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Environmental Aspects of the Future of Tanning Methods.

(Horizon 2050)

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1. The background situation by the year 2050

If in the year 2050 anyone should happen to read this, he certainly is going to wonder and to smile. Predictions of this kind are bound to be more or less perspicacious extrapolations of present trends, other things being equal. But other things are never equal.

In the following, I sometimes use the first person to indicate that the scenario is based on subjective considerations.

We have to think of a world with appr. 10 billions (10^9) inhabitants. This implies a strong pressure on the global food resources and consequently a strong demand for agricultural area and effectivity as well as sustainability of the agricultural production. This sustainability includes an effective preservation of e.g. the rain forest.

Probably around 2050, energy problems have been more or less solved, as fusion energy is being put into practical use (although there still will be an upper limit for how much energy it is acceptable to produce).

These factors will leave their mark on environmental measures and regulation. In many respects, environmental demands are going to be tightened up, in other respects alleviated. For instance, the use of sludge in agriculture is going to get a high priority, leading to stricter limits for some parameters and, on the other hand, repealing of limits and restrictions without any scientific justification.

Secondary or even more extensive waste water treatment will be obligatory for towns as well as for tanneries discharging into surface waters. This, added to the population increase, leads to a drastic increase of the amount of sludge generated. To some extent, this will be counteracted by cleaner production in the industry as well as preventive measures concerning waste water from other sources.

Environmental regulation as well as its enforcement has become uniform around the globe, with due consideration for local conditions. Generally, the required efficiency of environmental measure is going to be substantially higher than today, and cost are increasing with the efficiency more or less exponentially.

The leather industry is going to exist as long as meat is eaten. It is only going to disappear if the world goes vegetarian, or rabid animal protection activists gain power.

However, the population and the demand for e.g. shoes is growing faster than the meat consumption and hide production, and leather products become luxury items. This should leave room for the necessary environmental expenses. High efficiency of environmental measures presupposes a high level of technological competence, which is found in all tanneries existing in 2050.

2. Environmental Challenges.

Problems which have to be solved satisfactorily are:

Sustainable raw materials (hides, chemicals, etc.)

Satisfactory utilization or disposal of all kinds of wastes (waste water, sludge, solid wastes from the production), not only from the tannery itself but also from the leather consuming industries.

For all kind of wastes it is true that prevention is better than utilization and utilization better than disposal.

Occupational safety.

No health risks to consumers (allergies, etc.)

Environmentally acceptable disposal of final products (waste leather articles).

General good housekeeping is a matter of course in all tanneries existing in 2050.

3. Chromium

3.1.Environmental regulation and the philosophy behind.

Present limit values (cf. (1)) are very strict:

	Most strict values	"Median" values
	"ppm Cr"	
Discharge to sewer	0.8	3.5
Discharge to surface water	0.05	1.5
Sludge to agriculture	100	600

The limit values refer to Cr (III) where valency is specified; otherwise to total Cr.

To this must be added the fact that in some cases where a tannery discharges its waste water into a municipal treatment plant, and the municipality is not allowed to apply the sludge to agricultural soil, due to its chromium content, the tannery will have to pay the surplus costs arising from this. Already, a Danish tannery has to pay 150 USD per kg Cr discharged besides the normal waste water tax (appr. 3 USD/m^3). In another Danish municipality, the payment is 675 USD per kg Cr discharged.

Problems motivating this strictness towards Cr III are to a great extent without any risk based justification, but mainly of psychological nature. The psychological reasons are:

Cr is classified as a heavy metal and of many authorities considered to be similar to e.g. mercury.

While scientists almost uniformly recognise the important distinctions between trivalent and hexavalent Cr, environmental authorities often do not.

Waste Cr does not disappear, and due to modern technique of analysis and relatively low background values it is easy to demonstrate even a small introduction from outside.

This overshadows the fact that according to an overwhelming evidence in the scientific literature, Cr (III) has a very low toxicity, is only slightly soluble, and shows no biomagnification, but on the contary a biominification, as it is very poorly absorbed by plants or animals.

Any risk for ground water contamination does only exist in acid, sandy soils.

The question of oxidation of Cr III to Cr VI on agricultural soil, which was raised some 20 years ago, lost again its importance. Under certain circumstances, a small part of Cr III may become oxidized (on the surface of alkaline soils in the presence of manganese), but Cr VI is reduced back to Cr III by organic substance in the soil, and Cr III complexed by high molecular weight organic ligands is not readily dissociated and oxidized.

