JUMBO* purchased from *Aquaria* for air-quality analysis.

Analytical gas chromatography was performed on a *CLARUS 580* instrument from *Perkin Elmer* with a *SQ8 S* detector (EI) using an *ELITE-624 MS* capillary column (30 mt x 0.25 mm i.d.) and hydrogen as carrier gas. Static headspace analyses were carried out using a *TURBOMATRIX HS 40 TRAP* from *Perkin Elmer*, using hydrogen as carrier gas. Analytical gas chromatography was also carried out on a *CLARUS 400* instrument from *Perkin Elmer* using a FID detector for the quantitative determination of the volatiles prior chemical desorption with carbon disulphide (CS_2) from special designed cartridges *CARBON TUBE JUMBO* purchased from *Aquaria*. The chromatography was carried out using nitrogen as carrier gas and an *ELITE-624* (30 mt x 0.25 mm i.d.) as column.

The leather samples evaluated throughout this investigation were from different countries of origin and from different manufactures. It is noteworthy that this is a typical case scenario which occurs every day in most of the tanneries, and which is affected by strong differences from one to another sample within the same batch. Thus, to reduce such differences due to the raw material, it was decided to carry out the investigation on specially designed paper as substrate, which normalized any potential difference of matrixes; these papers were the BYKO-CHARTS DRAWDOWN CARDS purchased from *BYK*. However, investigation on leather was also carried out and has been considered of crucial importance. The application of the auxiliaries was carried out using a BYKO-DRIVE AUTO APPLICATOR 2122 from *BYK* and the appropriate spiral-bar coater, followed by drying *via* forced air oven at 105°C (UF 55 from *Memmert*).

The leather auxiliaries involved in the project implementation were provided and produced by *GSC Group spa* and used its facility; no commercial names and/or trademarks are reported in the description, but generic names adapted for the investigation. These products included PREGOUND, GROUND, INTERMEDIATE FOR EMBOSSING, BASECOAT, TOPCOAT and SILICONE auxiliaries; for our purposes, *GSC Group spa* produced also the corresponding LOW VOC versions of the abovementioned products.

2.1 General Procedure for the Preparation of the Novel Finished Samples

In order to verify the emission of the substrates treated with the novel finishing system, mixtures of finishing auxiliaries were prepared according to internal company procedures and specification. The matrix was then treated with a specific sequence of the chemicals to give the final article, followed by emission evaluation and physical-mechanical testing.

After the preparation of the auxiliaries, the application was carried out using the automatic film applicator and the appropriate spiral-bar coater (25, 50 or 100 µm), followed by 2 minutes drying *via* forced air over at 105°C. Herein, the composition and the sequence of the samples are reported; for this study, the sample was identified by the code **9384** followed by a suffix which identified the step of the application.

2.1.1 Sample 0 = standard chart

Sample 0 is the reference from the chart support.

2.1.2 Sample 0DA

0DA	
Demineralized water	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	

2.1.3 Sample 9384/ 0A

9384/0A	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	

Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	

2.1.4 Sample 9384/0B

9384/0B	
Preground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing LOW VOC	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	

2.1.5 Sample 9384/1

9384/1	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 0% (9384/1)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 0% (9384/1)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.6 Sample 9384/2

9384/2	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 1% Silicone STD (9384/2)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 1% Silicone STD (9384/2)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.7 Sample 9384/3

9384/3	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 3% Silicone STD (9384/3)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 3% Silicone STD (9384/3)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.8 Sample 9384/4

9384/4	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 6% Silicone STD (9384/4)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 6% Silicone STD (9384/4)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.9 Sample 9384/5

9384/5	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 0% Silicone LOW VOC (9384/5)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 0% Silicone LOW VOC (9384/5)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.10 Sample 9384/6

9384/6	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 1% Silicone LOW VOC (9384/6)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 1% Silicone LOW VOC (9384/6)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.11 Sample 9384/7

9384/7	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 3% Silicone LOW VOC (9384/7)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 3% Silicone LOW VOC (9384/7)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.12 Sample 9384/8

9384/8	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat STD	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 6% Silicone LOW VOC (9384/8)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat STD 6% Silicone LOW VOC (9384/8)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.13 Sample 9384/9

9384/9	
Preground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground STD	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing STD	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat LOW VOC	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat Low VOC 6% Silicone LOW VOC (9384/9)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat Low VOC 6% Silicone LOW VOC (9384/9)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.14 Sample 9384/10

9384/10	
Preground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing LOW VOC	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat LOW VOC	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat Low VOC 0% Silicone LOW VOC (9384/10)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat Low VOC 0% Silicone LOW VOC (9384/10)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.15 Sample 9384/11

