Comparison of tanning methods from an ecological viewpoint 1999

Collagen is a versatile biopolymer and, as a renewable resource, is of global significance. Every year, an estimated 4 million tons of pure collagen in the form of hides and skins is processed worldwide on an industrial and commercial scale. Some 70% of leather production is based on large animal hides from the meat industry (cattle, buffalo), ie the leather industry is a byproduct industry. Worldwide resources in large animals available for the production of raw hides have increased steadily over the last 25 years and today encompass an estimated 300 million slaughtered animals.

Approximately 80-90%of all common leather types are produced by chrome tannage. Practical experience has been available with regard to the production, processing and serviceability of chrome leather for at least 100 years. As heavy metals are, in general, considered pollutants, criticismof chromium salts has grown alongside an increased awareness for our environment. The reaction of industry and research institutes has been to provide a multiplicity of scientific investi-gations, new technologies and improved envir-onmental methods.

However, criticism of the production and use of chrome leather continues and there is an ever more widespread demand for the production of chromium free, so called 'organic' or 'bio' leather. Knowledge about the environmental impact of the technologies hidden behind these rather illdefined terms is lacking, or is at best sketchy compared with the information available on chrome tannage.

Doing away with chromium is often con-sidered to be an environmentally friendly action, without the new production methods ever having been assessed with regard to their total material and effective life cycle. It is, therefore, impossible to come to objective comparisons and conclusions in favour of alternative technologies.

High-quality leather for the upholstery and automotive industries made from large cattle hides is of major significance for value creation within the German leather industry. Theproducers are, therefore, very interested and eager to work with as little negative impact on the environment as possible, both with regard to processes and the productitself.

However, should tannage using chromium salts be replaced partially or altogether? Producers will have to cope with ecological, qualitative and cost implications which are extremely difficult to oversee at the moment.

Methods and processes

A product life cycle assessment (LCA) usually includes the gathering and processing of data on the whole life cycle of a product, from the extraction of raw materials to disposal. In this assessment, only the main leather production process, ie the tanning process, has been examined. The research method is based on the Draft Standard -Life Cycle Assessments / Principles and Framework: (prEN ISO 14040:1996).

The German Environment Protection Agency defines the objective of a life cycle assessment as: a comparison, which is as comprehensive as possible, of the environmental impact of two or more different products, product groups, Systems, processes or modes of action. The full definition can be found in reference 3.

One peculiarity of this research project is that nearly all Information has been gathered through experiments and not from a variety of sources in literature. The 'vertical analysis' included a risk assessment of auxiliaries and followed the production process from the limed and split hides right through to the fatliquored and dyed leathers, but without including the finishing processes.

The 'horizontal analysis' concentrated on effluents, sludge and waste, including their disposal and reuse. The ecological impact of the processes as expressed in inventory and impact analyses of the effluent and waste charges, was correlated to the costs and quality of the final product.

The objective of the project was not the generation of absolute environmental data, but to evaluate the selected tanning methods by direct experimental comparison. The quest for absolute figures did not seem conducive to the objective of the project, given the enormous technological breadth of Variation in leather production. In addition, in practice no tanning method for upholstery leather exists, which is restricted solely to tanning agents in the strict sense.

The production of high grade soft leather is based on combinations of different tanning agents and auxiliaries. Allocation to a particular tanning process is always derived rather than the predomi-nant mineral, synthetic or vegetable tanning agent.

Starting from the best chromium ffee tanning processes, three representative technologies for soft leather were selected. The recipes were based on the indications and recommendations of auxiliary manufacturers or were taken from literature and defined as technologies II - IV. Tannage I, a conventional chrome tanning process, was used as benchmark and control group. Tannage II represented wet white processes on the basis of glutaraldehyde and synthetic tanning agents. Tannage III represented the class of combination tannages with glutaraldehyde pretannage, followed by a chromium retannage. Tannage IV used a pure vegetable tannage on the basis of a spray-dried mimosa extract.

