LEATHER PRODUCTION: 
INDOOR INDICATORS FOR BATING PHASE IMPACT

Extended abstract

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Background

Traditional tanning processes for leather production have an important impact both on environmental and indoor conditions. The introduction in the 60s of rotating drums for tanning operations has permitted not only the perfect distribution of chemical agents and dyes the reduction of float volumes, but also a a significant reduction of indoor odour spread. This latter aspect can be further improved.

In the leather industry, the use of poultry dejections (PoDe) was historically abandoned on account of indoor odour impact as well. The use of technical products (TP) derived from PoDe as bating agents in the tanning industry to replace Standard Formulations (SF) was explored at the pilot scale in the LIFE project PODEBA (LIFE10 ENV/IT/365, Use of poultry dejection for the bating phase in the tanning cycle). Both TP and SF contain the proteolytic enzymes needed for de-limed pelt maceration, in order to obtain controlled weakening of the three-dimensional derma structure, through elastin and collagen breaking.

One of the main drawbacks of this kind of recycling is connected to foul smells that are typical of animal dejections but also of the tanning cycle. One of the project goals is to demonstrate how a poultry dejection treatment can reduce odorigen impact on the whole system, taking into account that standard conditions themselves are a source of foul smells (Dall’Ara et al., 2012).

Objectives

The goal of this paper is to present the strategy adopted to demonstrate PoDe deodorization after the treatment, and the evaluation of odor aspects connected with the use of this technical product in the bating phase compared with standard chemical formulations (SF).

Outline of the work

Because of difficulties in measuring indoor modifications or effects on the internal drum conditions (water, pelts and air during 0.5-1 hour rotation), the indoor impact of using TP during the bating phase was assessed by by experts of the tanning cycle (subjective perception), supported by objectively measuring the modification of standard odour conditions (obtained with SF).

The choice was to measure selected Sulphur compounds in TP and in the final bating floats, as incremental source of emissivity. The selection of indicators was made on the basis of scientific literature and technical data related to typical PoDe emissions. As evidenced in BREF (EC, 2003), ammonia is one of the main indicators of PoDe emissions; dimethyldisulphide (DMDS) is an indicator of poultry manure emissions in comparison with other manure generated by other animals (Asdrubali et al., 2005). Moreover, because of their heavy olfactometric impact, two additional sulphur compounds were selected (methylsulphide, and dimethylsulphide, DMS). In the bating phase, Ammonia contribution was not explored because its TP content (< 5%) is much lower than SF content (18%).
Furthermore input materials (TP) were characterized throughout their production: the indicators were detected along the production process, thus enabling the comparison of the final product with the initial conditions.

**Methods**

Odour emission analyses were performed for:

- TP production, on different type of TP (Poultry manure treated with a patented method and slight modification of it) contained in big bags, just before its use for the tanning test;
- Leather production, Bating phase, on volatile fraction of process wastewater samples (Bating floats), using different types of TP.

The experimental methodology, together with measurement methods used for emission indicators, are summarized in Table 1. First and Second generation TP were prepared by slightly changing the treatment recipe (AMEK, CTI, 2002), in order to select proper TP. Bating agents were tested in 2 different runs: a first run where SF was compared with W (a test without bating agent) and A (first generation TP); a second run where SP was compared with P (second generation TP).

To allow gas monitoring during TP production, a probe consisting of a Teflon piezometer (1,5” diameter) was inserted and left inside different big bags. The probe was closed at the bottom and equipped with a “T” and laterally perforated with small holes. Measurements of the selected indicators were made by gas-chromatograph (GC) coupled with the mass spectrometer (MS) in order to separate the analytes to be characterized, while MS could identify them (GCMS System Mass Agilent CG coupled to MS 5975C MSD, Agilent Technologies, Milan, Italy). Ammonia was detected by a spectrophotometrical method.