Concerning regulation of Cr content in sludge applied to agricultural soil, two philosophies exist: One is that limits (if any) must be risk based (cf. the decision of the United States Court of Appeals concerning Cr limits). The other, widespread in Europe, is that the concentration of Cr in any soil ought to remain what has been provided by nature.

Personally, I am sufficiently optimistic to assume that in the long run the first mentioned attitude is going to prevail. In a world with 10 billion people, it will be considered bad housekeeping not to utilize all sludge in agriculture, which has not been demonstrated harmful by scientific evidence. Any kind of fertilizers and soil improvers will be in great demand. Under these circumstances, chrome tanning will regain its importance. (Also restrictions on chromium in water and waste water may be alleviated, but in this case the impetus will be less strong).

The crucial question is: What is going to happen in the meantime? In the worst case tanners will have to learn chrome tanning technology once more.

<u>3.2 Future development and environmental consequences of the chrome tanning</u>

Anyhow, the specific chromium discharge is going to be further reduced. The future belongs to high-exhaustion tanning rather than precipitation and recovery, if not of other reasons, then because of the neutral salts discharge (cf.section 4) and because the high-exhaustion tanning also reduces the amount of Cr leaching out during the wet aftertreatments. Certainly, the high-exhaustion tanning methods are going to be improved, but any further reduction of the chromium discharge can be of limited importance, only, as a high exhaustion is already achievable, and a degree of exhaustion which makes it possible to comply with a limit of e.g. 100 ppm in sludge, will hardly ever become a reality.

In a global perspective, the greatest improvement in this respect will consist in the gaining ground of the high-exhaustion tanning (from appr. 25% to appr. 90% of all chrome tanned leather), supplemented with more extensive use of other known technologies such as lime splitting, reduction of the chrome offer (achieving boil resistance only when neccessary), and adequate pH control and a suitable selection of chemicals for the wet aftertreatments.

The technological competence necessary for carrying out all this is found in all tanneries existing in 2050.

With regard to environment, combination tannings including Cr have no specific advantages, as the reduction of chrome discharge obtained is of minor environmental importance. Environmentally, wet white technology may solve problems connected with solid wastes disposal, or be used in nonchrome leather production.

Taking a look on chrome tanning according to the list of environmental challenges found in section 2 may be a useful yardstick for an evaluation of alternative tannages:

a) Sustainable raw materials

Although chromium is not a renewable resource, the commercially extractable reserves are sufficient for several centuries, and the chromium consumption of the leather industry counts for only appr. 2.5% of the total consumption. On the basis of (2), the consumption of the tanning industry can be calculated to appr. 85,000 t Cr per year (referring to 1996).

b) Utilization or disposal of wastes

b1) Waste water

With the use of high-exhaustion tanning and secondary waste water treatment, chrome content in the discharge to recipient creates no problem.

b2) Sludge

The obvious way to dispose of the sludge is to utilize it in the agriculture. Other utilizations, e.g. as raw material in the building industry, are not promising. Incineration of the sludge should be avoided, as the sludge being alkaline during the incineration furthers the oxidation to Cr VI, but this will hardly be of interest in 2050.

For a tannery with its own waste water treatment it is impossible to comply with a limit of 100-200 ppm Cr in the sludge dry matter. Under present conditions, the absolute minimum achievable would be 1200 ppm, and that only in a few, optimal cases (3). Presumably, this figure is not going to be lower in 2050, as reduction of the chromium discharge and the suspended solids discharge are probably going to keep pace.

If the tannery discharges into a municipal plant, compliance may indeed be possible, according to the dilution.

Under the conditions prevailing in 2050, authorities and tanneries can probably agree on a concentration limit acceptable for both, say 3000 ppm.

What is said above (b1 – b2) refers to tanneries with a complete processing from rawhides to crust or finished leather. For tanneries processing wet blue, the situation is somewhat different.

b3) Solid leather waste

Unfinished chrome leather waste will be utilized. Probably, leatherboard production still exist and still consumes only a part of the waste. Most of the remaining is being hydrolyzed, and the fractions of the hydrolysate utilized. A substantial percentage of the protein hydrolysate is going to be used as an organic fertilizer.

Composting of chrome leather waste is not realistic, as it is too resistant towards biological degradation.

