LESS POLLUTING PROCESSES IN CATTLE HIDE BEAMHOUSE OBTENTION OF HIGH-YIELD LEATHERS PART I: WATER AND UNHAIRING MANAGEMENT

CROMOGENIA UNITS S.A.

Introduction

In times of increasing environmental awareness, the great interest on this formula shown by the chemical industry is excellent news, as is its constant commitment to innovation by way of more eco-friendly products and processes.

Many products and several well-proven chemical processes are currently available which allow obtaining wet blue leathers within technical and quality specifications.

We shall attempt here to select among all products and processes those that are less eco-unfriendly and those that provide best-yield leathers, both in area and selection operations, while ensuring water consumption optimization.

Keywords: collagen, in vitro, fibrils, tanning agents.

Environmental impact minimization

SUBSTITUTE.- Each product used must be replaced by another that performs the same function but pollutes less.

REDUCE.- The amount of each product must be the strict minimum required to obtain the desired item.

REUSE.- Use the same excess product again.

RECYCLE.- Recycle residual baths with the rest of non-reacted products.

Main wastewater pollutants

- Soluble salts: responsible for wastewater conductivity.
- Soluble organic matter: responsible for DQO and DBO5.
- Sulfides: responsible for foul odors. Removable by oxidation.
- Chromium III: risk of oxidation and of becoming Chromium VI, which is carcinogenic.
- Ammonia and total nitrogen.
- Suspended solid residues.

The present study is outlined as follows:

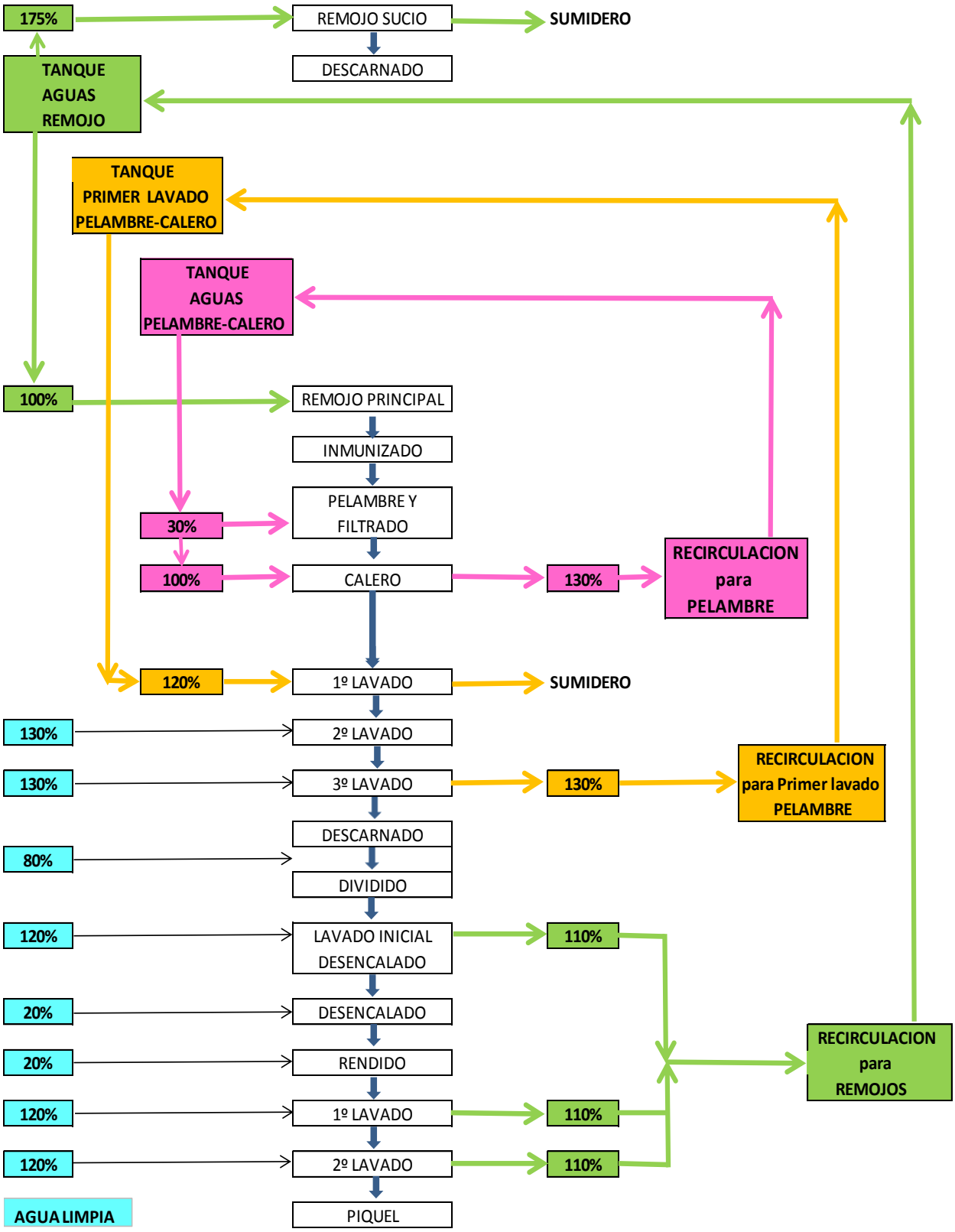
- 1st.- **WATER** management: water rationalization and recirculation. Minimum water consumption.
- 2nd.- Biodegradable **Soak baths**.
- 3rd.- **UNHAIRING**:
  - in the same soak bath.
  - with the minimum quantity of S= and SH-.
  - Nitrogen-free (amine-free).
  - with hair recovery.
  - hair with humidity lower than 50%.
  - with unhairing bath recovery and recirculation.
    - to provide leathers with:
    - no veininess.
    - no hair root.
    - no wrinkling.
    - better yield.

