OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

22425

9 August 2000

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

US/RAS/92/120/11-51

Regional Programme for Pollution Control in the Tanning Industry in South-East Asia

CHROME BALANCE IN LEATHER PROCESSING

Prepared by

J. Ludvík

UNIDO Consultant in Leather Pollution Control

Project Manager

J. Buljan, Agro-Industries and Sectoral Support Branch

V.00-56382

CONTENTS

1. INTRODUCTION

Chrome tanning is the most common type of tanning in the world. Chrome tanned leathers are characterised by top handling quality, high hydro-thermal stability and excellent user properties.

Chrome waste from leather processing poses a significant disposal problem. It occurs in three forms: liquid waste, solid tanned waste and sludge. In most countries, regulations governing chrome discharge from tanneries are stringent. Today, all tanneries must thoroughly check their waste streams. Chrome discharge into those streams is one of the components that has to be strictly controlled.

The environmental impact of chrome waste from tanneries has been a subject of extensive scientific and technical dispute. Statutory limits have since been set for chrome discharge and disposal, and relevant guidelines have been drawn up throughout the world.

Given the close correlation between chrome tanning and the environmental impact of leather processing, auditing the efficiency of processing operations takes on prime importance. Tanneries have to bear in mind that only some 53 % of the corium collagen and 15 % of the chemicals offered are retained in the finished leather, while the residue (47 % corium collagen and 85 % chemicals) enter the waste streams (1).

2. BASIC ASSUMPTIONS

Given the broad variations in raw materials, processing methods and equipment, as well as the different final product specification, certain basic assumptions have to be made. (See Annex 1 for the assumptions that have been made for the production of grain leather for shoe uppers). Although this chrome balance corresponds reasonably well to the situation in some factories, figures may differ considerably in many other factories. That notwithstanding, it is hoped that this paper will serve as a suitable working tool for tanners doing their own computations.

3. CHROME TANNING

Balancing chrome in leather processing, i.e. maximising the chrome uptake in the tanning process and minimising the amount of liquid/solid chrome wastes, is a matter of great concern to all tanners. In the following section, the chrome balance is computed for:

- Conventional tanning,
- High-exhaustion tanning,
- Tanning with chrome recovery/chrome precipitation.

3. 1. Conventional tanning

Offer

Basic chrome sulphate containing 25 % Cr_2O_3 in the amount of 8 %, corresponding to 2 % Cr_2O_3 on pelt weight.

Exhaustion

About 75 %, i.e. 1.5% Cr_2O_3, reacts with pelt collagen in the form of a binuclear basic chrome sulphate complex.

Ratio

$Cr_2O_3 \times 1.55 = Cr_2(SO_4)(OH)_2$

Typical chrome distribution in leather, split, solid waste and effluent according to (1) is shown in Table 1.

Table 1
Chrome distribution after conventional tanning
(related to pelt weight)

Chrome offer	Chrome input		Chrome output			
	%	kg	Grain leather kg	Usable split kg	Solid waste kg	Effluent kg
Basic chrome sulphate	8	88	-	-	-	62
Binuclear complex	-	-	12	4	10	-
Cr_2O_3	2	22	7.5 (34%)	2.5 (11%)	6.5 (30%)	5.5 (25%)

Table 1 shows that some 75 % of the Cr_2O_3 offer is retained in the collagen structure of wet blue (grain leather, usable split, solid waste) and 25 % remains in the effluent.

3. 2. High-exhaustion tanning

Offer

Basic chrome sulphate containing 25 % Cr_2O_3 in the amount of 4.6 % corresponding to 1.2 % Cr_2O_3 on pelt weight. Self-basifying chrome tannin with fixing effect containing 7 % Cr_2O_3 in the amount of 2.6 % corresponding to 0.2 % Cr_2O_3 on pelt weight. The total offer of chrome tannin is 7.2 % corresponding to 1.4 % Cr_2O_3 on pelt weight.