9384/11	
Preground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing LOW VOC	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat LOW VOC	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 1% Silicone LOW VOC (9384/11)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 1% Silicone LOW VOC (9384/11)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.16 Sample 9384/12

9384/12	
Preground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing LOW VOC	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat LOW VOC	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 3% Silicone LOW VOC (9384/12)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 3% Silicone LOW VOC (9384/12)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.17 Sample 9384/13

9384/13	
Preground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing LOW VOC	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat LOW VOC	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 6% Silicone LOW VOC (9384/13)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 6% Silicone LOW VOC (9384/13)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

2.1.18 Sample 9384/14

9384/14	
Preground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Ground LOW VOC	1 Application Film 100 µm
Forced Air Drying 2’ at 105 °C	
Intermediate for Embossing LOW VOC	1 Application Film 25 µm
Forced Air Drying 2’ at 105 °C	
Basecoat LOW VOC	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 6% Silicone STD (9384/14)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	
Topcoat LOW VOC 6% Silicone STD (9384/14)	1 Application Film 50 µm
Forced Air Drying 2’ at 105 °C	

Table 5. Application for 9384 samples.

	9384/1	9384/2	9384/3	9384/4	9384/5	9384/6	9384/7	9384/8	9384/9	9384/10	9384/11	9384/12	9384/13	9384/14
Preground	1X	1X	1X	1X	1X	1X	1X	1X	1X	-	-	-	-	-
Preground stripped	-	-	-	-	-	-	-	-	-	1X	1X	1X	1X	1X
Ground	2X	2X	2X	2X	2X	2X	2X	2X	2X	-	-	-	-	-
Ground Stripped	-	-	-	-	-	-	-	-	-	2X	2X	2X	2X	2X
Intermediate for Embossing	1X	1X	1X	1X	1X	1X	1X	1X	1X	-	-	-	-	-
Intermediate for Embossing Stripped	-	-	-	-	-	-	-	-	-	1X	1X	1X	1X	1X
Embossed by Rotopress6 m/min; 150 atm; 90 °C; Sandblasted														
Basecoat	1X	1X	1X	1X	-	-	-	-	-	-	-	-	-	-
Basecoat Stripped	-	-	-	-	1X	1X	1X	1X	1X	1X	1X	1X	1X	1X
Topcoat 0	2X	-	-	-	2X	-	-	-	-	-	-	-	-	-
Basecoat Low VOC 0	-	-	-	-	-	-	-	-	-	2X	-	-	-	-
Topcoat 1 %	-	2X	-	-	-	-	-	-	-	-	-	-	-	-
Topcoat 1 % sil Stripped	-	-	-	-	-	2X	-	-	-	-	-	-	-	-
Basecoat Low VOC 1 % Stripped	-	-	-	-	-	-	-	-	-	-	2X	-	-	-
Topcoat 3 %	-	-	2X	-	-	-	-	-	-	-	-	-	-	-
Topcoat 3 % sil Stripped	-	-	-	-	-	-	2X	-	-	-	-	-	-	-
Basecoat Low VOC 3 % Stripped	-	-	-	-	-	-	-	-	-	-	-	2X	-	-
Topcoat 6 %	-	-	-	2X	-	-	-	-	-	-	-	-	-	-
Topcoat 6 % sil Stripped	-	-	-	-	-	-	-	2X	-	-	-	-	-	-
Basecoat Low VOC 6 % stripped	-	-	-	-	-	-	-	-	2X	-	-	-	2X	-
Basecoat Low VOC 6 % Silicone	-	-	-	-	-	-	-	-	-	-	-	-	-	2X
Basecoat Low VOC 8 % stripped	-	-	-	-	-	-	-	-	-	-	-	-	-	-

2.2 General Procedure for the Analysis of the Leather Emission

As a general rule, the sample (i.e. leather or paper) was placed into an appropriate sealed container and heated, in order to saturate the inner atmosphere with its volatiles. Then, at specific timing, an aliquot of the volatile part was analysed by chromatography in order to determine the nature and the amount of the volatiles (qualitative and quantitative analyses). The techniques and methods involved in air quality analyses for the samples are briefly herein described. VOCs can be therefore defined according to the method used for their determination according to **Table 6Fehler! Verweisquelle konnte nicht gefunden werden.**.

Table 6. VOC classification according to analytical methods used throughout the investigation.