1st. Water management

The figure overleaf depicts the three most commonly used recirculation circuits. The objective is twofold: water saving and less pollution load in wastewater:

- SOAKING water circuit (green circuit).
- First UNHAIRING washing water circuit (ochre circuit).
- UNHAIRING-LIMING water circuit (pink circuit).

The use of these three circuits allows saving 40% of the water used in beamhouse operations.



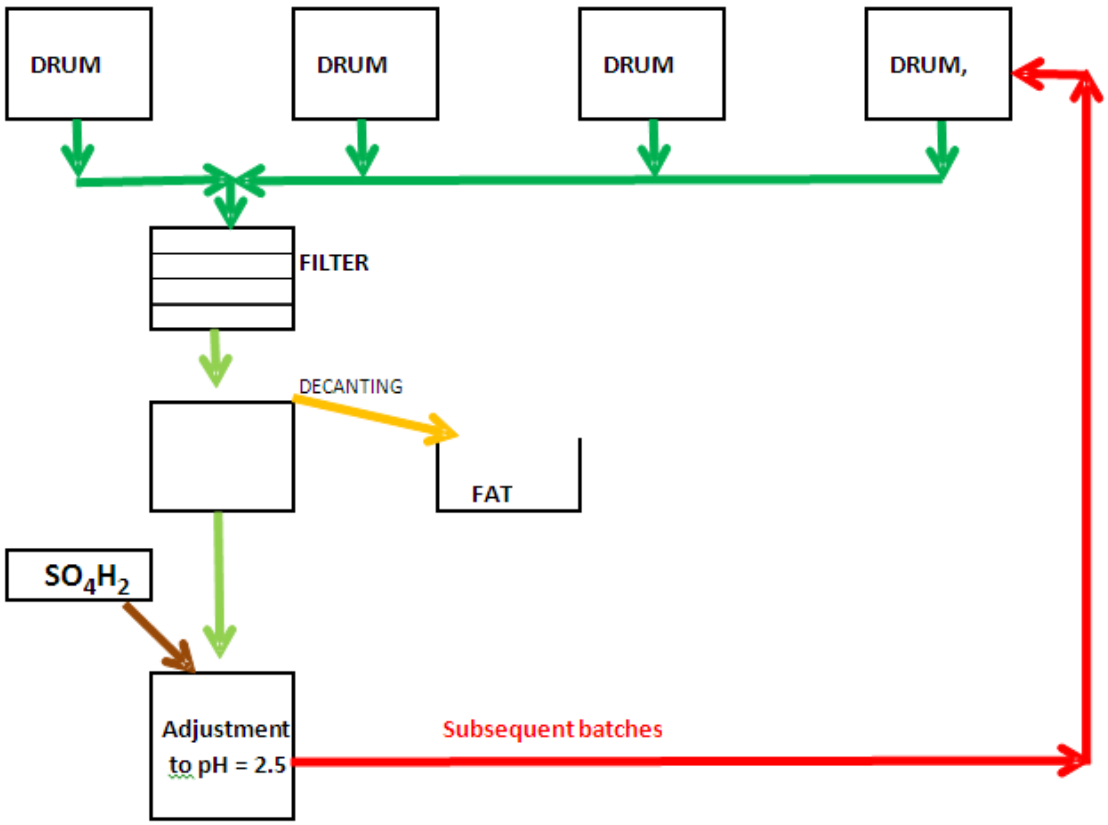
Legend:
[Green circuit] 110% → Soaking recirculation → Soaking water tank → 175% → Dirty soaking → Drain
[Ochre circuit] 130% → First unhairing washing recirculaton → First unhairing-liming washing tank → 120% → Drain
[Pink circuit] Unhairing recirculation → Unhairing-liming water tank
[Process, from top to bottom] Main soaking → Immunization → Unhairing and filtering → Liming → 1st washing → 2nd washing → 3rd washing → Fleshing → Splitting → Initial deliming washing → Deliming → Bating → 1st washing → 2nd washing → Pickel CLEAN WATER