Six salt cured, medium weight cattle hides were used for each test tannage. Identical process Steps in the beamhouse were used for all technologies. Only after lime

Splitting of the hides were the processes varied. As the quality of the raw material exerts a major influence on leather quality, each cattle hide was sided along the backbone after liming and further processed in two identical vessels, whereby all left sides were chrome tanned as the control group (tannage I), while the right sides were treated in accordance with the alternative tannages II - IV. The hides were marked accordingly to ensure precise classification at each stage. All outline conditions were kept as constant as possible in order to generate reliable and Substantive results. The aim was, in particular, to determine the differences in the environmental impact as a result of the tanning method used.

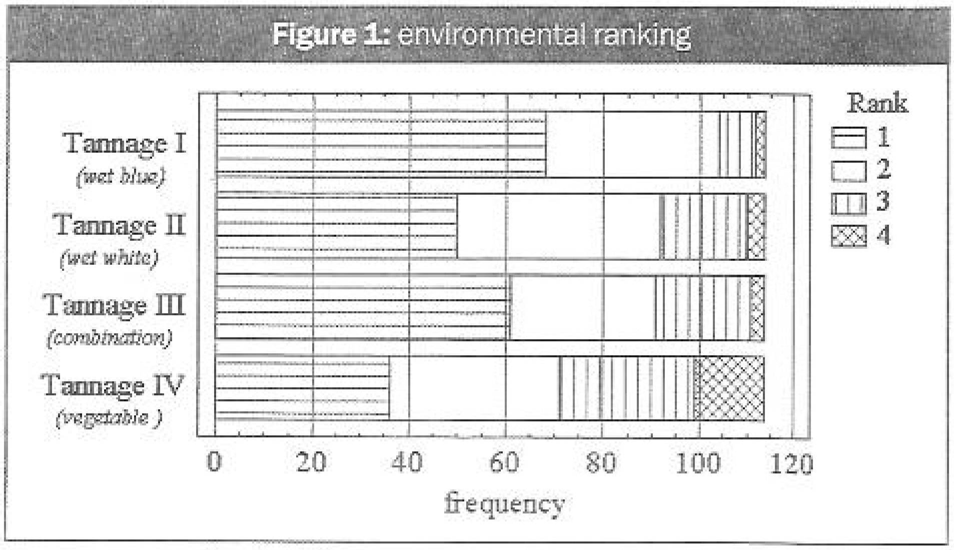
Results

The origin and extraction of the required auxiliaries is too complex to be able to include even one complete product path in the LCA. Different scenarios and allocations would have to be taken into account for each raw material or intermediate product. Even before their use, the choice of auxiliaries determines a possible environmental impact. Auxiliaries defined as haz-ardous products pose a risk during transport, handling and storage. In accordance with directive 91/155/EEC, every manufac-turer is obliged to provide comprehensive handling information for the users of their products in the form of safety data sheets. For all auxiliaries used, a risk assessment was carried out on the basis of these safety data sheets.

Ecological impact of the tanning methods

In the course of the project a multitude of data was generated which is impossible to present completely. Reference must be made to the project report (4). 114 parameters were selected from the totaldata material for presentation of the results in this paper.

Figure 1:



After comparing all four tanning method using these parameters, rankings from 1 to 4 were assigned. Rank 1 indicates the most favourable assessment of the relevant aspect. When the comparisons did not yield any significant differences between the different tanning methods or showed no differences at all the same rank could be assigned to several methods. The 114 parameters can be subdivided into the föllowing groups:

1. 37 ecological parameters with predominantly qualitative Statements
2. 26 ecological parameters with predominantly quantitative Statements
3. 17 environmental engineering parameters
4. 3 commercial parameters
5. 31 quality parameters for the finished leathers

Figure 1 shows how often each ranking has been assigned in the total assessment for tannages I - IV. It becomes evident that tannage I received the first rank almost twice as often as tannage IV. In comparison with tanning methods II and III, tannage IV again often ranks lower. This relatively poor Performance of the vegetable tanning technology (tannage IV) may surprise some, but can be explained relatively easily when the data material is analysed in detail.

The environmental impact associated with leather production is due mainly to the high water consumption and the specific composition of the tannery waste water. Important parameters for the quality of untreated wastewater types are indicated in tables 1 and 2. The significantly higher aquatoxicity of the post tanning floats compared with the floats drained up to the point of tannage is of particular interest. The so called GL value is a measure of this toxicity. It is the result of an accelerated photogenic bacteria test in accordance with DIN 38412 part 34. A comparison of the GL values in tables 1 and 2 shows that real pollution is shifted to the retannage/post-tanning stages. This holds particularly true for the alternative tannages II - IV. This is a fact which is often ignored or underrepresented in ecological assessments.

