

# TRANSFORMATION PLANT FOR CONVERTING CHROMIUM WASTE INTO CHEMICAL PRODUCTS FOR THE LEATHER INDUSTRY\*

by

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## ABSTRACT

The experience gained by our research team in recent years has led to the optimization of a quick and effective procedure for the complete dechromation of chromium waste. This procedure is based on the oxidation of chromium (III) to chromium (VI) through the action of hydrogen peroxide in an alkaline medium. The highly toxic chromium (VI) is stored in a stainless steel tank before being subsequently reduced to chromium (III), which can be reused in the tanning process. The oxidation reaction, at room temperature, leads to the formation of peroxochromates that have great oxidizing power and which significantly accelerate the pre-hydrolysis; corresponding to the maceration stage in the gelatine production process. In this way, gelatine or any other type of collagen biopolymer can be obtained in a single stage and with an excellent yield. We have designed an industrial transformation plant for chromium waste in chemical products used by the tanning industry. This plant consists of the following equipment: defibering machine, hydroextractive centrifuge, two reactors (dechromation and for obtaining biopolymers), tank for storage and reduction of chromium (VI), atomizer (optional), simple equipment for heating concentrated biopolymer solutions, transportation truck. Given that the overall investment has a payback back in five years, the cost of the plant can easily be borne by the tanner.

This project has two objectives: firstly, to help solving an important environmental problem faced by the leather industry, which incurs significant costs in managing this type of waste; and secondly, to enable acceptable financial gains in terms of

obtaining chemical products designed for the tanning industry. These products are: basic chromium (III) salts from the chromium waste, collagen biopolymers suitable for retanning, filling, basifying, deliming and glazing finishes that can partially and/or totally replace casein. Our proposed transformation plant for chromium waste was designed in such a way as to be adaptable to the individual circumstances of all interested leather industries, thus avoiding the need to build a communal plant, where the costs of transporting waste would have a negative effect on final savings.

The plant is designed to process all types of chromium waste produced during the tanning process and in the subsequent stages of manufacture (fatliquoring, retanning, dyeing and finishing), and includes chromium waste with wool/hair (double-face).

A financial study of the overall installation and the corresponding cost in obtaining the new chemical products was also been carried out and reveals significant savings for the tanner.

## RESUMEN

La experiencia obtenida por nuestro equipo de investigación en años recientes ha conducido a la optimización de un procedimiento rápido y eficaz para el descromado completo de los desperdicios al cromo. Este procedimiento se basa en la oxidación del cromo (III) a cromo (VI) por medio de la acción del peróxido de hidrógeno en medio alcalino. Debe ser recalcado que el altamente tóxico cromo (VI) obtenido es almacenado en un tanque de acero

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inoxidable, antes de ser reducido a cromo (III) para poder ser reutilizado en el proceso de curtido. La reacción de oxidación, a temperatura ambiente, conduce a la formación de los peroxocromatos que tienen gran poder de oxidación y que aceleran significativamente la pre-hidrólisis, correspondiente a la etapa de la maceración en el proceso de producción de la gelatina. De esta manera, la gelatina o cualquier otro tipo de biopolímero del colágeno se puede obtener en una sola etapa y con un rendimiento excelente.

Hemos diseñado una planta de transformación industrial de los residuos al cromo en productos químicos usados por la industria curtidora. Esta planta consta de los siguientes equipos: una máquina desfibradora, una centrífuga hidroextractora, dos reactores (para descromar y para obtener los biopolímeros), un tanque para el almacenaje y la reducción del cromo (VI), atomizador (opcional), un equipo simple para la calefacción de las soluciones concentradas de biopolímero y un vehículo para transporte. Dado que la inversión total se puede amortizar en cinco años, el coste de la planta puede ser fácilmente asequible por el curtidor.

Este proyecto tiene dos objetivos: en primer lugar, ayudar a solucionar un problema ambiental importante enfrentado por la industria de cuero, que incurre en costes significativos en el manejo de este tipo de residuos; y en segundo lugar, permitir ganancias financieras aceptables en términos de obtener productos químicos diseñados para la industria curtidora. Estos productos son: las sales básicas de cromo (III) y biopolímeros de colágeno adecuados para recurtir, rellenar, basificar, desencalar y para acabados brillantables reemplazando parcial o totalmente las caseínas.

Nuestra planta transformadora propuesta para los residuos con cromo se ha diseñado a fin de poder adaptarse a las circunstancias individuales de todas las industrias de cuero interesadas, evitando así la necesidad de construir una planta comunal, en donde los costes de transportar los residuos tendrían un efecto negativo en los ahorros finales.

La planta se diseña para procesar todos los tipos de residuo con cromo producidos durante el proceso de curtición y en las etapas siguientes de fabricación (engrase, recurtido, teñido y acabado), y también incluye el residuo al cromo con pelo/lana (doble faz). Un estudio financiero de la instalación total y del coste correspondiente en la obtención de los productos químicos nuevos también se ha realizado y revela los ahorros significativos para el curtidor.

## INTRODUCTION

In a globalized world like ours, it is increasingly important to put sustainable environmental policy into practice. Many productive sectors in Spain, Europe and worldwide are making a real effort to invest in facilities and processes. Examples include: installing effluent treatment plants (physical-chemical; biological; biomembrane reactors; reverse osmosis; etc.); replacing conventional manufacturing processes with others that use what is known as "clean technology"; trying to process solid waste materials; etc. However, there is still a long way to go in this field.