Exhaustion

About 98 %, i.e. 1.37 % Cr_2O_3, reacts with pelt collagen in the form of a binuclear basic chrome sulphate complex.

Ratio

$Cr_2O_3 \times 1.55 = Cr_2(SO_4)(OH)_2$

Typical distribution of chrome in leather, split, solid waste and effluent is shown in Table 2.

Table 2
Chrome distribution after high-exhaustion tanning
(related to pelt weight)

Chrome offer	Chrome input		Chrome output			
	%	kg	Grain leather kg	Usable split kg	Solid waste kg	Effluent kg
Chrome tannins	7.2	80	-	-	-	56
Binuclear complex	-	-	11	4	9	-
Cr_2O_3	1.4	15.4	6.9 (45%)	2.3 (15%)	5.9 (38%)	0.3 (2%)

Table 2 shows that about 98 % of the Cr_2O_3 offer is retained in the collagen structure of wet blue (grain leather, usable split, solid waste) and only 2 % remains in the effluent.

3. 3. Tanning with direct and indirect chrome recycling

In practice, two ways of chrome recycling and re-use are practised: direct and indirect recycling. The direct form entails spent float being recycled direct to the chrome tanning processing for re-use. The indirect form entails precipitating and separating the chrome from the float containing residual chrome, and then re-dissolving it in acid for re-use. The efficiency of both methods can be very high (more than 90 %); it depends on the effectiveness of the float collection process and the recycling/reusing technique. Of the two approaches, chrome recovery is more widely used than chrome precipitation.

Normally, chrome recovery is used in conjunction with convential tanning. In high-exhaustion tanning, however,the chrome can, as a rule, only be precipitated, separated and de-watered, but not re-used in processing.

3. 3. 1. Conventional tanning in conjunction with direct chrome recycling

A model for chrome balance in tanning using direct chrome recycling has been presented in other papers (2,3). On the basis of that model and the assumptions given above for a conventional tanning process, computation shows that about 24 % of the chrome offer can be recovered from the spent tanning float and sammying/draining water, and 1.4 % is discharged in effluent. In principle, the chrome so recovered can be recycled and re-used in the form of a basic chrome sulphate solution for the subsequent tanning batches.

3. 3. 2. High-exhaustion tanning in conjunction with chrome precipitation

A model for chrome balance in high-exhaustion tanning using chrome precipitation has also been presented in other papers (2,3). On the basis of that model and the assumptions given above for a high-exhaustion tanning process, computation shows that at the most some 1.9 % of the chrome offer can be precipitated from the spent tanning float and sammying/draining

water, and about 0.1 % is discharged in effluent.

4. POST TANNING

The range of post tanning wet-work formulations applied by tanners is very broad. For the purposes of this paper, two basic post tanning processes are considered: post tanning with or without chrome retanning.

4. 1. Post tanning with chrome retanning

Offer

Basic chrome sulphate containing 25 % Cr_2O_3 in the amount of 5 % corresponding to 1.25 % Cr_2O_3 on shaved weight.

Exhaustion

About 40 %, i.e. 0.5 % Cr_2O_3, interacts with wet blue grain leather in the form of a binuclear basic chrome sulphate complex.

Ratio

$Cr_2O_3 \times 1.55 = Cr_2(SO_4)(OH)_2$

Typical distribution of chrome in crust leather, waste crust and effluent is shown in Table 3.

Table 3
Chrome distribution after post tanning with chrome retanning (related to shaved weight)

Chrome offer	Chrome input		Chrome output		
	%	kg	Grain crust kg	Waste crust kg	Effluent kg
Basic chrome sulphate	5.0	13	-	-	11.0
Binuclear complex	-	-	1.97	0.05	-
Cr_2O_3	1.25	3.3	1.27	0.03	2.0

Table 3 shows that about 40 % of the Cr_2O_3 offer is retained in the leather material (grain crust, waste crust) with 60 % remaining in the effluent. This proportion has to be adjusted slightly, given the leaching of unfixed chrome during neutralisation, retanning with organic tannins, dyeing and fatliquoring. In conventional tanning, we can reckon with leaching in the order of 0.7 kg Cr/t of wet salted weight (w/s) (or 0.3 kg Cr/t w/s in high- exhaustion tanning) (3, 4, 5).