For bating floats, the extraction of volatile substances from the aqueous sample was carried out by means of two techniques: in the first run Purge & Trap (8 ml sample were flushed by means of inert gas (He) flow -purging, which was then conveyed into a concentration trap; from there the substances were injected into the GC-MS system using thermal desorption) . In the second run, Head Space (performed with HS autosampler, three grams of float samples were placed in a 10 mL vial heated at 60°C for 1800 s). In both cases, volatile compounds were identified and semi-quantified by same GCMS System Mass.

**Results and discussion**

During TP production, the results of emission indicators show a significant reduction in all parameter concentrations, demonstrating a reduction of odour emission in final TP (start-end). In particular, the “emissions” of DMS were reduced by 89% v/v, while concentrations of the DMDS and methanethiol were both reduced by about 99% v/v. The goal of reducing ammonia g emission by 80% compared with initial conditions was achieved.

With reference to bating float characterization, the chromatogram graphs related to the first run are reported in Fig. 1, which represents the overlapping chromatograms: W (1foro-black), SF (2fori-red), A (5fori-blue). The detected substances, corresponding to the chromatographic peaks, were identified by comparing their fragmentations with those stored in the N.I.S.T. library. Among the detected substances the ones of interest were: the carbonyl sulfide (COS), the methanethiol (CH\(_3\)SH), dimethyl disulphide (CH\(_3\)SSCH\(_3\)), and dimethyl trisulphide (CH\(_3\)SSSCH\(_3\)). The peak areas are directly proportional to substance concentration; therefore, as a first approach, a comparison of odour impact of the three floating baths can be schematized with the peak area ratio. Taking into reference SF, W presented the following ratio: 47%; 25%; ND respectively for CH\(_3\)SH, CH\(_3\)SSCH\(_3\), CH\(_3\)SSSCH\(_3\). Similarly, A presented the following ratio: 259%; 463%; 222% respectively for CH\(_3\)SH, CH\(_3\)SSCH\(_3\), CH\(_3\)SSSCH\(_3\).

The chromatograms related to the second run are reported in Fig. 2, which represents the HS-GCMS chromatograms of bating floats: SF (M1, red), P (P1, green). The chromatograms of the two samples showed peaks with similar heights, indicating similar concentrations for volatile compounds in the two samples SF and P.
The assessment of odour impact modifications was made by technicians and process developers as far as bating process conditions compared with standard process (SF), they are summarized as follows:

- the W test showed foul smells during the bating process as well as bad quality in the final tanned leather;
- the A test showed foul smells during the bating process, but good quality of tanned leather;
- the P test showed very similar smells to SF during bating process and good quality of tanned leather;
- the A and P tests had no odour impact on finished leather, just as SF.

Only second generation TP can assure odour conditions similar to a standard process; nevertheless, all bating agents based on PoDe had no odour impact on finished leather and do not influence them.

PoDe treatment, which is necessary to assure final product sanitation, is a key factor to produce a TP suitable for its use as bating agent in leather manufacturing.

At the moment, according to tanning experts, the results of these activities indicate the reduction of olfactive impact in the use of TP in comparison with first generation TP. In addition they do not show a change in bating phase odour impact taking into reference SF with the use of second generation TP. These results, together with the positive effects on leather structure and cleaning surface, indicate that second generation TP is suitable for tannery

**Concluding remarks**

The strategy adopted for the control of odor aspects connected with the use of poultry dejections PoDe in the bating phase to replace standard products (chemical formulations containing proteolytic enzymes as well) was useful to select the proper optimized TP and its process production. In fact, second generation TP affords a reduced olfactive impact in comparison with first generation TP samples, and has a very similar impact compared to SF. In addition, TP performs well as a bating agent, in terms of leather structure and cleaning surface. All poultry manure samples had no impact on finished leather (as confirmed by their historical use).

The selected measurement system checking TP production and bating phases in leather production have led to analytical results in agreement with subjective assessment by the experts and are, therefore, indicative of actual indoor conditions.

**Keywords:** bating phase, leather production, odour impact, poultry dejections
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References