The pollution load can be significantly reduced in chromium tanning residual baths. Two systems can be used:

A- Residual bath recirculation

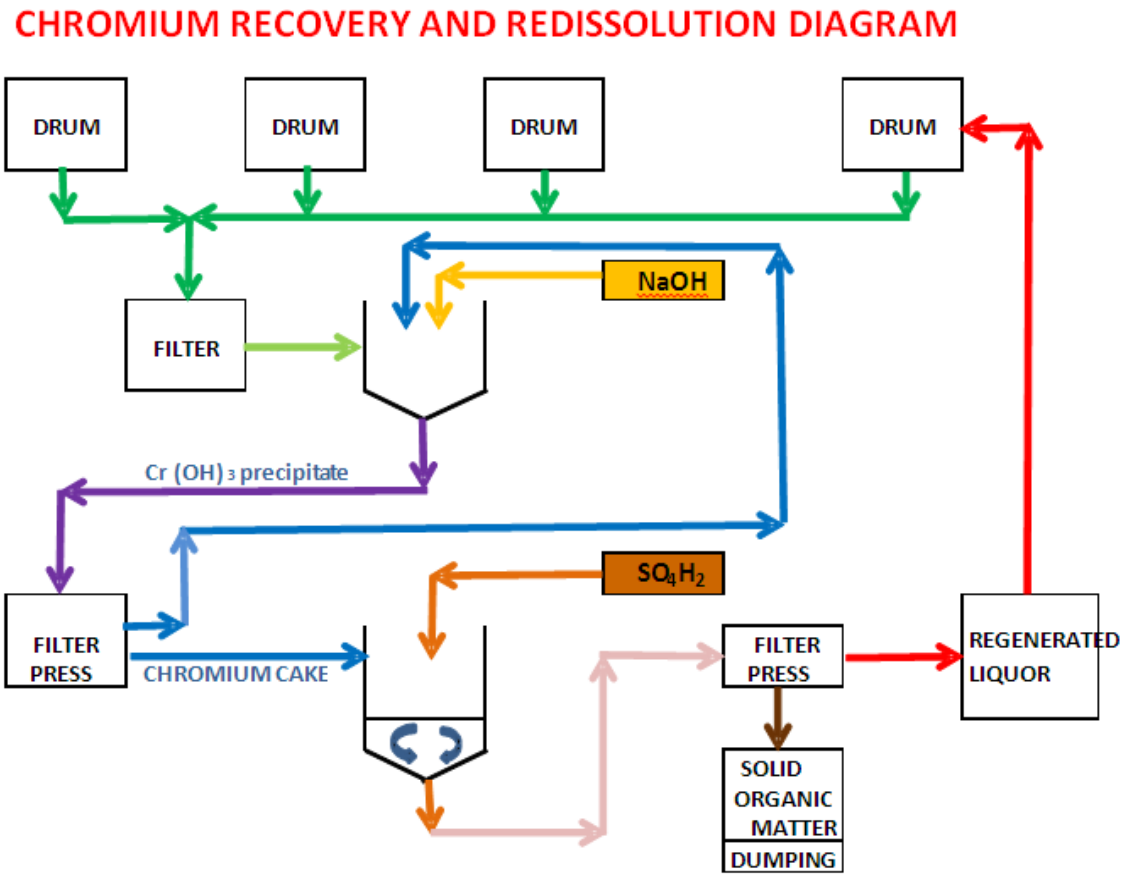
As shown in the following diagram, the residual tanning bath first undergoes filtration to separate solid parts (pieces of flesh, trimmings,…), then the small amount of supernatant fat is decanted, then water is transferred to a storage tank where pH is adjusted to 2.5 with sulfuric acid. The bath is now ready to be used in subsequent tannings.
This system also makes residual pickel bath recirculation mandatory.
In practice, the bath is usually changed every three months.

CHROMIUM TANNING BATH RECIRCULATION DIAGRAM



B- Chromium oxide precipitation and further redissolution.