Our research team has proven experience. It has specialised in the last 20 years in subjects related to the environment and specifically focused on the treatment of solid meat industry waste. Currently the research team is taking part in a major European project, called RESTORM, reference: GIRD-CT-2002-00772. The team's basic, general research area has focused on problems in treating collagen waste materials generated by the meat industry (in abattoirs) and by the tanning industry in particular. The tanning industry's raw material is skin, which is a waste material from the meat industry. Why has the team focused on the tanning industry? Firstly, because this industry generates large amounts of collagen waste, as do related industries (e.g. shoe, clothing and upholstery, etc.) that generate different products mainly from skin (leather). As an example, only 300 kg of each 1000 kg of cowhide that enters the tanning industry is used to make saleable leather. Most of the remaining 700 kg represent solid collagen waste. The second reason for carrying out research in this area is the collagen content of this waste itself. Collagen is a very special, high valued protein. It is the most abundant protein in the animal and human kingdom. This opens up a range of potential applications for collagen in fields such as pharmacology, cosmetics, veterinary science, medicine, etc. Thirdly, many members of our research team have also accumulated experience in the technology of the chemical processes used by the tanning industry.<sup>1,2</sup>

It is important to bear in mind that the tanning industry uses a raw material, skin, that is in turn a by-product of the meat industry. This skin is the tanning industry's raw material. In fact, in the distant past, tanners were the first environmentally friendly industrialists, as they made use of a by-product that would otherwise have been disposed of. However, synthesized chemical products have gradually been introduced to the tanning process. These have created extrinsic (external) pollution, in addition to other factors.<sup>3,4</sup>

Clearly, in recent years, much of the tanning industry has moved from Europe to Asia (mainly China). However, there are still many tanneries in Europe and thus associated environmental problems still persist. It is also true that the development of innovation in processes designed to obtain biopolymers is perfectly exportable to other countries. Soon, more countries will also have to better manage their waste materials. This possibility could represent a considerable source of income in terms of royalties, knowledge transfer, etc.

Knowledge obtained in the last National Plan R+D and R+D+I projects and current participation in the European project RESTORM, reference:GIRD-CT-2002-00772 (leading some of the Workpackages (WP1) that specifically deal with the management of collagen waste), has helped to draw up the report for this new Research Project. Objectives have been determined that constitute a real scientific challenge; such as obtaining new high value-added biopolymers. From the experience acquired in carrying out previous projects, the team has perfected specific technology for processing collagen waste. This technology is particularly aimed at waste that is cross-linked (tanned) with basic chromium (III) salts, as used in 85% of the tanning industry worldwide. In this way, bioproducts that belonged to the low-price market segment are obtained. The main applications of these bioproducts have been in the tanning industry itself as filling, retanning and finishing agents or in the paper industry as binding agents that either partially or totally replace casein (which is much more expensive and has to be imported). However, the industrialist, in this case the tanner, has to deal with real environmental problems related to collagen waste materials. Chromium waste causes particular problems; under current European legislation the accumulation in otherwise approved dumps of waste materials containing chromium (III) is forbidden. This is because, depending on the length of time, temperature, pH, microorganisms, etc., some of the chromium (III) can be oxidised to chromium (VI). Chromium (VI) is highly toxic and pollutes the ground and groundwater. So tanners continue to accumulate waste materials in their tanneries and pay high prices for "someone" to remove them. Therefore, one of the objectives of past projects and of this one has not only been to obtain bioproducts but also to "physically" eliminate collagen waste from tanneries; separate metals and/or potentially toxic compounds; and gain financial benefits from obtaining industrially reusable bioproducts.<sup>4</sup>

Experimental mathematical models are used to study the degree of significance of the most important variables. In addition, the corresponding interaction between the variables in the processes established to obtain new types of biopolymers can be analysed using such models. Thus, the experiment can be rationalised and a mathematical equation defined that will control the whole process and enable us to determine the optimum zone in each case.

## EXPERIMENTAL

### Description of the Global Process Diagram

CSIC's research team has developed a special dechroming technology in which the chrome (III) wastes are oxidized to chrome (VI) by the action of hydrogen peroxide (optimum selected oxidizer compound), in alkaline medium (sodium carbonate) at room temperature, in a range between 20°C ± 2°C. Chromium (VI) has lost all its coordinating capacity; therefore, all types of ligands are liberated into the bath and then conducted into a storage tank for its final recovery as chromium (III). The main advantages of this process is summarized as follows:

- a) High-speed oxidation reaction means considerable economic savings, such as operating costs (chemicals, energy, labour, time, etc). It presently may be considered the fastest dechromation treatment; it can be set up in an average of 1 hour. It should be remembered that other processes, such as; change of pH (acid/alkaline); alkaline-based enzymatic, and/or masking-based chemical compounds take over 6 hours.<sup>1,2,3,4</sup>
- b) In contrast, this process is based on the oxidation of chromium (III) to chromium (VI) using peroxides, generally hydrogen peroxide, in an alkaline medium. The collagen fibres of the leather are left with very little residual chromium and, with their physical and chemical characteristics completely unaffected. By means of this process, the chromed collagen fibres are left at a stage previous to the tanning phase, remaining in the raw or pickle stage, not stabilised or crosslinked.<sup>4,5,6</sup>

### Basic Steps of This Process

Process Diagram (see Figure 1)

#### *1st Step - Ground up chrome-tanned wastes.*

Collagenic chrome (III) wastes are ground into a "defibered size"; achieving a diameter of 1 to 5 mm; so giving a more homogeneous material with a greater surface and therefore saving chemicals and shorten reaction time ( Grinder : J-110 as shown in Figure 1).