Table 1 and 2

Table 2: Wastewater analysis, combined effluents from tanning

Analysis	Tannage I	Tannage II	Tannage III	Tannage IV
COD [g O_2 $\cdot l^{-1}$]	4.3	7.1	3.6	14.9
DOC [g$\cdot l^{-1}$]	1.0	1.5	1.7	5.6
AOX [mg$\cdot l^{-1}$]	5.9	1.0	5.8	8.4
Phenol index [g$\cdot l^{-1}$]	0.3	1.2	0.1	1.3
Aldehydes [mg$\cdot l^{-1}$]	«1.0	9.9	22.0	0.9
GL value	14	18	44	340

Table 3: Wastewater analysis, combined effluents from retannage/post tanning

Analysis	Tannage I	Tannage II	Tannage III	Tannage IV
COD [g O_2 $\cdot l^{-1}$]	6.2	10.6	4.7	16.7
DOC [g$\cdot l^{-1}$]	2.6	4.4	1.7	6.1
AOX [mg$\cdot l^{-1}$]	0.2	0.15	0.08	0.1
Phenol index [g$\cdot l^{-1}$]	0.15	4.25	0.2	1.5
Aldehydes [mg$\cdot l^{-1}$]	9.7	19.6	14.0	16.9
GL value	≤1,400	9,000	2,000	≥2,000

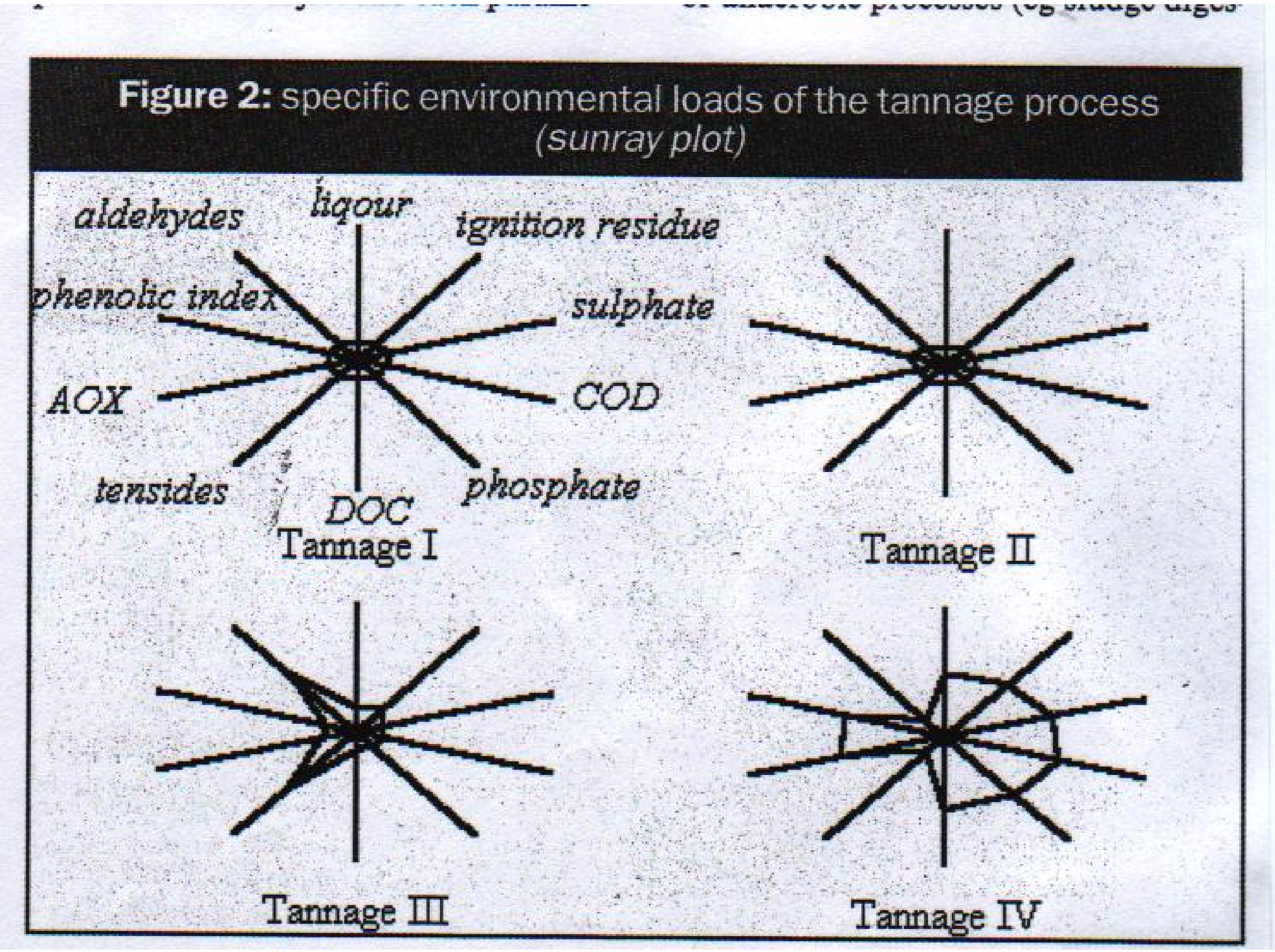
Apart from the qualitative aspects of ecological assessment, the issue of the efficient use of natural resources must also be considered. The total costs of a tannery with full in-house tannery stages can be broken down as follows: 62 - 65 % are caused by the raw material, 15 -18 % by auxiliaries, 12 -14 % by personnel costs, 5 -10 % by disposal and environmental costs and 3 - 4 % by energy. Any overheads must be added to these amounts.