Method	VOC Quantification	Extraction Conditions
VDA 277	All peaks from GC trace	5h @ 120°C
ISO 12219	All peaks from GC trace	1h @ 65°C (variant #4 small chamber)

2.2.1 Emission Evaluations via VDA 277

This method provided information of the emission of organic compounds using static headspace analysis combined with GC-MS analysis using a 2 g sample placed into a glass vial prior heating at 120°C for 5 hours. In such way, the most volatile compounds saturated the inner atmosphere of the vial, establishing an equilibrium with the same compounds to be released from the sample; however, in this case, the presence of high volatile compounds influenced the composition of the volatiles, since they were enriched of the more volatile derivates, whilst the less volatile would have been kept from the matrix. The results are converted to acetone carbon (used as external standard) and expressed as µg C/g sample.

Table 7. Results for VOC emission according to VDA 277 test method.

Entry	Description	VOC (ugC/g)
ZERO-01	Chart	-
ZERO-DA	Chart After Washing	-
9384/0A	Intermediate for Embossing STD	73.19
9384/1	Silicon STD	23.08
9384/2	Silicon STD 1%	3.25
9384/3	Silicon STD 3%	14.31
9384/4	Silicon STD 6%	25.42
9384/5	Topcoat STD	29.57
9384/6	Topcoat STD + Stripped Silicone 1%	24.03
9384/7	Topcoat STD + Stripped Silicone 3%	23.17
9384/8	Topcoat STD + Stripped Silicone 6%	44.88
9384/9	Basecoat + Stripped Silicone 6%	40.93
9384/10	Topcoat Low VOC	19.09
9384/11	Topcoat Low VOC + Stripped Silicone 1%	9.18
9384/12	Topcoat Low VOC + Stripped Silicone 3%	28.99
9384/13	Topcoat Low VOC + Stripped Silicone 6%	19.49
9384/14	Low VOC Auxiliaries + STD Silicone 6%	52.42

2.2.2 Emission Evaluation via ISO 12219-4 (Small Chamber Test)

This method allowed the qualitative and quantitative determination of the emission of volatile species from samples heated at 65°C for 5 hours, under a constant purified air stream and sampling at specific timing. The samples were conditioned for approximately 10 days at 25°C, 50% R.U. In this case, no static headspace analysis was performed, but the continuous air sampling from the sample placed into a stainless-steel chamber in which purified air was streamed continuously. The airstream was passed into special cartridges in order to concentrate the analytes emitted (the choice of the cartridges depended on the kind of species to be analysed), and was also force upon gentle vacuum which provided continuous and constant air flow. For this investigation, *CARBON TUBE JUMBO* cartridges were used for the volatile VOC analyses and *DNPH TUBE JUMBO* cartridges were used for the aldehydes and ketone analyse. This is a major difference compared to static headspace analysis, since it allows to continuously sample and analyse all the chemicals emitted from the sample at a certain temperature, and their emission is not influenced by the presence of the most volatile species since purified air is continuously purged into the chamber. It is noteworthy that due to the high dimensions of the stainless-steel chamber and the corresponding oven required for the constant heating, a reduced dimension chamber was used for the investigation, particularly for the preliminary study of the VOCs emission. The smaller chamber was built considering the correct ratio of sample area /chamber dimension/air reported in the method ISO 12219-4; for our purposes, the chamber was of approximately 192 litres volume.

2.2.3 Emission Evaluation via GS 97014-3 (BMW Summer Test)

This method is very close to the ISO 12219-4, although it required more stringent conditions; the testing conditions also refer to ISO the sample was heated at 65°C for 5 hours and at 105°C for additional 3 hours.

A component is placed into an approximately ideally intermixed 0.24 m^3 or 0.98 m^3 test room and stored there at the prescribed temperature, humidity and air exchange rate. Organic substances that escape from the component accumulate in the test room and are discharged by means of the exhaust flow. Due to the high dimensions of the stainless-steel chamber and the corresponding oven required for the constant heating, a reduced dimension chamber was used for the investigation.

2.3 Physical and Mechanical Testings

The quality of the leather was also assessed and characterised through standard automotive tests such as stick-slip, abrasion trials with Taber tester and Martindale machine, ball plate method, fogging test; rub fastness provided with Veslic tester (wet, dry, alcohol, gasoline), dry-rubbing trial with Gakushin tester. For this study, the physical and mechanical tests for stick-slip, abrasion and rub-fastness are reported.

2.3.1 Wet-Rubbing Test

Wet rubbing tests were performed with *Veslic Giuliani* IG/10/MOD, following the guidelines of ISO 11640. Before the specimen preparation, the materials were stored for at least 24 h under normal climate conditions (temperature 23 +/- 2°C, humidity: 50 +/- 5% relative humidity).
The sample size for the wet rubbing test was 100 mm x 50 mm.