#### *2nd Step - Dechroming process.*

Uses a stainless steel stirred reactor (oxidation reaction) and/or a modification of a conventional tannery drum (non-wooden) with a suitable filter mesh (1 to 5 mm of diameter). Tannery selected drum should be placed at least two meters height in order to facilitate charging of the oxidized bath into a storage tank. Tannery drum can serve as a proper reactor to obtain different types of biopolymers, providing that the temperature inside the tank can be increased to 80°C. However, the authors strongly recommend the first option (Reactor: R-120 as shown in Figure 1).

The oxidation takes place in basic medium; therefore, a pH 12 should be reached using sodium carbonate or sodium hydroxide. The oxidation is carried out with hydrogen peroxide that allows a faster kinetic reaction and in addition does not generate any residues. This reaction only forms water as show the following reaction.<sup>5,6</sup>



Published thermodynamic functions allows the calculation of the final Gibbs Energies of Formation for this reaction; its negative value shows that under such a conditions is totally displaced towards the formation of chromate anion and water, meaning there is a complete oxidation of the original chromium (III)

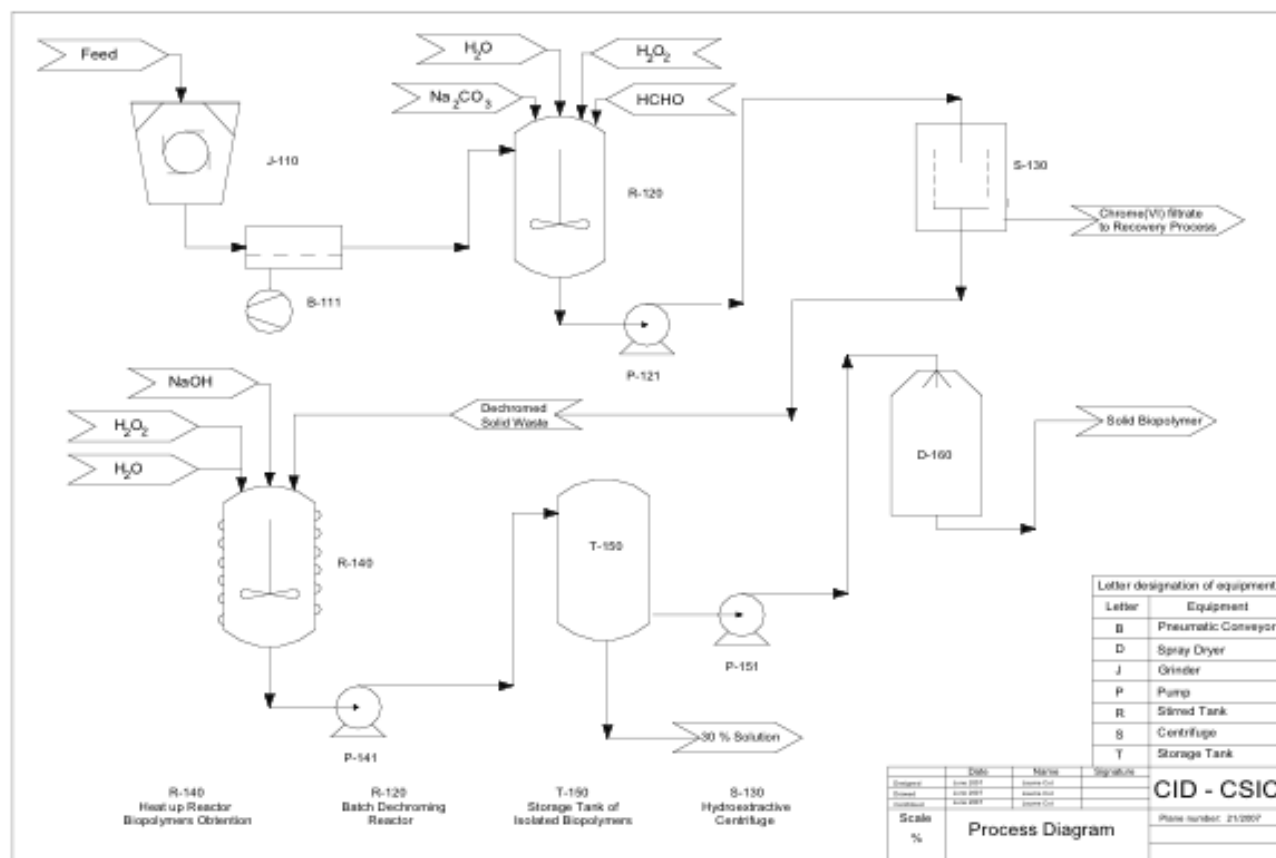


Figure 1: Process diagram

## Gibbs Energies of Formation:

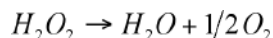
Component	Gibbs Energies of Formation,
$\text{Cr}_2\text{O}_3$	-1053
$\text{OH}^-$	-157.28
$\text{O}_2$	0
$\text{CrO}_4^{2-}$	-727.85
$\text{H}_2\text{O}$	-228.61
$\text{Cr}_2\text{O}_7^{2-}$	-1301.2
$\text{H}^+$	0

## Gibbs Energy, both reactions:

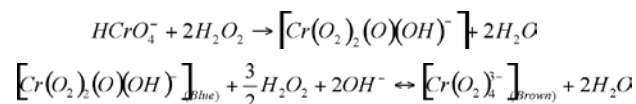
$$\Delta G_f^\circ = -4 \times 727.85 - 4 \times 228.61 - (-2 \times 1053 - 8 \times 157.28) = -461.6 \text{ kJ/mol}$$

It is a question of the kinetics of the above-mentioned reactions that have been studied in various publications.<sup>7,8</sup>

The compound acting as oxidizing agent is oxygen that comes from hydrogen peroxide decomposition.