The price of soft leather for the upholstery and car upholstery industries is determined by the surface area sold. For this reason and due to the high proportion of costs attributable to the raw material, the quality and the yield, relative to the raw hide quantity purchased, are of the utmost significance for the economic viability of the leather production. In most research studies investigating pollution caused by leather production, one ton of saltcured raw hide is used as the functional unit. One of the known facts of leather production is, however, that given raw hides of identical quality, the technology determines the final surface yield. For this reason, the establishment of a quantitative balance from which waste and pollutant quantities were extrapolated was based on the production of 100m² of leather. This approach is illustrated in figures 2 and 3. In these figures, values originating from the process stages tanning (deliming ti the end of tanning) and post-tanning (retannage, dyeing, fatliquiring) are compared. A sunray plot allows a quick comparison of a multitude of paramters of several objects. The appropriate measured value is plotted for each object and each parameter, and the relevant points are connected. The distance to the centre is not a absolute figure, but illustrates the relationship of the observed objects to each other. The form of the diagram changes with the combination of the objects. In this case the four tanning methods are the object and the different wastewater pollutanes are the parameters. Without further knowledge of the mathematical function the plots can be interpreted in a simplified way.

The individual peaks of a tanning method represent the problem parameter compared with other technologies, while the total surface area of the polygon expresses the sum total of the pollution compared with other technologies, ie with the increase of the surface area, the pollution also increases. This data presentation allows a very straightforward comparison of the environmental burden caused by each technology. The parameters indicated have the following significance:

- Float m³/100m² :denotes the generated waste water quantity and, besides the surface yield and the concentration values, in the central parameter for calculating waste water pollution.
- GR kg/100m² : includes all dissolved mineral constituents, including heavy metals. The ecological significance lies in the salinisation and in the discharge of persistent and toxic substances (heavy metals).High salt concentrations hamper waste water treatment and cause corrosion.
- Sulfate kg/100m²: poses, apart from salinisation, the danger of microbia hydrogen sulfide and acid formation and the related damages caused by corrosion (concrete corrosion) and the disturbance of anaerobic processes (eg sludge digestion).