It is more difficult to convert finished leather waste into usable products, and probably part of this waste will still have to be incinerated. The incineration must be carried out in a way that generation of Cr VI is avoided. (Experience shows that when smaller amounts of chrome leather are incinerated with domestic refuse, oxidation does not take place to any demonstrable extent).

c) Occupational health and safety: No problems which have not been overcome.

d) Health risks to consumers. No demonstrable traces of Cr VI are allowed in the finished leather. Cr III does not provoke allergies, but nonchrome leather articles of any kind are available to allergics.

e) To sum up, the most important environmental drawback of chrome tanning is the solid wastes disposal (except perhaps the neutral salts discharge, see section 4). A minor problem is that chromium is not a renewable resource strictly speaking although more or less inexhaustible. Also when the attitude to chromium has become less negative, the disposal of leather waste may be more difficult when containing chrome.

   Of the two life cyclus assessments (LCA's) concerning chrome tanning, known to the author (4) (5), the first compares chrome tanning to vegetable tanning. The conclusion is: "Vegetable tanned leather generates less environmental impact through its life cyclus than chrome tanned leather. However, the difference is not great and is mainly a consequence of the chromium emission and the high energy consumption in the production of chrome tanning agents". As mentioned above, both these factors are going to have lost much of their importance in 2050.

   In the second LCA, rather to be called an ecological comparison comprising only the leather production, waste water, sludge, and leather wastes, chrome tanning is compared to glutaraldehyde plus chrome tanning, and to purely vegetable tanning. In this case, it is concluded that each method has its own advantages and drawbacks, and that chrome tanning must be considered an environmentally not very harmful method. Also in this case, the major drawback is considered to be chrome in the sludge.

4. Neutral salts

Without any doubt, neutral salts are going to become a more serious problem than chromium. Restrictions on the discharge of dissolved solids are becoming a reality, not only in dry climates but generally, in order to protect the fresh water resources of the earth. This development is relevant not only for chrome tanning, but for any kind of tanning.

Already at present, the discharge limits necessitate cleaner production. On the basis of (1), present limits can be summarized as follows:

		SO_4^{--} mg/l	**Cl^- mg/l**	**COD mg/l**
Discharge to surface water	Most strict values	40	200	30
	"Median" values	1000	1000	225
Discharge to sewer	Most strict values	100	300	100
	"Median" values	300	2250	850

The limits are inevitably going to be lowered.

Unless reverse osmosis or suitable technologies for salt removal become economically viable for tanneries, chrome tanning must be carried out with a salt free pickling or without any pickling. Any concomitant increase of the COD must be avoided.

Furthermore, the content of surplus sodium sulphate in the tanning agent preparation must be phased out. Concerning the chrome tanning agent itself, a substitution of sulphate complexes with basified chromium salts of an organic acid is desirable, although it entails an increase of the COD. Also the discharge of neutral salts deriving from basification must be minimized.

Some relocation of the tanning industry to sites near the open sea is going to take place.

5. Nonchrome tannages

5.1 General

In reality, as stated in section 3.2, chrome tanning has only a few ecological drawbacks. This means that any alternative tannings must have a low environmental impact and, compared to chromium, make easier the solid waste disposal.

All tanning agents react by definition with protein. However, at the same time as they have to react strongly with collagen, they should ideally not react at all with human tissue or micro- and macroorganisms. The keyword is selectivity, a quality chrome tanning agent possesses to a high degree. As far as possible, any other tanning agent must be comparable to chromium in this respect.

Another important aspect is the environmental consequences of producing the tanning agent in question.

5.2 Mineral tannages

The only other practical possibilities seem to be aluminium, titanium, and zirconium.

Compared to chromium, aluminium has two psychological advantages: It is not a heavy metal, and it is ubiquitous in nature, which means that an introduction of aluminium is less easily observable than is the case for chromium. Aluminium is used as a coagulant for waste water.

However, the use of aluminium raises its own environmental problems. Aluminium is substantially more soluble than chromium; in water with a pH below 5.5, as it is found in naturally acid waters or in regions with acid rain, it can be dissolved in water in concentrations toxie to fish or to harmful effects on plants roots.

Acid rain is probably no problem anymore in 2050, but nevertheless a weighing of the environmental advantage of aluminium (generation of a sludge without chromium) against its drawback (higher solubility and toxicity), there is nothing to gain environmentally by substituting chromium with aluminium.

In some countries, aluminium levels in waste water, surface water, or drinking water, are lower than the corresponding limits for chromium III.