During this phase, a brown precipitate is observed, that can be identified as peroxochromates of hard isolation. The reactions are presented in the following equations.

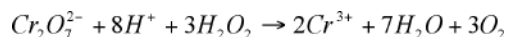


The blue complex is present in neutral medium and the brown complex in an alkaline medium. This is favored by hydrogen peroxide excess and the basicity of the sample. This reaction is influenced by the oxygen diffusion in reaction medium.

**3rd Step - Centrifuge operation.**

The use of a hydroextractive centrifuge is suggested when tanners prefer to invest money in building up a new treatment plant near by, instead of modifying the traditional drums. The authors also recommend installation of a hydroextractive centrifuge (Centrifuge: S-130 as shown in Figure 1).

This operation produces a filtrate (liquid effluent) and dechromed collagen fibres (solid state). The filtrate, which contains chromium (VI), is stored into a stainless steel stirred tank for further reduction to chromium (III), and adjusted to the correspondent basicity (33° Sch); then this basic chromium (III) solution can be mixed up with the addition of chromium (III) salts powder to the suitable concentration for the tanning operation. The main reductions agents are the following:

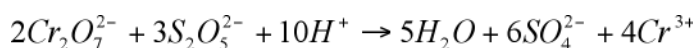
*Reduction with hydrogen peroxide.*

$$\begin{aligned}\Delta G_f^\circ &= -2 \times 1301.2 - (-2 \times 1053 - 2 \times 228.61) \\ &= -39.18 \text{ kJ/mol}\end{aligned}$$

for acidic medium.

*Reduction with sodium disulphide.*

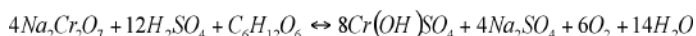
The method of obtaining chromium liquor with disulphide is very similar to the one using the sulfite. In this case, disulphide reacts with the acid forming sulfite that acts as reducer and yields bigger quantities of sulfates. The following equation shows the global reaction that governs this process.



This reduction generates an important amount of complex and neutral salts. The experience shows that the reaction could be developed in cold and also without using sulfuric acid.

*Reduction with glucose.*

This is one of the most widely used reduction methods in chromium recovery process. In this reaction, glucose is not completely oxidized to carbon dioxide, but some intermediate compounds are formed, generally organic acids that play an interesting role because of their influence diminishing the basicity and masked effect on chromium. The following equation shows the reaction when the glucose undergoes a complete oxidation.



The masked effect increases as the quantity of glucose is increased favoring the formation of organic acids. On the contrary, the temperature decrease produces a diminishing effect upon the basicity. One problem that arises when using this method is the doubts about if it is much better adding glucose to the acid-dichromate mix or adding acid to the glucose-dichromate mix. Alternatively, the squeezed dechromed collagenic fibers are driven through a conventional pump into the next step.

*4th Step - Isolation of collagen biopolymers.*

In this step a jacketed stainless steel stirred reactor designed for viscous products is used in order to obtain different types of biopolymers (Reactor: R-140 as shown in Figure 1). Treated dechromed collagen wastes undergo a second process of highly controlled topochemical hydrolysis. The method of control depends on the degree of interaction of the following variables: macerators - alkaline, acid, liotropic, activators - hydrogen peroxide, sodium percarbonate, sodium perborate, etc.

It is important to note that during the process, a certain amount of peroxochromates are generated in situ, which in turn are very active and possess a high oxidation capacity. These compounds contain 2, 5 peroxy groups for each chromium atom, and are strongly linked to the ionic groups of the collagen structure. The presence of such peroxochromates during the second hydrolytic process, carried out at a temperature of - 60°C - 70°C, accelerates the kinetics of the reaction; allowing the production of the bioproducts, such as gelatine with acceptable physical and mechanical properties. After two hours a yield of 98% or higher was reached.<sup>9,10,11,12</sup>

*5th Step - Storage.*

These biopolymers can be commercially available in several states; usually as a 30% solution which can be stored into a jacketed agitated tank. When temperature goes down below 14°C it is necessary to heat it up around 40°C with special equipment; thus converting it into a viscous liquid when needed (Storage Tank: T-150 as shown in Figure 1). It can also be in the form of a solid powder achieved with a spray drier unit (Spray Dryer: D-160 as shown in Figure 1). It should be kept in mind that according to the strict EU environmental legislation, it is totally banned to landfill this sort of chrome (III) wastes.

By the CSIC's Process, which consists of two main steps, the chromium content of the chrome-tanned waste can be fully recovered and reused back to Tannery.

Step one is based on a dechromation reaction of chrome (III) to chrome (VI) by the action of hydrogen peroxide in an alkaline medium; and subsequently reducing (steel storage tank) to chrome (III) by the action of hydrogen peroxide in an acidic medium. A final adjustment of its basicity will make the basic solution of chrome (III) reusable for the Tannery Operation.

