



VOCs in the tanning sector: characteristics, reduction and treatment⁽¹⁾

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

Constraints have been defined in the EU directive 99/13/EC. Implementation, for some European countries, began on March 30, 2005 and it should come into effect in all countries on March 30, 2007. These constraints refer to the "total area of coated leather 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 metre of leather produced.
- For solvent consumption above 25 tonnes per year, total emission limit values are 75 grams of VOC emitted per square metre of leather produced.
- For leather coating activities in furnishing and in particular for leathers used as small consumer goods such as bags, wallets, etc., total emission limit values are 150 grammes of VOC emitted per square metre of leather produced.

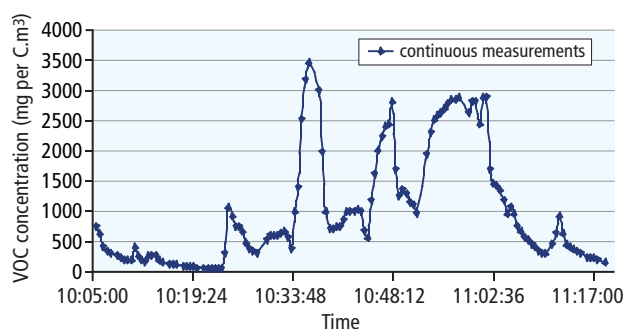
VOCs in the tanning industry vary in terms of composition and concentration versus time. A typical composition of a tannery VOC includes the following substances: acetone, butyl acetate, cyclohexanone, isopropyl alcohol, methyl ethyl ketone (2-butanone), 2-pentanone or ketone C ≤ 5, ethyl acetate, cyclohexane, di-isobutylketone (DIBK), xylene, butane-diol isomere, methyl iso butyl Ketone (MIBK), toluene, ethylbenzen.

Concentration varies from 100 to several thousand milligrammes per cubic metre during finishing operations. The extractions of the finishing booth have a flow that may reach 10,000 or 12,000 m³/hour for one finishing line.

Typical emissions of VOCs in the tanning industry are shown in Panel 1:

Considering these emission characteristics, it was clear that there was no simple method of treatment available. However,

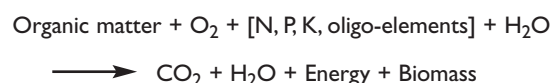
Panel 1: Emissions of VOCs in the tanning industry



following a survey of the different technologies available on the market—including efficiency, flow rate, concentrations, the type of VOC treated, and economic aspects—two techniques were identified and tested.

1. Biological treatment

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



With regards to air treatment, the bioreactor needs to fully accommodate both the transfer of the pollutant from the gas to the liquid phase, and the biodegradation.

THE BIO-FILTER

A filter is made of a packed column used as a support for the microbial growth. In this investigation a bio-filter of 1,600 mm height and 2,300 mm diameter was used. This reactor was divided into four compartments in order to test four different materials used as support for the bio-mass:

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

THE BIO-WASHER

In addition to the bio-filters, a bio-washer was tested simultaneously. The bio-washer comprised three different steps:

An absorption column: The water circulates at counter current for the transfer of VOCs from the gas to liquid phase. The use of a packed column is more effective than a non-packed unit because the increased contact area improves the pollutant exchange from one phase to the other. The column diameter was 465 mm and 3 metres high.

An activated sludge basin: A biological reactor in which an aerobic biodegradation takes place. Air bubbles are introduced using a compressor to provide:

- Homogenisation
- Oxygen, as required by the micro-organisms

**Panel 2: The bio-washer and bio-filter**

- Suspension of the sludge
- Contact between the polluted liquid phase and the biomass.

A decanter: To remove excess biomass from the system.

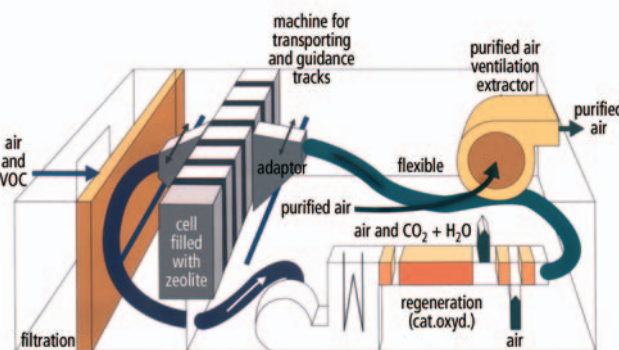
The bio-washer and bio-filter are shown in *Panel 2*. The main results for the removal of VOCs as purification yields and the

Panel 3: Purification yields of the pilot unit

	On site trials (Finishing booth)	Recovered cleaning solvents
Bio-filter with activated carbon	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%

Panel 4: Degradation by VOC type (comparisons of results obtain with a bio-filter with peat and the biowasher)

	Degradation with peat biofilter	Degradation with Bio-washer
Acetone	38%	46%
Isopropyl alcohol	100%	100%
MEK	53%	61%
Butyl acetone	85%	81%
Cetone > C5	100%	98%
Cyclohexanone	97%	91%

Panel 5: Principle of the treatment**Panel 6: The SORBICAT pilot plant**

degradation according to VOC type are shown in *Panels 3* and *4* respectively.