Figure 2:



- COD kg O_2/ 100m²: is a general parameter for the oxygen exhaustion in the wastewater. Using this parameter, the required purification input for industrial wastewater can be determined. The COD correlates with other parameters such as BOD5 or TOC. These correlations only apply, however, within strict limits for the wastewater in question.
- Phosphate g/100m²: is classified as an eutrophicating wastewater constituent.Phosphorus compounds of usually only contained in small quantities in tannery effluents. Frequently, additional phosphate must be added during a biological Purification stage.
- DOC kg/100m²: characterises in total the pollution of the wastewater with dissolved organic carbon compounds which may include easily degradable, persistent,88 well as toxic constituents.
- Tensides g/100m²: in the context of this study, the anionic and nonionic tensides were determined. Tensides may lead to disturbances in the wastewater treatment (foam problems, oxygen feed). In water bodies they impair the interfacial tension and, therefore, the living conditions of lower water organisms and Bucroorganisms. If tensides are not completely degraded during wastewater treatment, they can find their way into the sewage sludge, where they can endanger the ground water by facilitating the elution of essential elements or heavy metals.
- AOX g/100 m²: is a parameter summarising the presence of halogenated hydrocarbons absorbed by activated carbon. Substances in these groups are either not degraded at all or are degraded, but only with difficulty. Both types are toxic. In effluents they may indicate, for example traces of preserving agents or be derived from auxiliaries containing such substances

(eg fetliquors)

- Phenol index kg/100m²: denotes the analysis of the total Phenol index (substances with oxidative coupling capacity).Using this parameter, the presence of synthetic and vegetable tanning agents in the effluent can be checked. A high phenol index is always coupled with high aquatoxicity
- Aldehydes g/100m²: this parameter is derived from the sum of formaldehyde and glutaraldehyde levels. Both substances are considered strong pollutants and have a high level of aquatoxicity. Their effect is Particularly marked against nitrifying and anaerobic bacteria

The relevant type of tanning method is reflected when wastewater pollution caused by tannage and retannage/post tanning processes (see Figures 2 and 3) is compared. Tannage I is characterised by a peak for sulfate, while the use of syntans in tannage II is reflected by a peak in the phenol index. With the exception of the strongly toxic subsatnce groups aldehydes and phenol index, tannage I is clearly distinct from the other tanning methods.

Figure 3 and 4

Figure 3: specific environmental loads of the wet dressing process *(sunray plot)*