Step two is based on the isolation of biopolymers (gelatine) from the already dechromed collagenic waste, thus producing a yield of 98 -99% on this new bioproduct.

The remaining 1 - 2% of not recovered waste can be submitted to a repeat "Step two" raising the temperature, in order to isolate a more hydrolyzed biopolymer. That will make a 100% of yield on bioproducts and all chrome (VI) generated is fully converted to chrome (III). According to this process the biopolymers isolated contain a low amount of chrome (III), 30- 40 ppm making available for Tannery use.

With the CISC's process, two main targets were reached: a) sort out a serious environmental problem as a consequence of dealing with chrome-tanned waste and b) an economical benefits including: recovery of chrome(III), isolation of biopolymers to be applied as retanning, filling, and finishing agents in tannery.

CSIC's process has been adjusted to treat other types of chrome (III) tanned waste, produced during different tannery operations; such as: Full chrome tanning, fatliquoring, retanning, dyeing, finishing and, also double-face waste, separating the wool/hair with a proper filtration unit.

## MAIN NOVELTIES

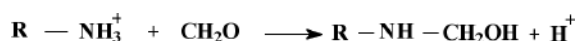
### Size Reduction by Grinding

The experience acquired by this research group in the recent environmental projects, especial mention to PPQ-2000-0213-P4-04, upon processing these types of wastes, it is essential to submit them to a size reduction operation (defibering) to achieve fiber size between 1 to 5 mm of sieve diameter. In this way, it is possible to reduce considerably the concentration of the chemical compounds employed, and lower the reaction temperature. The level of defibering of the residues obliges the use of very large baths, since the collagenic fibers absorb large amounts of water. To achieve good dechroming action, residues ought to be totally submerged in the treatment bath, since the oxidation of chromium (III) to chromium (VI) requires a high concentration of hydroxyl ions (supplied by the alkali). It has been proved that when parts of the wastes do not remain soaked in the alkaline bath, they fail to be dechromed. Another important aspect of the system is agitation, using an adequate stirrer capable of vigorously mixing action of the defibered wastes.<sup>13,14</sup>

### Formaldehyde Crosslink of Chrome Wastes

One of the most innovative aspects of this study is the possibility of retanning chromed collagen waste products with formaldehyde; this reaction, takes place with the amino and imino groups of collagen, producing an additional crosslinking to that corresponding to the coordination of chromium (III) with carboxylic groups of collagen. Clearly, some of the formaldehyde also reacts with the chromium (III) salts that are coordinated with collagen and/or free. However, the benefit of 'formaldehyde tanning' is proportional to the stability of the collagen wastes that is acceptable once they are dechromed. Dechromed collagen wastes behave like if they were in a raw state (unstabilised), and therefore undergo swelling in aqueous solution, both acid and alkali, consequently it is necessary to add neutral salts.<sup>13,14</sup>

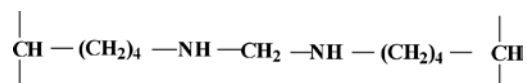
Stabilization with formaldehyde permits the elimination of sodium sulfate (in alkaline medium) and sodium chloride (in acidic medium), and prevents the dechromed collagen fibers from swelling and hydrolyzing during dechroming and subsequent treatments. Acid treatment, in the presence of hydrogen peroxide (reducing medium), is able to partially reverse the formaldehyde-mediated stabilization of collagen (a form of detanning) in such a way that the rest of the crosslinked with collagen does not interfere with the subsequent obtaining of the bioproduct (gelatin) and can even be said to give some interesting properties to that bioproduct. Various reactions take place in the combination of formaldehyde and collagen. At pH values between 3 and 4, in other words in the acidic region with respect to the isoelectric point of skin, a reaction takes place between collagen and formaldehyde.



This reaction causes a small increase in the contraction temperature, but the condensation reaction between

formaldehyde and the skin tissue occurs more intensely in the alkaline zone with respect to the isoelectric point, that is to say, in that zone in which the free basic groups of collagen are encountered in an un-dissociated form. Up to a pH of 8 the amino groups of lysine are the main reactive species, but if an even more alkaline medium is used guanidine groups will also participate. For this reason it is convenient to use an alkali, e.g. sodium bicarbonate that produces the desired alkalinity without causing swelling of the hide.<sup>13,14</sup>

The tanning effect, manifested by the increased contraction temperature, is probably due to the formation of bonds between collagen adjacent chains; e.g., lysine amino groups, so as described in the following scheme:



### Elimination of the Ion Exchange Equipment

In the CSIC dechroming Process the original chromium (III) is oxidized to chromium (VI) by means of the action of peroxides, generally based, on the hydrogen peroxide, in alkaline medium ; on this way the collagen fibres are left with very little residual chromium, and, more importantly , their original physical-chemical properties remain unaffected. By means of this process the chromed-collagenic fibers are retro gradated in a stadium(sic) prior to the tanning, that is, in a raw or pickle state- not crosslinked.<sup>13,14, 15</sup>

On the chromium (VI) solution, the excess of peroxide is eliminated, then acidified to a form of "dichromate anion" and subsequently it is made pass through a column of ionic exchange resin where the fixation of the dichromate is total. Once the resin is completely saturated, reduction of chromium back to level (III) takes place "in situ". By using an acidic medium, also with the addition of hydrogen peroxide, chromium (III), which has the same positive charge as that of the matrix of the resin, can be easily eluted. A very concentrated solution of chromium (III) is obtained, and, with final adjustment to the right basicity, offers the possibility to be reused back to tannery.