Neither titanium nor zirconium compounds have any known biological significance. Generally, they have a low solubility, are poorly absorbed and retained by plants and animals, and have an extremely low toxicity when in contact with human or animal tissues.

From an environmental point of view they are ideal tanning agents, but their low reactivity which make them harmless in the external and internal environment, at the same time reduces their practical value as tanning agents.

5.3. Organic tannages

5.3.1. General

Contrary to mineral tanning agents, organic tanning agents "disappear" when reacting with collagen, with activated sludge, or with substances in the soil. Consequently, leather waste and tannery sludge do not appear substantially different from other organic wastes. Furthermore, organic tanned leather is normally more easily biodegradable than chrome leather.

5.3.2. Vegetable tanning

Tannins are not regarded as hazardous, as they occur in the nature, in plants as well as in soil. However, they are produced by plants as a protection against biological enemies, which implies that they are toxic towards these organisms. They are reasonably compatible with the human physiology (as an inveterate teadrinker I can bear witness to that).

Vegetable tannins are only going to be qualified as a renewable resource, insofar they are obtained either within eco-compatible plantation programmes or by harvesting from natural species (fruits, leaves, roots, etc.). As far as possible, remaining parts of trees felled or material harvested must be utilized for other purposes. Because of the great need of area for food production, production of vegetable tannins will necessarily get a lower priority and is probably going to be concentrated in areas which cannot be otherwise utilized. The production of vegetable tannins is hardly going to increase, rather the opposite.

Use of genetically modified species for increased tannin production is a possibility. In 2050, genetically engineering is going to be a normal and necessary practice in agriculture and is consequently not considered ecologically negative. However, it is doubtful whether tannin production is found important enough for a development of this kind.

According to Germann (7), the present consumption of vegetable tanning agents is appr. 250,000 t/yr. A complete substitution of chrome with vegetable tannins would entail a yearly consumption of 2-3 mill. t/yr, which is totally unrealistic.

Environmental pollution, occupational health problems, and energy consumption by the production of the tanning agent are less than is the case with chrome tanning agent.

Vegetable leather is easily biodegradable and compostable; vegetable tannins are ubiquitous in decaying plant materials in or upon the soil, and vegetable tannins in sludge or decaying leather make no difference in this respect.

Vegetable leather is not allergenic.

However, the waste water is problematic. The colour may be difficult to eliminate, and COD before and after waste water treatment is higher than is the case for chrome tanning, and a third treatment stage, e.g. with activated carbon, is going to become necessary.

Most problematic is the discharge of neutral salts, deriving from the salt content of the extracts as well as from the pretreatments. It is desirable or probably necessary to optimize the tanning itself, to eliminate non-tannins from the extracts (this might be possible through membrane technologies, but would the costs be viable?), and to eliminate pretreatments with sodium sulphate or phosphorus compounds.

In the environmental analysis (5), vegetable tanning was found to result in the highest loads of waste water, sludge and other solid wastes. The advantage, indeed, was the easy disponibility of the solid wastes.

The argument, heard in the present time, that it is a positive property of vegetable leather that it is "natural", has no real value. As Heidemann rightly points out (6), the natural function of the vegetable tannins is to defend the plant by killing other organisms; and in general, "nature" comprises not only life and death, but also killing and murder. Probably the fascination of the notion "natural products" is going to lose its its force.

Vegetable tanning is never going to be an alternative to chrome tanning. Its relative importance is rather going to decline, due to problems with supply as well as waste water. However, in 2050 it is probably still used for various purposes.

5.3.3. Synthetic organic tannages

Real alternatives to chrome tanning must be found among the synthetic organic tanning methods. All crosslinkers for proteins are potential tanning agents, and it must be expected that in 2050, also organic substances and reactions are used for tanning which nobody as yet have thought of for this purpose.

Also these tannages must fulfil the same requirements as chrome tanning (high exhaustion, low discharge of neutral salts and COD, and a low occupational health risk).

Problems with regard to internal and external environment following from the production of synthetic tanning agents are too varied to be discussed here.

The problem is occupational health and safety risks. Tanning agents should at the same time crosslink proteins and have no negative physiological effects, a more or less self-contradtictory demand.

Monomer organic tanning agents are toxic and consequently demand protective measures in the working place. On the other hand, polymers used in the tanning process are in most cases physiologically harmless but can only be used as auxiliary tanning agents.

