VOCs in the tanning industry: Caracteristics, reduction and treatment

Thierry PONCET
CTC

VOC EMISSIONS IN THE TANNING INDUSTRY

The solvents used during the finishing operations represent the main source of Volatile Organic Carbons (VOC) for tanneries.

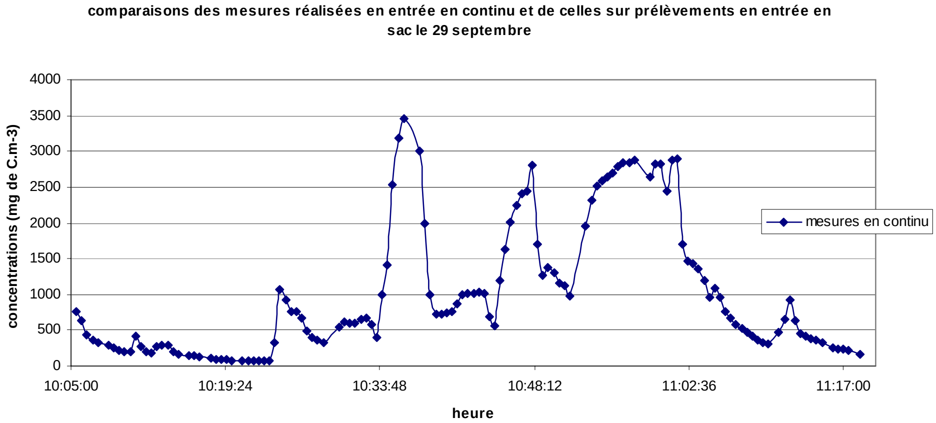
Constraints have been defined in the UE directive 99/13/EC. Implementation has begun on 30th march 2005 for some European countries. It should be implemented in all countries on 30th March 2007. These constraints refer to “total area of leather coated produced” and to “the solvent consumption”.

- For solvent consumption between 10 and 25 tonnes per year, total emission limit values are 85 grams of VOC emitted per square meter of leather produced.
- For solvent consumption above 25 tonnes per year, total emission limit values are 75 grams of VOC emitted per square meter of leather produced.
- For leather coating activities in furnishing and particular leather goods used as small consumer goods like bags, wallets, etc… total emission limit values are 150 grams of VOC emitted per square meter of leather produced.

VOC’s in the tanning industry have a composition that varies in composition and concentration versus time. A typical composition a tannery VOC includes the following substances: acetone, butyl acetate, cyclohexanone, isopropylic alcohol, methyl ethyl ketone (2-butanone), 2-pentanone or ketone C <= 5, ethyl acetate, cyclohexane, di-isobutylketone (DIBK), xylene, butane-diol isomere, methyl iso butyl Ketone (MIBK), toluene, ethylbenzen.

Concentration varies from 100 to several thousands of milligrams per cubic meter during the finishing operations. The extractions of the finishing booth have a flow that may reach 10.000 or 12.000 m^3/hour for one finishing line.

Next figure is a typical emission of VOCs in the tanning industries.



Emissions of VOCs in the tanning industries

Graph 1

Considering these emission characteristics, not all technologies could fit. Thanks to a bibliographical survey of the different technologies available on the market. This survey included technical aspects such as efficiency, flow rate, concentrations, type of VOC treated and also economical aspects. Two techniques have been identified and tested:

- Biological treatment by bio-filter or by bio-washer
- Combination of adsorption and catalytic oxidation (SORBICAT system®).

BIOLOGICAL TREATMENT

Biological processes are applied to the degradation of biodegradable molecules in low and medium concentrations in the air. The principle is described in the following equation:

$$\text{Organic matter} + O_2 + [N, P, K, \text{oligo-elements}] + H_2O$$

$$\longrightarrow CO_2 + H_2O + \text{Energy} + \text{Biomass}$$

Regarding air treatment, the bioreactor needs to realize at the same time the transfer of the pollutant from the gas phase to the liquid phase and the biodegradation.

Bio-filters

A filter is made of a packed column used as a support for the microbial growth. CTC has used a 1,600 mm height bio-filter, 2,300 mm in diameter. That reactor was divided into 4 compartments in order to test 4 different materials as support for the biomass:

- Granular peat for its adsorption properties thanks to its specific surface
- Active carbon usually used for its adsorption properties and not for biological growth.
- Corn cobs for its low cost and for its availability almost everywhere.
- Mixture of coconut fibres and granular peat found in some bio-filter installations.

A test was also conduct on shaving because of its high capacity of absorbance and its availability in tanneries.