Nevertheless, in order to reduce the investment cost in the equipment of global pilot plant installation, the authors decided to eliminate this unit and the collected chromium (VI) effluent produced by this procedure is stored into a stirred stainless steel tank where the aforesaid reduction process will take place at. Although the chromium (III) content is rather low (0.4 %), a calculated amount of solid commercial chromium (III) basic salt can be added to this effluent; so can be ready to use it in the tanning operation.

Thus, the chromium (III) can be completely recovered from the collagen containing chrome-tanned wastes and re-used into the Tannery.

### Recommended Physical State of the Isolated Biopolymers

The biopolymers obtained according to this process can be prepared either in a completely dry state or in a solution of 30% concentration. Referring to the first option the investment

cost is considerably higher due to the Spray Drier equipment. Therefore, we recommend to use the 30% solution; however it has to bear in mind that at this concentration and in function of the temperature, e.g.: below 14°C this biopolymer will be converted in a solid-jelly product that will need to be heated up. It would be advisable to use a jacketed stainless steel storage tank; in order to heat it up around 40°C, then the biopolymer solution will easily become lightly viscous and therefore can be poured into the drum or other vessel.<sup>12,13,16</sup>

## STATISTICAL TREATMENT OF THE RESULTS

### Experimental Design

As can be seen in the global Process Diagram showed in the Figure 1, this is subdivided in two complementary treatments, both were submitted to mathematical experimental designs: a) Dechroming of the chrome (III) –tanned wastes, and b) Isolation of collagenic biopolymers from the dechromed wastes. In order to evaluate the significance of the experimental factors and their interactions on the residual Chromium an Analysis of Variance was performed. Factors and interactions that have not reached a minimum significant level of 10% were removed from the model.

### Dechroming Process

All factors are highly significant, especially the oxygen peroxide concentration at linear and quadratic components that are significant at 0% level. The linear component of the Na<sub>2</sub>CO<sub>3</sub> concentration is also significant at 0.96%, and the time in its linear and quadratic components is significant at the 2.7 and 7.8% respectively. Lastly, the linear component of the HCHO is significant near at the 10% level, although an interaction between the HCHO and the H<sub>2</sub>O<sub>2</sub> is significant at 4.5%. The effect of the significant interaction between HCHO and H<sub>2</sub>O<sub>2</sub> is shown in Figure 2. It can be seen that the effect of the HCHO at low H<sub>2</sub>O<sub>2</sub> level is reverse to the effect of the HCHO at high H<sub>2</sub>O<sub>2</sub> level. Also the effect of the H<sub>2</sub>O<sub>2</sub> on the residual Chrome is different depending on the level of the HCHO concentration. Using the same methodology the influence of the four factors on the efficiency has been examined. Non

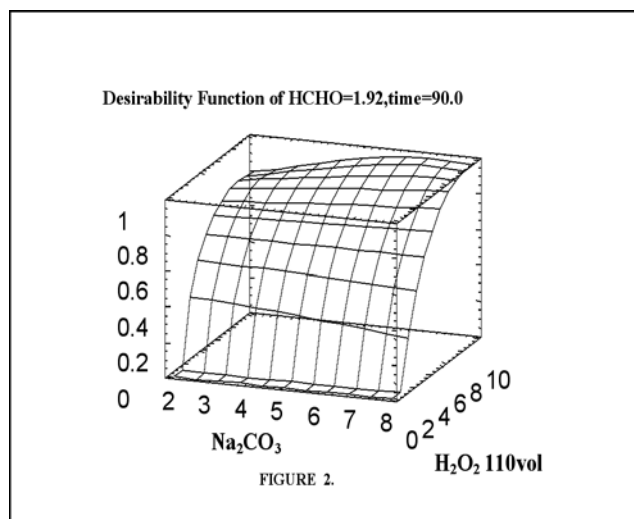


Figure 2

significant effects and interactions were removed and the significant effects are those shown in the following table of the analysis of variance. It can be seen that the HCHO, H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> exert a high significant effect on the Efficiency. Nevertheless, being that the quadratic effect of HCHO is significant an optimal concentration of HCHO can be observed. Two interactions were significant (HCHO x H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> x Na<sub>2</sub>CO<sub>3</sub>). According to the effect of the first one it seems that at high H<sub>2</sub>O<sub>2</sub> concentrations the presence of HCHO improves the efficiency, while at low H<sub>2</sub>O<sub>2</sub> concentrations no effect of HCHO on efficiency was noticed. The second interaction shows that at low concentrations of H<sub>2</sub>O<sub>2</sub> no effect of Na<sub>2</sub>CO<sub>3</sub> was observed on the efficiency, while at high concentrations of H<sub>2</sub>O<sub>2</sub> the Na<sub>2</sub>CO<sub>3</sub> improves the efficiency.

$$\text{Effic.} = 105.474 + 7.11458 \cdot \text{HCHO} - 0.803472 \cdot \text{Na}_2\text{CO}_3 - 7.11542 \cdot \text{H}_2\text{O}_2 - 7.49917 \cdot \text{HCHO}^2 + 2.74688 \cdot \text{HCHO} \cdot \text{H}_2\text{O}_2 + 0.508958 \cdot \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2$$

The equation explains the 80.1% of the squared variations of the efficiency. Non significant influence of the time over the efficiency was observed, Figure 2. In order to reach the best experimental conditions for both efficiency and residual chromium the desirability function has been used.<sup>17,18,19</sup>