2.3.2 Stick-slip test VDA 230-206

This is test method is meant for determining the stick-slip tendency of material pairs. The measurements were carried our using a *STICK-SLIP TESTER* from *Ziegler*.
The sliding carriage with the material specimen A is moved relative to a spring element (short steel spring) against the material specimen B. The force with which the material specimens are pressed against each other as well as the speed of the sliding carriage are given.

The spring's movement behaviour which is created during the change between adhesion and slipping (stick-slip effect) is a measurement of the stick-slip tendency according to VDA 230-206. Before the specimen preparation, the materials were stored for at least 24 h under normal climate conditions (temperature 23 +/- 2°C, humidity: 50 +/- 5% relative humidity). The sample size for the spring was 50 mm x at least 20 mm; the sample size for the sliding carriage was 100 mm x 50mm, preferably using a punching process. Measurement are done during three periods with the results averaged to a total result. Each measurement must be done on two specimens in order to confirm the test results.

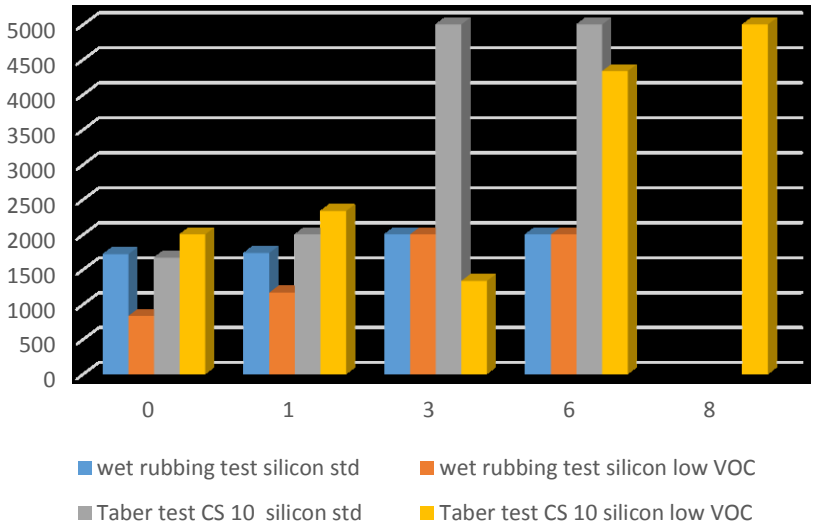

Figure 1. Physical performances comparison between standard silicon and low emitting derivative.

3 Results and Discussion

Our preliminary study showed that silicon compounds family brought an important contribution to the emission from a qualitative and quantitative perspective: these substances play a crucial role in terms of the final article performances (such as resistance), and quality.

From the preliminary results, it was therefore decided to compare two set of finishing auxiliaries: from one side the standard finishing chemicals, whilst from the other a novel series of auxiliaries designed for low VOC contribution. High performances leather with respect to abrasion resistance and wet rub-fastness require the utilisation of high quantities of silicone; as a consequence, the increase of such compounds is related to an increase VOC value.

So, our investigation focused on innovative low emitting silicones to give low contribution to the emissions the leather compared with the same performances of the original silicon containing finishing (see 2.1 and **Table 5**). The gradual increase in standard silicon content showed an increase in VOC emission, as expected (**Table 7**), whilst in the case of low-emitting silicones the VOC values are less than the respective counterparts. It is remarkable that the low-emitting derivatives showed equal wet rub-fastness performances (**Figure 1**), but they lacked in abrasion resistance; in order to obtain satisfactory results it was necessary to use 8% of low-emitting silicones in the formulation,

whilst only 6% was required for the standard derivative. It was also noted that the low VOC formulation with 3% of STD silicone showed higher VOC content that the 6% test, but also higher than the standard preparation entries (see **Table 7** entry 9384/13). This was not explicable and unexpected; several trials were carried out, although the VOC content form VDA 277 test method was confirmed throughout the investigation.

The set of result showed that standard leather containing silicon compounds on the finishing produced high VOC emission and high-performance articles, thus contributing to VOC emission. Conversely, the novel finishing auxiliaries had low VOC emission, less quantity of silicones, yet high performance leather and therefore should be chosen from a more environmental point of view as depicted in **Figure 2**.