Probably, before 2050 systems with a satisfactory tanning effect but at the same time less hazardous have been developed. Nevertheless, more extensive – and expensive – protection measures than in the case of chrome tanning will probably still be necessary.

Many syntans in the classical sense are polymers and at the same time fully satisfactory tanning agents due to their phenolic and sulphonic acid groups. Syntans making possible the production of high quality leather with minor environmental consequences are still going to be used in 2050.

The syntans found at present are of a strongly varied biodegradability in waste water. Syntans with a low biodegradability and consequently a low efficiency of COD elimination are going to be phased out..

Of the four tanning methods compared in (5), glutaraldehyde pretanning followed by a main tanning with syntan had the lowest discharge of neutral salts, but a significantly higher COD discharge than the chrome tanning.

Even if, a I suppose, chromium has been rehabilitated by 2050, is it hardly going to regain its market completely, as there after all probability will be developed synthetic organic tannages which can compete with or surpass chromium tannage with regard to leather properties and/or process technology.

5.4. Economy

A Danish upholstery leather tannery has converted more than 50% of their production to leather without chromium. The costs of tanning agents is 20% higher, the total production costs 2-5% higher than the corresponding costs for chrome leather (8).

Other information indicates surplus production costs in the magnitude of 30% (9) or even 150% (10). This is probably a question of the choice of tanning agent and the production scale.

6. Environmental management

6.1. Environmental management schemes, life cyclus assessments, and eco-labelling.

Environmental management schemes have come to stay; future schemes are going to resemble EMAS rather than ISO 14000, including demands to the environmental standard of subcontractors and a continuous improvement of the environmental standard. Environmental accounts of companies become a normal feature.

Life cyclus assessments (LCA's) are certainly going to be important, also in 2050. However, in the last resort, a LCA is a subjective evaluation as selection and weighing of the various parameters forming parts of a LCA is subjective, depending on the prevailing scientific opinions, a priori assumptions, practical circumstances, and political correctness at the time the LCA is carried out (e.g. does the "greenhouse" problematic turn out to be real or a hoax, and if real, is a warming of the atmosphere going to be evaluated as positive or negative, all things considered, in 2050? Furthermore, is the energy produced from fossile fuel or by fission at that time?). Nobody can tell how the weighing is going to be carried out in 2050, and consequently it is hardly possible to predict the impact of LCA's on the leather industry at that time.

Whether eco-labelling does still exist in 2050 depends indeed on the consumers' interest. Eco-labelling may become obsolete when environmental regulation and its enforcement have reached a uniform high level around the world, but it is also very well possible that there still exists a demand for articles produced even more environment-friendly than prescribed. The attitudes of customers are if possible even more difficult to predict than the weighing of parameters in LCA's.

Also the attitude of customers is going to become more uniform around the world.

The buy and throw-away mentality discourages the interest for eco-labelling, but the trend towards leather becoming a luxury item will make leather articles belong to the categories of goods whose quality, durability, and probably also ecological properties distinguish them from cheaper materials.

Sooner or later, at least before 2050, the leather industry will have to provide for removal of discarded leather articles and their utilization for some purpose or other. Incineration must be the last resort. This raises the question whether a chromium content is a hindrance for any potential utilizations.

6.2. Perspectives for leather marketing

After all possibility, leather has a future as an ecologically sound material, not least because the hides are a renewable ressource and a byproduct which is best utilized for leather production.

From a rational point of view, the nonchrome tanning methods should provide the tanner with a useful alternative, not completely replace chromium. The main ecological advantage of the nonchrome tannages is that they open up for more possibilities with regard to utilization or disposal of solid wastes, important in at least the nearer future.

If nonchrome leather is marketed as environmentally preferable, it follows by implication that chrome leather is environmentally unfriendly.

The Danish tannery, referred to above, developed their nonchrome leather, not because of marketing reasons, but because they had to pay an exorbitant tax for their chromium discharge (cf. section 3.1). Only very few of their customers ask for a nonchrome, "ecological" leather; most customers are only interested in the leather itself; some customers demand that the tanning method is not mentioned, as they also use chrome leather in their production.

Within some years, the tannery may be compelled to stop the production of chrome leather and then market their leather as "eco-leather".

More generally, the situation may become that in some part of the world (e.g. Europe) predominantly nonchrome leather is demanded, whereas in other parts of the world, chrome leather is in greatest demand. In 2050, however, the situation has probably stabilized in the way that both leather types are appreciated according to their respective inherent qualities.

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