4. 2. Post tanning with chrome retanning and chrome precipitation

In principle, the chrome remaining in the spent retanning float can be precipitated, separated and dewatered, but it cannot be re-used.

A model for chrome balance in post tanning with chrome retanning and chrome precipitation was also presented in earlier papers (2, 3). On the basis of that model and the assumptions given above for chrome retanning , computations show that in chrome retanning some 50 % of the chrome offer can be precipitated and 10 % of the chrome offer is drawn off in effluent. Here again, however, the proportion of chrome offer discharged in effluent must be slightly adjusted to account for chrome leaching(0.3 - 0.7 kg Cr/t w/s).

4. 3. Post tanning without chrome retanning

The post tanning formulation is subject to various modifications. In order to balance the chrome in leather processing, account has to be taken of the amount of chrome that might leach.

5. SUMMARY TABLES AND FIGURES

A general chrome balance in leather processing by various types of chrome tanning and post tanning is given in Table 4. The balance expressed in a proportional chrome distribution is illustrated in Figure 1.

Table 4
General chrome balance in leather processing

Legend:

I Conventional tanning without chrome retanning.

II Conventional tanning with chrome recovery and without chrome retanning.

III Conventional tanning and chrome retanning.

IV Conventional tanning with chrome recovery and chrome retanning.

V Conventional tanning/chrome retanning with chrome recovery/ precipitation.

VI High-exhaustion tanning without chrome retanning.

VII High-exhaustion tanning with chrome precipitation and without chrome retanning.

VIII High-exhaustion tanning and chrome retanning.

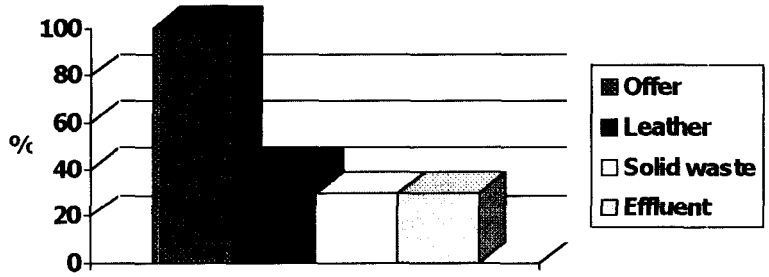
IX High-exhaustion tanning with chrome precipitation and chrome retanning.

X High-exhaustion tanning/chrome retanning with chrome precipitation.

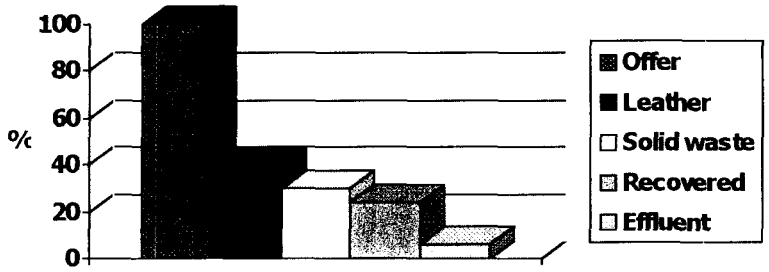
Type of tanning/ post tanning	Distribution	Amount	
		kg Cr/t w/s	%
I	Offer	15.00	100
	Leather	6.05	40
	Solid waste	4.50	30
	Effluent	4.45	30
II	Offer	15.00	100
	Leather	6.05	40
	Solid waste	4.50	30
	Recovered chrome	3.54	24
	Effluent	0.91	6
III	Offer	17.24	100
	Leather	6.91	40
	Solid waste	4.52	26
	Effluent	5.81	34
IV	Offer	17.24	100
	Leather	6.91	40
	Solid waste	4.52	26
	Recovered chrome	3.54	21
	Effluent	2.27	13
V	Offer	17.24	100
	Leather	6.91	40
	Solid waste	4.52	26
	Recovered chrome	3.54	21
	Precipitated chrome	1.12	6
	Effluent	1.15	7
VI	Offer	10.50	100
	Leather	6.00	57
	Solid waste	3.99	38
	Effluent	0.51	5
VII	Offer	10.50	100
	Leather	6.00	57
	Solid waste	3.99	38
	Precipitated chrome	0.20	2
	Effluent	0.31	3
VIII	Offer	12.74	100
	Leather	6.86	54
	Solid waste	4.01	31
	Effluent	1.87	15
IX	Offer	12.74	100
	Leather	6.86	54
	Solid waste	4.01	31
	Precipitated chrome	0.20	2
	Effluent	1.67	13
X	Offer	12.74	100
	Leather	6.86	54
	Solid waste	4.01	31
	Precipitated chrome	1.32	11
	Effluent	0.55	4