Picture 1 – Bio-washer and bio-filter

Bio-washer

The bio-washer consist in 3 different steps:

- An adsorption column where water circulates at counter current for the transfer of the VOC from the gas phase to the liquid phase. The use of a packed column is more effective than a non-packed column because of the contact area to perform the exchange of the pollutant from one phase to the other. Column diameter was 465 mm and column height was 3 metres.
- An activated sludge basin is a biological reactor in which an aerobic biodegradation takes place. A compressor provides the homogenisation by air bubbles providing
    - The oxygen required for the micro-organisms
    - The suspension of the sludge and the contact between the polluted liquid phase and the biomass.
- A decanter to remove the excessive biomass of the system.

Main results are presented in table 1 and 2.

	On site trials (Finishing booth)	**Reconstituted VOC**
Bio-filter with activated sludge	95%	95%
Bio-filter with granular peat	60%	60%
Bio-filter with coconut fibres	55%	55%
Bio-filter with corn cobs	50%	45%
Bio-washer	55%	50%

Table 1 - Purification yields of the pilot unit

	peat	**Biowasher**

Acetone	38%	46%
Isopropyl alcohol	100%	100%
MEK	53%	61%
Butyl acetone	85%	81%
Cetone > C5	100%	98%
Cyclohexanone	97%	91%

Table 2 – Degradation by VOC type

Degradation yields depend on the type of support used and on the type of VOC emitted. The degradation yield depends on the solubility of the VOC. Chemical with the higher solubility give the higher yields.

ADSORPTION AND CATALYTIC OXYDATION (SORBICAT SYSTEM ®)

Principle

The idea of this technology is to couple an adsorption followed by a catalytic oxidation.

- Zeolite is used for the adsorption
- Platinum is used for the catalytic oxidation

The pilot used by CTC for these trials is a 1.000 m^3/h.

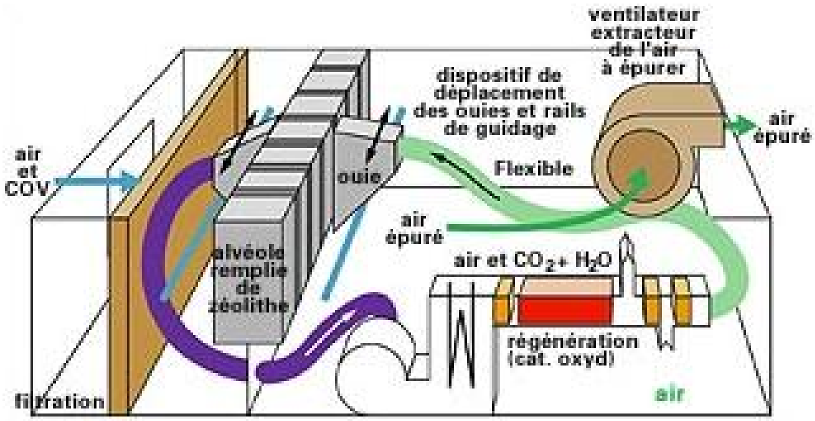
Adsorption and catalytic oxidation are integrated within a caisson as described on scheme 1 and showed on picture 1.

The adsorption system is composed of 7 cells of zeolite. VOC are adsorbed on 6 cells at the same time while the last cell is being treated through the catalytic system.

Regeneration of the cells is possible thanks to a counter courant, closed loop of heated air.

VOC are extracted thanks to heated air and oxidized through the oxidation system (electric resistance with the platinum catalyser). Each cell is being automatically regenerated one after the other.