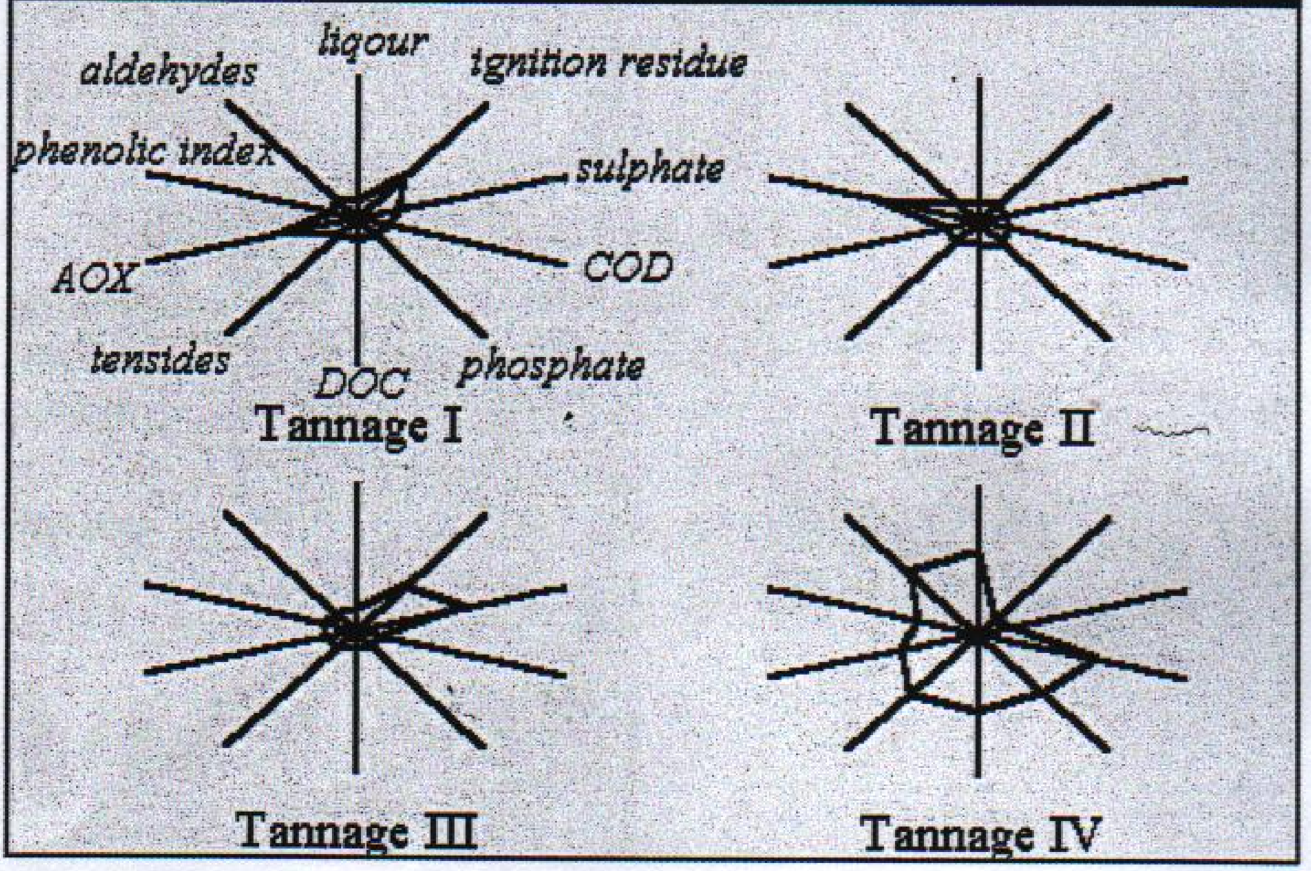
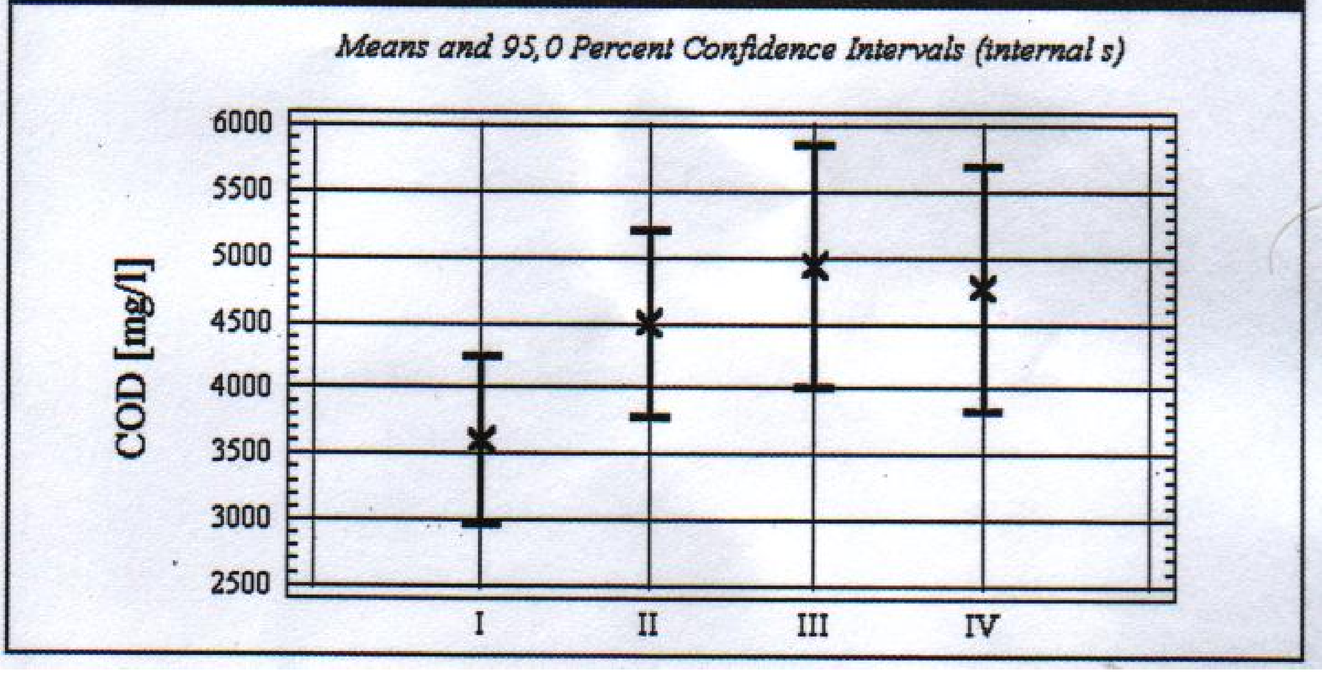


Figure 4: mixed effluents of beamhouse & tannage



With the exception of sulfate pollutionand the well-known chromium problem, tannage I caused the lowest wastewater pollution per production unit. In the pickle of tannage II, the inorganic components were substituted by organic acids and salts, this reducing the salt load dramatically.