### Isolation of Collagenic Biopolymers

Experiments were carried out according to a Box and Hunter Central Rotatable and Orthogonal Composite Design [a] for four variables. The variables were the following: X<sub>1</sub>, Temperature [°C], X<sub>2</sub>, time [min], X<sub>3</sub>, M of NaOH and X<sub>4</sub>, mL of H<sub>2</sub>O<sub>2</sub>.<sup>11,12,13</sup>

A first cycle of experiments, in order to reach optimal conditions was designed. It has to be taken into account that only NaOH concentrations and Temperature were the variables that showed significant influence on Bloom. Therefore the Two-Level Factorial Plan in which the experimental plan is based was centred on this experiment and the range of variation of the variables was as follows;

Central Point:

- X<sub>1</sub>, Temperature = 70°C – 80°C
- X<sub>2</sub>, time = 60 -90 min
- X<sub>3</sub>, NaOH concentration = 0.2 M
- X<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> = 1 mL

Neither the amount of H<sub>2</sub>O<sub>2</sub> nor time significantly affected Bloom results. Therefore the H<sub>2</sub>O<sub>2</sub> amount was fixed at constant 1 mL and time was slightly modified between 40 to 50 minutes.<sup>20</sup>

In some cases a second set of experiments centred on that ought to be designed. It is important to underline that hydrogen peroxide should not be added all at once, but in three or four doses.

### Industrial Applications

The isolated biopolymers were tested; either on a lab scale or on a pilot- plant one and the following chemical products for Leather Industry were found:

- As a casein substitution in some especial glazing finishing articles. It can also be used mixed up with casein (biodegradable films).
- As a filler and/or retanning agents for the leather industry. The main purpose is that each Tannery could process their own chrome (III) – tanned wastes and/or raw ones; in order to produced a type of protein – based retanning compound to be used alone or mixed up with other conventional ones. Finished leather treated with these new retanning agents has shown no negative variation of their standard physical and mechanical properties (tearing, tensile strength, etc); on the contrary, these parameters were increased in some leathers.
- As a delimiting agent.
- As a basifying agent.

Several types of bioproducts obtained at the optimum zone according to the response surface given by the factorial experimental design described previously on this paper, were used on different industrial applications at the following: Pielcolor S.A (Spain), Trumpler Espanola S.A (Spain), Incusa (Spain), Pittards (U.K.), BLC (U.K.) and ECCO (Netherlands).<sup>20,21</sup>

#### Biodegradable Films used as Finishes in Tanneries

Pielcolor SA, is a chemical supply firm for leather industry, dealing with polyurethane, acrylics, and correspondent copolymers for finishing of leather. One combination of these materials produces the glossy finish for a specific manufacture article very popular throughout the world. Traditionally, this type of glossy finish is based on casein.

Several pilot-plant trials carried out at this industry in comparing the whole set of casein-based products to biopolymer-based ones, have allowed to conclude that :

- a) There were no major differences between casein and collagenic biopolymer application to leather.
- b) Collagenic biopolymer possesses excellent binding properties for pigments, dyes, waxes, etc.
- c) Good fastness to dry rub fastness test and less when referring to wet rubbing test, However, this property can be modified by changing the crosslinking agent; e.g., a new compound, "ethylene glycol diglycidyl ether", which has improved final results. It has been tested according to ISO – 11640 (IUF/50) - Colour Fastness of Leather to Rubbing.
- d) Good glossy and transparency effect.
- e) Similar resistance to flexometer, lastometer.
- f) Similar resistance to water absorption and to solvents.

It is important to bear in mind that there are three parameters that should be taken into account; such as: viscosity, low residual chromium content and concentration of collagenic biopolymer within the range of 20% -30%. With respect to viscosity, it is established that such a solution stored to 4°C would have to be viscous or fluid, capable to pour out easily from the barrel or container- an average of 1.400 - 1.600 cps. A similar solution of casein behaves in such a manner; however,

the bio product is entirely different protein - spaghetti-like rode, while the casein is globular protein. In the majority of collagenic biopolymers their physical state at this temperature is completely solid-jelly stuff. Therefore, it is necessary to install a jacketed stirred tank at a temperature of 40°C to turn the biopolymer into a fluid viscous liquid.

Furthermore, gelatine does not stick during ironing process - 110°C-120°C of temperature, a pressure of 80 - 100 Kg/cm<sup>2</sup> and during a period of time of 20- 60 seconds.

Several pilot-plant trials were run using a type of collagenic biopolymer, obtained according to CSIC's Process, instead of casein. Final conclusions were quite similar; thus biopolymer-based compounds showed an excellent binding capacity, good glossy and transparency effect, increasing by mechanic rubbing strong action; good to dry and/or wet rub fastness test, and finally a similar resistance to bleeding out of the ink in function of temperature, time and atmosphere conditioning.

#### Retanning and Filling Agents

Incusa (Spain); Pittards (U.K.); ECCO (Netherland); BLC (U.K.); Trumpler (Spain) are leather industries specialised in bovine leather; except from the last one, which is a chemical supply company settled in Spain. Although it can be paradoxical, an industry like this produces this type of chrome-collagen wastes at a level of a few tons/per year, but at the same time by using CSIC's Process is capable to reuse both chrome (III) recovered, and collagenic bio product; transformed them into a *pretanning* and/or *retanning agent*. The main target of this hypothesis is to substitute synthetic acrylic, polyurethane resins and protein based retanning products by the isolated biopolymers.