Picture 2 – SORBICAT pilot plant

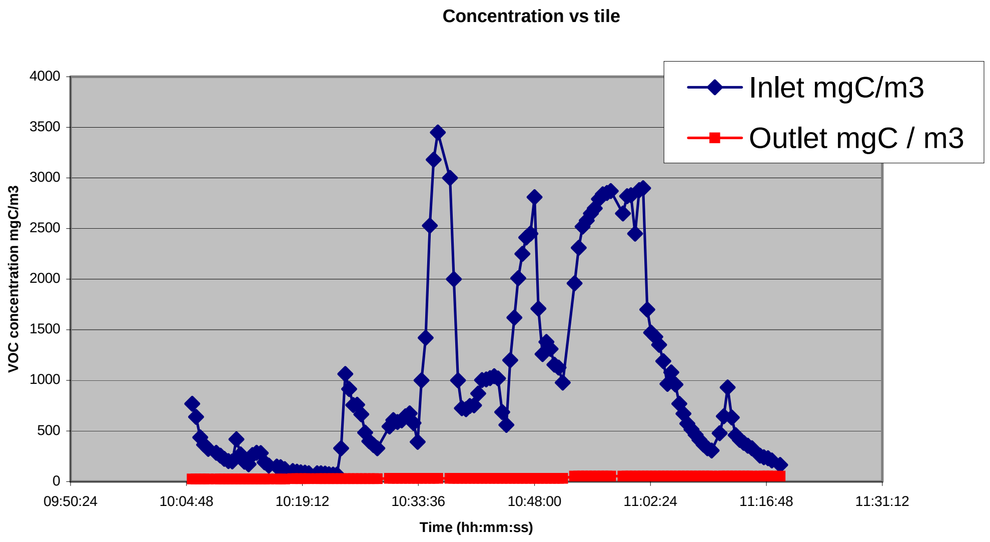


Scheme 1 – Principle of the treatment

Results

Graph 2 presents the concentration of VOC before and after treatment.

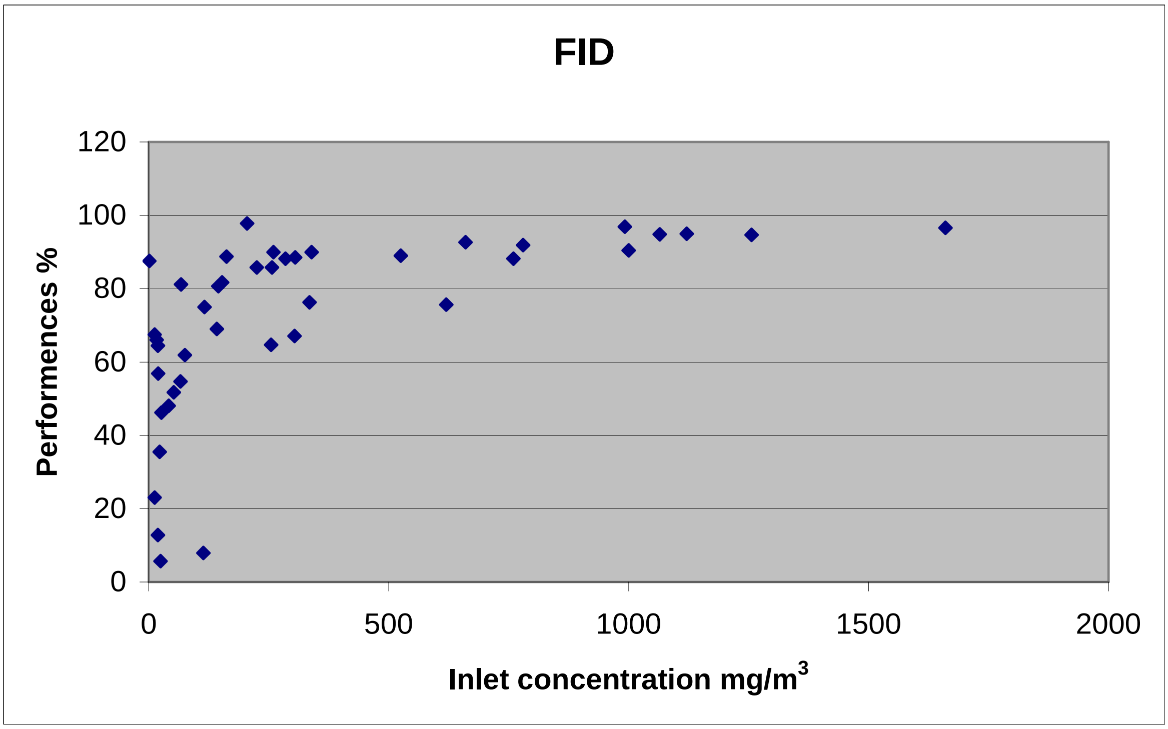
Whatever the concentration is before treatment (up to 3.500 mg/m^3), concentration after treatment remains below 100 ppm.



Graph 2 – VOC concentrations at the inlet (blue) and outlet (red) of the pilot plant

Graph 3 indicates

- Above 200 ppm of VOC, the performances of the pilot are rather constant, from 80% to 97%.
- Below 200 ppm, the performances are lower indicating that the system has less efficiency for some chemical. Results indicate that performances vary depending on the nature of the substances and their affinity for the zeolite. Acetone and iso-propylic alcohol are less adsorbed than butyl acetate.



Graph 3 – Performances (%) versus VOC inlet concentration

CONCLUSION

- The best way to avoid VOC emissions is to avoid solvent during the finishing operations. Improvements have been done by the chemical suppliers and by the tanners.
- Concentrations fluctuation from the finishing operations has been confirmed.
- Flame Ionisation Detector (FID) enables the detection of total VOC even if a 20% error remains.
- Both biological treatment and adsorption followed by and catalytic oxidation have shown their possible use for VOC treatment in the tanning industry.