Within the context of the overall project, the effectiveness of other known processes for wastewater cleaning was investigated. As in practice, the effluents from the beamhouse and tannage were treated togeher for this study. The strongly alkaline effluents from the beamhouse floccuate spontaneously with the acidic residual tanning floats and tanneries traditionally make use of this synergistic effect.

The created primary sludge was separated off before testing. Figures 4 and 5 indicate the relevant arithmetic mean values and the confidence levels of the COD before and after a biological cleaning process. This is in accordance with the activated sludge process.

The spontaneous flocculation of the mixed effluents significantly levelled off the differences between the four raw effluents; the effect was most pronounced with tannage I due to the precipitating effect of the chrome hydroxide flocs. After biological treatment, no significant differences could be ascertained between the mean COD values. The activated sludge treatment demonstrated comparable effective-ness for all technologies. The degradation rates reached 70 - 80 % for the COD and 97 - < 100% for the BOD5, whereby the difference between the parameters indicates persistent substances. Only when the tanning methods are related to the functional unit of the LCA, calculated as the residual COD load in kg O_2 per 100 m^2 of leather, can they be distinguished. When the theoretical residual charges are calculated for tannages I - IV from the data generated through experiments, the ratio is 1.0 : 1.7 : 1.8 : 2.0. To achieve the same production result, tannage IV would, therefore, generate about twice the COD Charge of tannage I after the wastewater treatment described.

Within the framework of the project, the effect of anaerobic-biological (fixed bed reactor) and chemical-mechanical wastewater treatment (flocculation/precipitation) was checked.

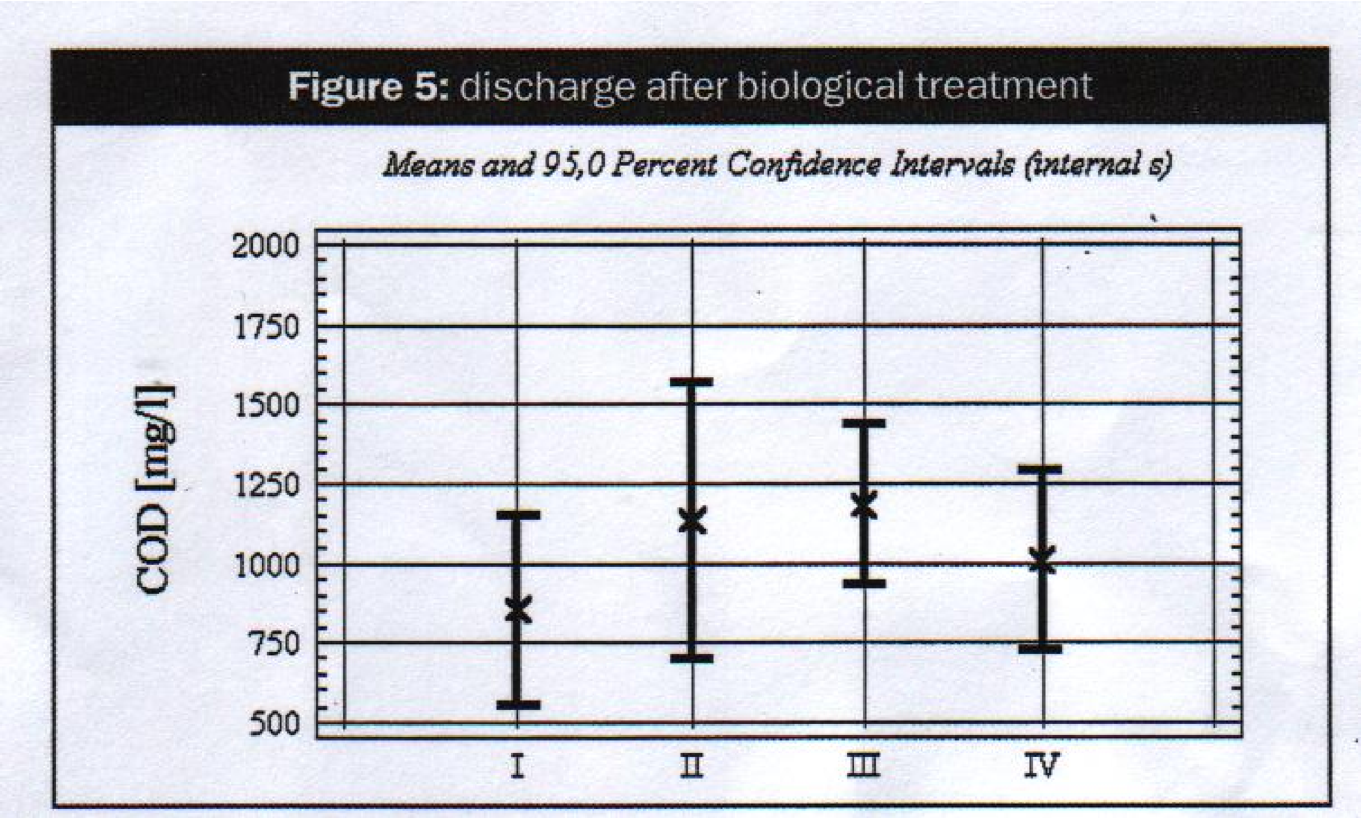
The former treatment proved to be an unsuitable method for all four tannages in question. In precipitation tests in accordance with a unified method, the wastewater from vegetable tanning (tannage IV) yielded a voluminous sludge which was difficult to dewater.