Figure 1
Proportional distribution of chrome in leather processing
Legend: see Table 4

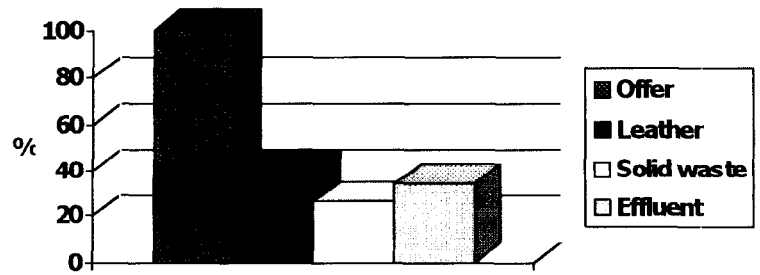
I



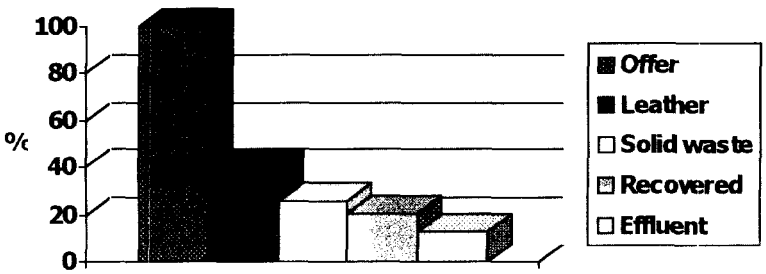
II



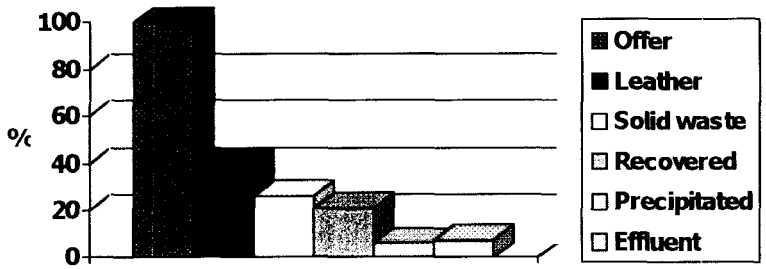
III



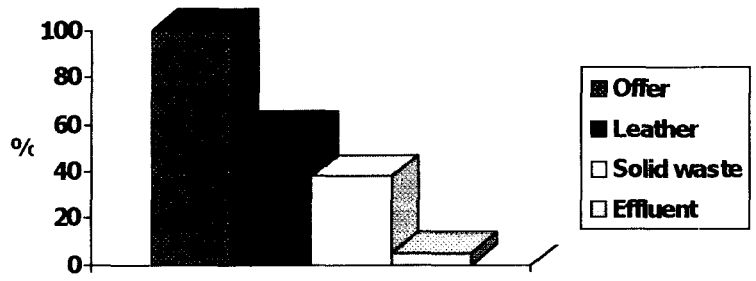
IV



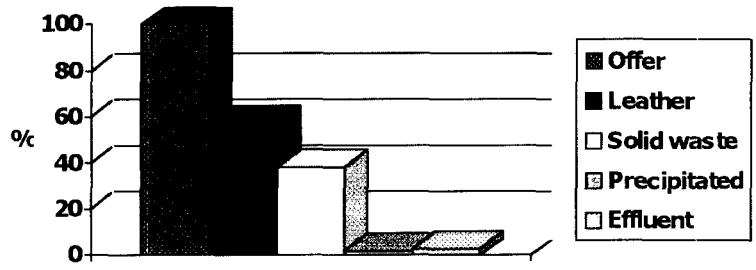
V


100
80
60
%
40
20
0
Offer
Leather
Solid waste
Recovered
Precipitated
Effluent

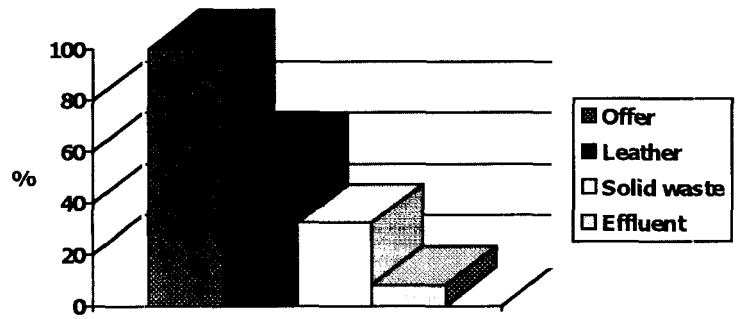
VI


100
80
60
%
40
20
0
Offer
Leather
Solid waste
Effluent

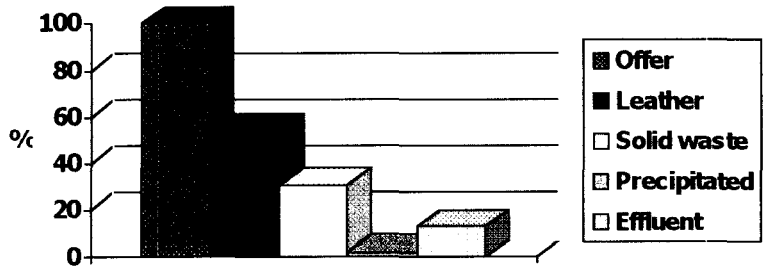
VII


100
80
60
%
40
20
0
Offer
Leather
Solid waste
Precipitated
Effluent

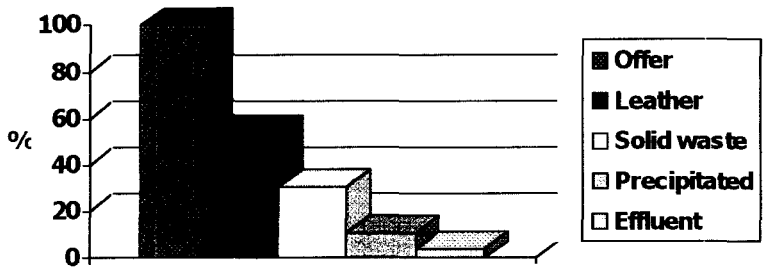
VIII


100
80
60
%
40
20
0
Offer
Leather
Solid waste
Effluent

IX



X



The following basic information can be derived from the general balance and chrome distribution:

The type of chrome tanning and post tanning significantly affects the balance and distribution of chrome.

When processing leather by conventional tanning and/or chrome retanning with a chrome offer of 15-17 kg Cr/t w/s, 40 % of the chrome offer remains in the leather, 26-30 % in the solid waste and 30-34 % enters the effluent. A certain amount of the chrome entering the effluent can be recovered from the tanning float and sammying/draining water (21-24 % of chrome offer) or precipitated from the retanning float without being re-used (6 % of chrome offer).