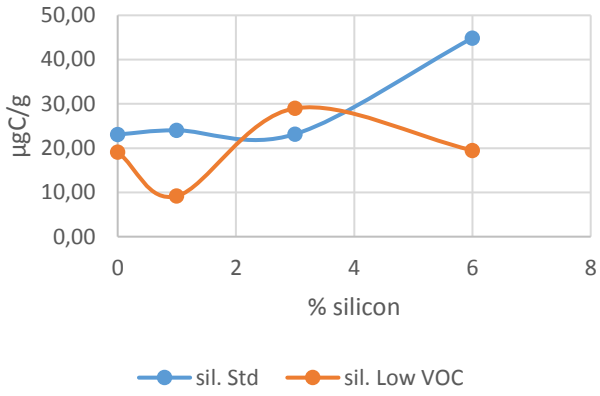

Figure 2. VOC emission according to VDA 277 for standard and low emitting silicone derivatives.

Furthermore, low emitting silicones promoted an unexpected positive effect towards the VDA 230-206 (Stick-slip test): an increase in concentration of the standard silicones usually raises the values of the VDA 230-206, which is therefore a negative effect. As depicted in **Figure 3**, in the case of the low emitting auxiliaries the effect is positive since the results did not increase.

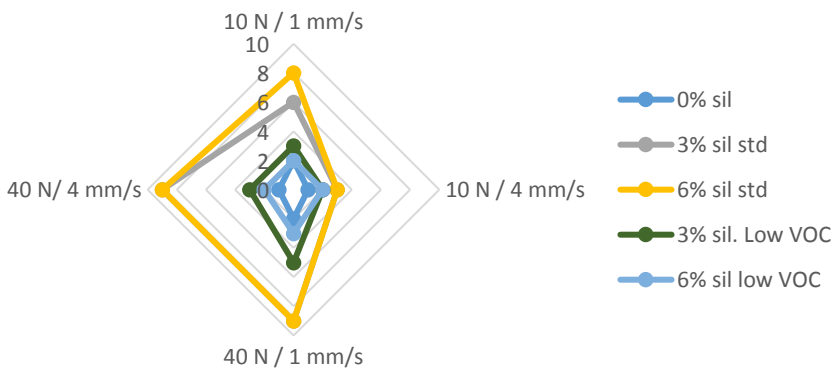

Figure 3. Stick-slip test VDA 230-206 comparison.

4 Conclusions

The major components found from the leather emissions were silane-based compounds, regardless the method used for the analysis. Taking into account the fact that some of the silanes and the organic volatiles are currently object of safety evaluation from authorities (EC), it is appropriate to make all efforts to minimize the presence of these species and their contribution to VOCs.

The silane compounds come from the finishing auxiliaries, although also from retanning; silicons can take part in fatliquor formulation as retanning agents, yet it is important to choose the correct species to ensure to provide chemicals which are in compliance with the regulations and the customers' requests. However, it was demonstrated that a free from silanes leather matrix, can be provided (LIFE GOAST), which also exhibited low to negligible emission compared to standard leather. It is therefore stressed the importance of prompting new research to alternative tanning systems to traditional chrome tanning substrates, which could lead to more sustainable and less impacting manufactures from the emission point of view.

This investigation is a proof that leather auxiliaries' producers are active part of the supply chain: if the presence of the silane-compounds from the emission could give problems in terms of emissions and safety concerns, the leather performances could not be met if they were not included in finishing auxiliaries. So, the chemical supplier in entitled of an important work, which will use inter-disciplinal competences to show that new finishing system could solve the safety issues and maintain the leather performance, without losing the final article.

5 Acknowledgments

This investigation was fully supported and sponsored by GSC Group spa, which carried out all the leather production, auxiliaries production and leather chemical and physical testing. It is therefore important to thank all the GSC Group R&D team, the analytical staff, the experimental centre and the production department. A special mention has to be given to Lorenzo Diddi, Annamaria Marangon, Elisa Zordan and Arturo Bortolati for the samples preparation and testing; this study was integrated with the analytical support of Francesco De Laurentiis, Giacomo Chiodarelli and Mariana Moretto. A special thank has to be given to all the customers and partners that since 2013 had contributed to screen and monitor the VOC emissions by using our expertise.

References

1. *ADIENT. (2018, 02). Adient - Taking automotive seating to the next level .*
2. *Drive Sustainability, Responsible Minerals Initiative, The Dragonfly Initiative. (2018, July). MATERIAL CHANGE.*
3. *Faber, J., Brodzik, K., Gołda-Kopek, A., & Łomankiewicz, D. (2013). Air Pollution in New Vehicles as a Result of VOC Emissions from Interior Materials. Pol. J. Environ. Stud. , 22, 6, 1701-1709.*
4. *Fedoruk, M., & Brent, K. (2013). Measurement of volatile organic compounds inside automobiles. Journal of Exposure Analysis and Environmental Epidemiology , 13, 31–41 .*