The specific filter cake resistance was determined for all four tannery sludges. The value for tannage IV was twenty times higher than that of sludges from tannages I to III. The problem can be solved, albeit at the expense of a high dosage of auxil-iaries which in turn cause an even larger quantity of sewage sludge.

The dewatered sludge from the mechanical physical wastewater treatment and the shavings generated during thickness regulation of the leather were subjected to an eluate test in accordance with DIN 38314 S4 in order to check their dumping ability.

When measured against the legal stipulations of the Technical Directives on Waste Disposal (TA-Abfall) or Municipal Waste (TA-Siedlungsabfall), the TOC eluates for the sludge and leather samples investigated proved to be inadmissibly high. The shaving eluates from tannages I and III generated very high concentrations with regard to the phenol index. The tannage I sludge generated an eluate of 0.4 mg/l, and the wet-blue shavings 113.5 mg/l.

Figure 5:



Apart from a literature search on types of waste disposal, practical investigations were also carried out. The shavings were submitted to two manufacturers of leather fibre board and protein hydrolysates for testing.

As expected, the leather fibre board samples made of shavings from tannages I and IV demonstrated good to very good properties, while the wet white tanned shavings from tannages II and III yielded inferior leather fibre board products. The shavings hydrolysis tests demonstrated that only the chromium shavings from tannage I were suitable as a raw material basis for the creation of hydrolysate.

Conclusion

The results of the comparison can be summarised as follows:

Tannage I proved efficient and was associated with reasonable costs. It gave a relatively low wastewater, sludge and waste load per leather surface produced.

Tannage II gave the lowest salt wastewater pollution of all the tannages.

No problems with heavy metals and sewage sludge could be determined. The general wastewater pollution (DOC, COD) was significantly higher than for the control group.

The aquatoxicity of the raw wastewater was particularly high in retannage/post tanning. Substances characterised by Parameters in the phenol index and for aldehydes were particularly striking.

Tannage III was a compromise between chrome tanning and alternative technologies. This method required the smallest number of auxiliaries, but required more process water than the control group.

The raw wastewater from the retannage/post tanning processes demonstrated the lowest level of aquatoxicity of all the post tanning floats tested.

Tannage IV caused the highest tanning costs. At the same time, it was the most involved technology (water consumption, process times), and it led to the highest wastewater, sludge and leather waste pollution by a wide margin.

The second part of the paper, concerning the leather quality produced from the four tannages, will be published in the Jan 2000 issue of Leather.

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