When processing leather by high-exhaustion tanning and/or chrome retanning, the chrome offer can actually decrease from 15-17 kg Cr/t w/s to 10-13 kg Cr/t w/s and it is used more effectively: 54-57 % remains in the leather, 31-38 % in the solid waste and 5-15 % enters the effluent. A certain amount of the chrome entering the effluent can be precipitated from both the tanning and retanning floats without being re-used (2-11 % of chrome offer).

An overview of the chrome content in tannery effluent by type of chrome tanning and post tanning is presented in Table 5 and Figure 2.

Table 5

Chrome content in tannery effluent, by stream

Legend: see Table 4

STF spent chrome tanning float

SDW sammying/draining water

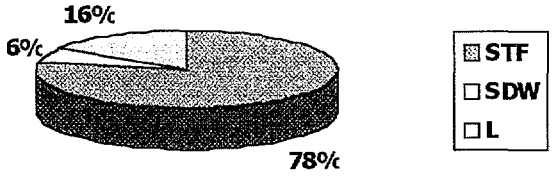
SRTF spent chrome retanning float

L leachable chrome

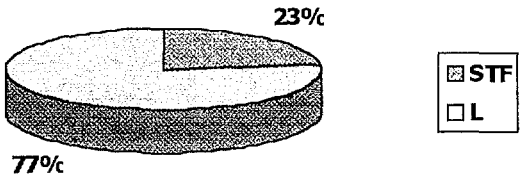
Type of tanning/ post tanning	Origin	Amount	
		kg Cr/t w/s	%
I	STF	3.49	78
	SDW	0.26	6
	L	0.70	16
	Total	4.45	100
II	STF	0.21	23
	SDW	0	0
	L	0.70	77
	Total	0.91	100
III	STF	3.49	60
	SDW	0.26	4
	SRTF	1.36	24
	L	0.70	12
	Total	5.81	100
IV	STF	0.21	9
	SDW	0	0
	SRTF	1.36	60
	L	0.70	31
	Total	2.27	100
V	STF	0.21	18
	SDW	0	0
	SRTF	0.24	21
	L	0.70	61
	Total	1.15	100
VI	STF	0.20	39
	SDW	0.01	2
	L	0.30	59
	Total	0.51	100
VII	STF	0.01	3
	SDW	0	0
	L	0.30	97
	Total	0.31	100
VIII	STF	0.20	11
	SDW	0.01	1
	SRTF	1.36	72
	L	0.36	16
	Total	1.87	100
IX	STF	0.01	1
	SDW	0	0
	SRTF	1.36	81
	L	0.30	18
	Total	1.67	100
X	STF	0.01	2
	SDW	0	0
	SRTF	0.24	44
	L	0.30	54
	Total	0.55	100