Just like the above system, this system undergoes previous filtration to remove solid matter, then supernatant fat is decanted, then chromium is precipitated as hydroxide Cr(OH)3. It is further separated with a filter press and then redissolved with sulfuric acid to yield regenerated chromium liquor ready for use in subsequent batches. This process is depicted in the diagram below:



In both processes, only a minimum amount of chromium is likely to reach the sewage plant because chromium can only come from the tanning bath and from the chromium sammying machine.

2ª.- Biodegradable soak baths

- In order to reduce the conductivity of the residual soak bath in the case of salted leathers, DESALTING by means of a "milling" drum of raw salted hide or by manual shaking is highly desirable.

- It is always best to perform PRE-FLESHING in hair. The proteins and fats separated at that time are not polluted by unhairing liming chemicals.
- Use ANTIBACTERIAL AGENTS at the strictly MINIMUM AMOUNT required. Preferably use bacteriostatic agents instead of antibacterial agents.
- Always use biodegradable TENSOACTIVE AGENTS. Never use nonylphenol ethoxylates.
- Use one single biodegradable product that combines wetting, degreasing and pH buffering properties, WETTING AGENT (A).

The hide section must be WHITE at the end of the soaking process, and crossed GREENISH with Universal Indicator control.

3º.-Unhairing process with amine-free hair imnunization.

In the standard formulation below, 5 phases can be clearly differentiated:

PHASE 1: CONDITIONING
Se puede considerar un puente entre el remojo y el pelambre.

A "bridge" between soaking and unhairing can be considered.
BATH RECOVERED AT 22ºC 20–30% (50% actual) (Bath temp.:25ºC) (d<1,2ºBè)
EMULSIFIER (B). 0 – 0.2% (according to leather fat)
THIOGLYCOLATE (C) 0.5-0.8% (according to leather thickness)
SODIUM SULFHYDRATE .0.1 %
LIPASE (D) .0–0.02% (according to leather fat)
Run 50 min (3 rpm).
Controls: Bath pH = 9.5
Green-bluish color with Universal Indicator

Not crossed

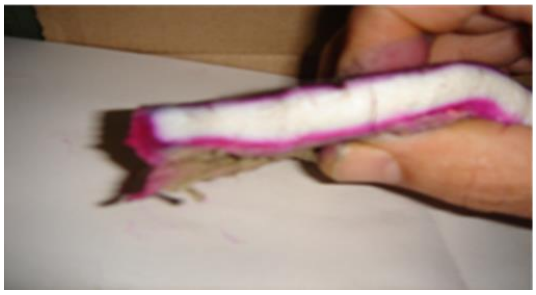
Correct crossing and pH

PHASE 2: INMUNIZATION
LIME……1.2 %

Run 20 min. (1.5 rpm).
Stop 15 min. Run 15'.
Stop 10'

Controls: Bath pH = 12.5

PINK color down to the hair root only, with Phenolphthalein.



Insufficient

Excessive

Correct penetration

PHASE 3: UNHAIRING

SODIUM SULFHYDRATE ……0.6 – 0.8 %
SODIUM SULFIDE . ……..0.6 – 0.8 %
Run 20 min. Stop 20 min. Run with filtration 20 min.
Stop 30 min. Run 3 min. Stop 30 min. Run 3 min. Stop 30 min.

*FILTER 60 – 90 min. (1.5 rpm)
(* Should a bath need to be added, use the recovery bath of previous unhairings)

KERATIN REMOVAL control. If removal is insufficient, add:
SODIUM SULFIDE……..0 – 0.6 %
(according to cleanliness)
KERATINASE (E)……..0 – 0.1 %
(according to cleanliness)
Run 30 min.

KERATIN REMOVAL control. Increase duration if necessary (up to 2 hours).

Adhered keratin

Lose keratin

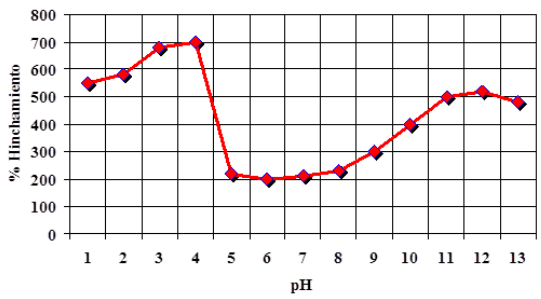
PHASE 4.- STRUCTURAL LOOSENING
LIME 1.8 – 2.3 %
(according to size and thickness)
EMULSIFIER(B). 0 – 0.2 %
(according to animal fat)
THIOGLYCOLATE(C) 0 – 0.2 %
(according to leather size)
Run 15 min. Stop 30 min.
Increase time for greater fiber loosening in larger leathers (up to 7 hours in case of upholstery leathers).