With reference to *Panel 3*, the main trials were performed directly on the finishing booth exhaustion. However, during a vacation period as the finishing booth was not operating, the trials were organised with recovered cleaning solvent. This emission composition is similar to that of the main trial but concentration versus time is relatively constant.

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

2. Absorption and catalytic oxidation

This technology couples an absorption with a catalytic oxidation. In this system, Zeolite is used for the absorption, and platinum is used within the catalytic oxidation.

The pilot used for these trials is a Sorbicat SystemR with a capacity of 1,000 m³/h. The absorption and catalytic oxidation are integrated as indicated in the schematic shown in *Panel 5*. The VOCs are absorbed in zeolite-containing cells set in series, before oxidation within the catalytic component. Regeneration of the zeolite cells, one after the other, is enacted using a counter-current, closed loop of heated air.

The VOCs are extracted using heated air, then oxidised within the oxidation system (*electric heating elements with the platinum catalyser*). The pilot plant is shown as *Panel 6*.

PERFORMANCE AND OBSERVATIONS

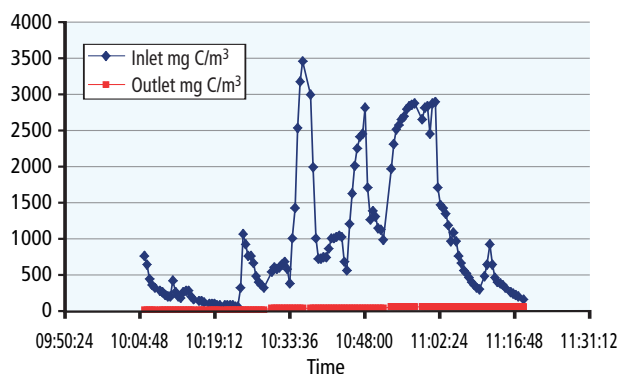
The concentration of VOC before and after treatment is shown in *Panel 7*.

This shows that whatever the concentration before ➤

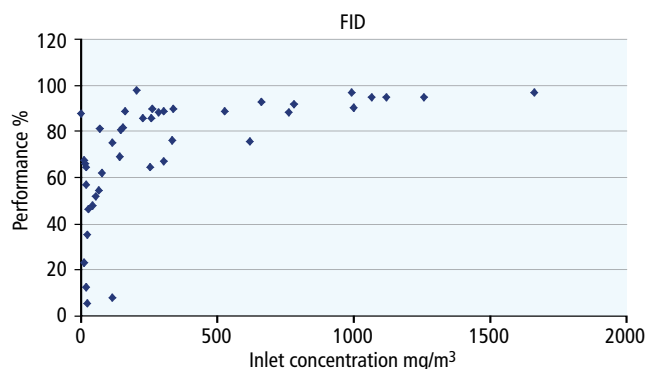
VOCS IN THE TANNING SECTOR



Panel 7: VOC concentrations at the inlet and outlet of the pilot plant



Panel 8: Performances (%) versus VOC inlet concentration



treatment (up to $3,500 \text{ mg/m}^3$), the concentration after treatment remains below 100 ppm. The performance, expressed as a percentage, is given in *Panel 8*.

This indicates that:

- Above 200 ppm of VOC, the performance of the pilot was very constant—from 80% to 97%.
- Below 200 ppm, the performance is lower indicating that the system is less efficient for some chemicals.
- Results indicate that performance varies depending on the nature of the substances and their affinity with the zeolite. Acetone and iso-propylic alcohol are absorbed less than butyl acetate.

Conclusions from the investigation

- The best way to avoid VOC emissions is to avoid solvents during the finishing operations. Improvements have been made by both chemical suppliers and by tanners.
- Fluctuation in VOC emissions from finishing operations has been confirmed.
- Flame Ionisation Detector (FID) enabled the detection of total VOC, although a 20% error margin remains.
- Both biological treatment, and absorption followed by catalytic oxidation, have proved possible for use for VOC treatment in the tanning industry. 

Acknowledgement

(1) This project was financed by the Région Rhône-Alpes, France, to a value of €40,000.

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