Figure 2
Chrome content in tannery effluent
Legend: see Tables 4 and 5

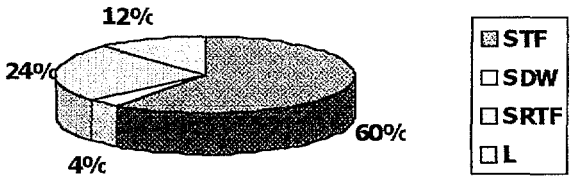
I



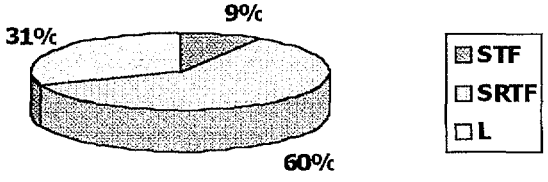
II



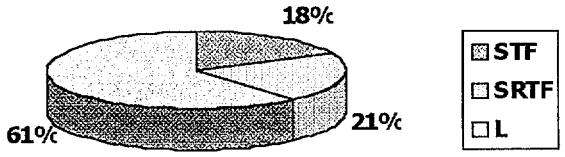
III



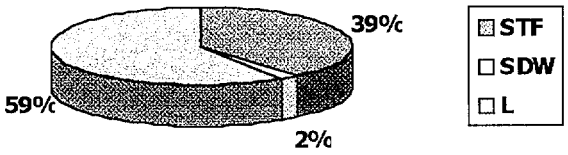
IV



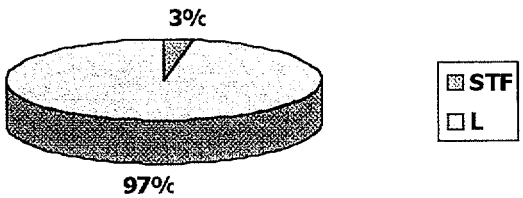
V


18%
61%
21%
STF
SRTF
L

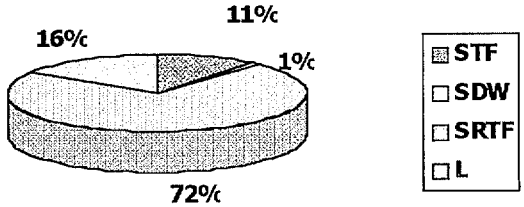
VI


39%
59%
2%
STF
SDW
L

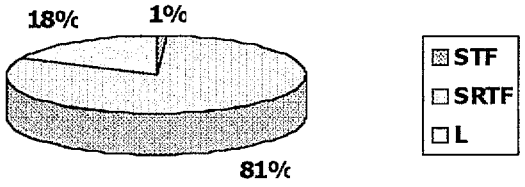
VII


3%
97%
STF
L

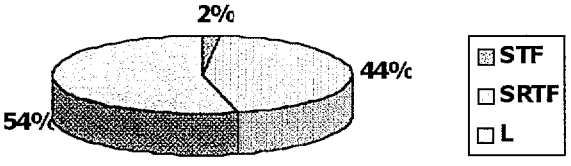
VIII


11%
16%
1%
72%
STF
SDW
SRTF
L

IX



X



The following main conclusions can be drawn with respect to the quantities presented in Table 5 and Figure 2:

The lowest level of chrome in effluent, i.e. 0.31 kg Cr/t w/s, is achieved when the leather is processed by means of high- exhaustion tanning with chrome precipitation, but without chrome retanning in the post tanning process. If the leather has to be retanned using chrome tannins, it is advisable to precipitate the chrome from both the spent tanning float and the separated spent retanning float. The level of chrome in the effluent can thus drop from 1.67-1.87 kg Cr/t w/s to 0.41 kg Cr/t w/s. The actual chrome concentration might be slightly higher owing to such residues as shavings and buffing dust.

In many instances, the main source of chrome in effluent (up to 97 %) is the unfixed chrome leaching from the leather. This could be considered a challenge to tanners to improve tanning and post tanning formulations in order to enhance chrome fixing in leather.

Selected figures relating to the levels of chrome concentrate in mixed effluents are to be seen in Table 6.

Table 6
Chrome concentration in mixed effluents.
Amount of effluent 30 m^3 /t w/s

Type of tanning/post tanning	Chrome in effluent	
	Amount kg Cr/t w/s	Concentration mg/l
Conventional tanning without chrome retanning	4.45	148
High-exhaustion tanning/chrome retanning with chrome precipitation	0.55	18.3
High-exhaustion tanning with chrome precipitation and without chrome retanning	0.31	10.3

Legislative requirements governing chrome content in effluents and its discharge into surface water vary greatly from 0.05 to 10 mg Cr/l. In the case of discharge into sewers the range extends from 1 to 50 mg Cr/l (7). However, the most frequent requirements range from 1 to 4 mg Cr/l.

In order to meet the rigorous requirement of 1 mg Cr/l in mixed effluent, it is essential to start by collecting all waste streams emanating from the tanning and chrome retanning operations after precipitating the chrome,, as well as all waste streams, i.e. spent floats from other post tanning operations (neutralisation, dyeing, fatliquoring). The latter waste streams which contain residual chrome in soluble/insoluble form also have to undergo precipitation. Calcium hydroxide is the most frequently used precipitant. In order to achieve complete chrome precipitation, ferric and/or aluminium salt is added together with lime.