Liming PENETRATION control.
Do not add water or recovered bath until the inner hide is fully BROWNISH-GRAY and at least 2 hours have elapsed.

No penetration

Correct penetration

Water added to non-penetrated liming results in alkaline swelling that depends on hide pH, as shown in the **Heidemann** graph below:



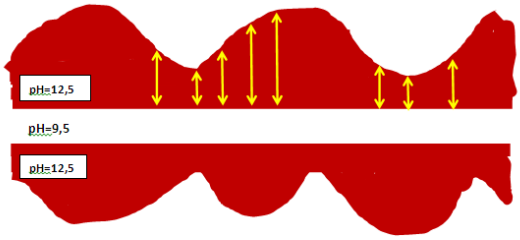
Y: Swelling %

In other words, the part of the hide at pH=12.5 swells to a much greater extent than the inner part, which maintains pH=9.5 (soak pH): the outer part of the hide increases in size while the inner part remains unswollen at its central area.

This leads to internal stress:

fiber breaking (loose grain, worse physical resistance: traction, tearing, grain burst ….).

area differences between the inner and the outer part (neck wrinkles, mesh in cheeks and chanks,….).



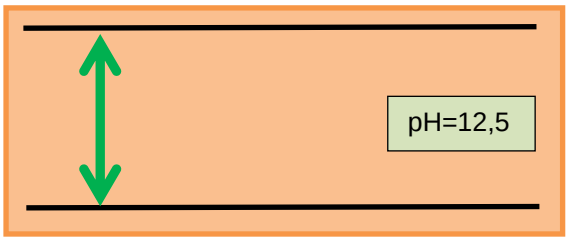
PHASE 5.- SWELLING

BATH RECOVERED FROM PREVIOUS LIMINGS AT 26ºC…….100 %

Run 30 min. Stop 30 min.

Automatic, running for 5 min. Every hour.

Total Unhairing-Liming time from the beginning: 16 hours



Water —or better still, recovered bath— must be added only after liming is fully penetrated in order to obtain uniform, tension-free swelling..

Liming baths account for 50% of the wastewater pollution load, and liming bath recycling allows to drastically reduce this environmental impact. In addition, Unhairing-Liming recovered baths result in:
- savings in chemicals.
- important savings in purification tasks.
- a more open leather without neck or cheek wrinkles.

The results of the analysis of Unhairing-Liming baths are shown in the table below:

DIAS	CONDUCTIVIDAD (µs / cm)	SNa_2 (mgr / l)	$Ca(OH)_2$ (mgr / l)
1º	66.800	1.533	5.960
2º	68.300	1.614	6.435
3º	69.900	1.571	7.231
4º	70.500	1.502	8.016
5º	75.100	1.708	6.784
8º	80.200	1.618	6.932
15º	92.300	1.584	7.485
20º	98.900	1.638	6.822
30º	114.700	1.653	7.539
MEDIA		1.602	7.023

Legend: DAYS (1st, 2nd, 3rd…) – CONDUCTIVITY – MEAN

SNa2 and Ca(OH)2 values suggest a reduction in the amount of the following batches of each of these products.
130% of bath added at Unhairing (initial 30% + final 100%) results in average recovery and further recirculation of 100% (part of the bath is drained with filtered hair and the other part remains in the leather upon leather swelling).
Saving in 100 Kg of gross weight:
In Ca(OH)2:7.023 gr.Ca(OH)2/liter of recovered bath x 100 liters = 0.702 Kg Ca(OH)2
In SNa2: 1.602 gr.SNa2/liter of recovered bath x 100 liters = 160.2 gr = 0.160 Kg SNa2
That is, **product saving would amount to 0.7% for 0,7% de Ca(OH)2 and 0,16% de SNa2**

Hair filtration system and further transfer to the filtered bath drum.

CONCLUSIONS

In view of the above, Part I can be summarized as follows:

Water rationalization and residual bath recirculation results in significantly reduced volume of water used.

The use of unhairing processes using hair immunization and suitable products results in less polluting residual baths (conductivity, DQO…)

LIST OF PRODUCTS USED of CROMOGENIA UNITS S.A.

A.- Wetting agent	*HUMECTOL RAPID*
B.- Emulsifier	*CELESAL BE-50*
C.- Tioglycolate	*RIBERSAL LA*
D.- Lipase	*DEFAT 50*
E.- Keratinase	*RIBERZYM MPX*

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