According to recent information (7) it has been demonstrated that chrome can be almost totally precipitated from waste stream residues in tanning/post tanning operations. It has been claimed that concentrations of 1 mg Cr/l corresponding to 0.03 kg Cr/t w/s can be obtained in mixed effluent. In some countries, tannery sludge containing chrome cannot be re-used and must be dumped in special landfills.

6. CONCLUSION

Building on our previous work on mass balance in leather processing (1), the attempt was made to design a specific model for computing chrome balance. Computations were made on the basis of an input of one ton wet salted cattle hide processed into grain leather for shoe uppers using the most common types of tanning/post tanning procedures.

A survey of chrome balance shows that when processing leather by means of conventional tanning and/or chrome retanning with a chrome offer of 15-17 kg Cr/t w/s, some 40 % of the

chrome offer remains in the leather, 26-30% in the solid waste and 30-34 % in effluent. A certain amount of the chrome entering the effluent can be recovered from the tanning float (21-24 % of chrome offer) and re-used or precipitated from the retanning float without being re-used (6% of chrome offer). When processing the leather by high-exhaustion tanning and/or chrome retanning with a chrome offer of 10-13 kg Cr/t w/s, 54-57 % of the chrome offer remains in the leather, 31-38 % in the solid waste and 5-15 % in the effluent. A certain prportion of the chrome entering the effluent can be precipitated from the tanning/retanning floats without being re-used (2-11 % of the chrome offer).

The lowest practically attainable chrome content in effluent ranges somewhere between 0.3-0.6 kg Cr/t w/s. With a level of standard effluent production of 30 m^3/t w/s, chrome concentration thus ranges between 10 and 18 mg Cr/l. However, statutory requirements most frequently stipulate levels in the range of 1 to 4 mg Cr/l. In that case, all waste streams from tanning/post-tanning operations have to undergo further precipitation after precipitating the chrome. Calcium hydroxide combined with ferric and/or aluminium salt is considered the most suitable precipitant. Only after further precipitation can a concentration of about 1 mg Cr/l corresponding to 0.03 kg Cr/t w/s be obtained.

REFERENCES

(1) *Buljan, J., Reich, G., Ludvik, J: Leder u. Häutemarkt No.4 (1998), p.30, No.5(1998), p.25*

(2) *Covington, A.D: Chrome Management. Proceedings of the Workshop on Pollution* Abatement and Waste Management in the Tanning Industry. Ljubljana, 1995

(3) *Ludvik, J: Chrome Management in the Tannery. UNIDO, Vienna, Rev. 1, 2000*

(4) *Ludvik, J: Study on the Scope for Decreasing the Pollution Load in Leather Processing. UNIDO, Vienna, Rev. 1, 2000*

(5) *Francke, H: Das Leder 44 (1993), p. 89*

(6) *Bosnic, M., Buljan, J., Daniels, R.P: Pollutants in Tannery Effluents. UNIDO, Vienna, Rev. 2000*

(7) *Rydin, S: Reduction of Chrome Discharge from the Leather Industry. Minutes of the European Workshop on Environmental Technologies in Leather Industry. Bologna, 1995*

Annex 1

BASIC ASSUMPTIONS

Rawhide	1000 kg wet salted cattle hides. Weight class of 25-29.5 kg green weight
Technology	Soaking Liming with hair burning Fleshing, trimming Deliming, bating Pickling Tanning Conventional chrome tanning with/without chrome recovery High exhaustion chrome tanning with/without chrome precipitation. Sammying, splitting, trimming, shaving. Post tanning Neutralisation Retanning with/without chrome precipitation, dyeing, fatliquoring Drying Finishing
Leather	Lightly corrected shoe upper grain leather
Weight ratios	Green weight 1100 kg Wet salted weight 1000 kg Pelt weight 1100 kg Shaved weight 262 kg Finished grain leather 195 kg