After the correspondent set of pilot-plant trials it has been determined that collagenic biopolymer introduces an important filling effect to leather, similar to the other resins, and raises up the colour intensity of the dyestuffs. Nevertheless when this biopolymer compound was applied alone, the leather produced is rather hard, but when mixing up with fatty acid o some type of triglycerides, its original hardness can be changed to a softer handle. Our research will go towards the copolymerization of this bio product with a long chain fatty alcohols or acids to give a permanent soft feeling to the finished leather. However, what is most relevant is that in all trials the colors of dyed leathers were significantly deeper, stronger and more intense in comparison to other retanning agents. In addition, the newly created protein retanning biopolymers also produced a significant filling effect, thus raising the thickness of treated leathers. Figures 3, 4 and 5 show the most fundamental physical tests in order to reflect a comparison trial of this bio product obtained by CSIC's Process and some other commercial protein-based retanning products.

Figure 3, corresponds to Measurement of Tensile Strength and Percentage or Elongation – ISO -3376 (IUP/6).<sup>22</sup>

Figure 4, corresponds to *Measurement of Tear Load* – ISO – 2417 (IUP/8).<sup>23</sup>

Figure 5, correspond to *Measurement of Distension and Strength of Grain by the Bull Burst Test*- ISO – 3379 (IUP/6).<sup>22</sup>

Specimen 1 corresponds to the control test (not retanned). Specimen 4, 5 and 6 correspond to different types of commercial protein-based retanning agents. Specimen 2 and 3, correspond to the collagenic biopolymer obtained according to CSIC's Process.

It can be concluded that the application of such collagenic biopolymers have produced both a retanning and filling effect comparable, and in some cases, even showed higher values, to the already existing commercial protein-based retanning agents (see Figures : 3,4,5). In addition, what is really relevant to mention is that in all trials the colour of dyed leathers were significantly, deeper, stronger and more intense in comparison to other retanning agents. Furthermore, some other appreciated qualities such as acceptable handling, smooth grain (like soft nappa), and firm full leather were imparted.

### Deliming Agent

Due to the amphoteric nature of these biopolymers, isolated by CSIC's Process, it is possible to use them both as a delimiting or basifying agents. For these special uses, the conditions of the controlled hydrolysis of the dechromed collagenic fibres are taking place in stronger hydrolysis conditions, in order to isolate polypeptides chains of shorter lengths. When using this biopolymers as delimiting agents, the final pH is adjusted to 3- 4,5 with sulphuric acid; thus converting the biopolymer into a cationic form, in which the carboxylic groups can mask the calcium already fixed in the skin/hides. This proteinaceous biopolymer produces a uniform neutralization of the internal

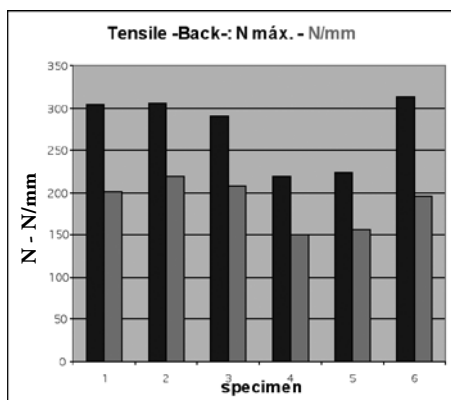


Figure 3

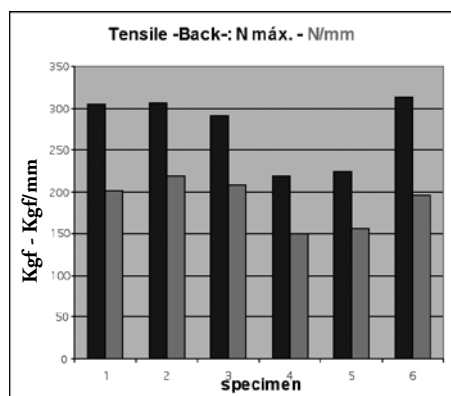


Figure 4

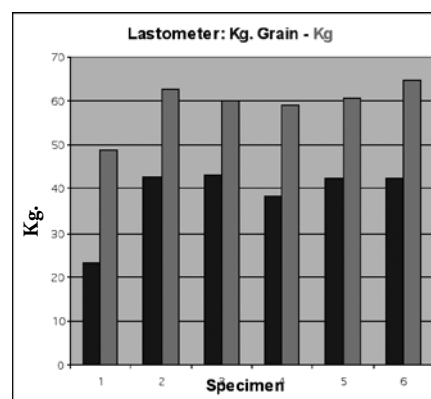


Figure 5

layers of the skin/hides without swelling them, so as happens when strong acids are applied.

### Basifying Agent

In a parallel way and adjusting the pH to an alkaline range; such as: 10 – 12 with sodium hydroxide, ammonium hydroxide, sodium carbonate. The optimum results were obtained when these biopolymers were mixed up with oxazolidine, in a proportion of 1:1; thus producing a type of synergy that helps a gradual basifying action during the tanning operation.

Another advantage is that can be added together with the powder chromium (III) basic salts direct to the tanning bath, without need of a periodical control of the pH and gradual addition of the basifying agent (e.g. sodium bicarbonate, etc). After five hours running in the drum, chromium (III) has completely stabilized the skin/hides in a uniform penetrated layers and producing a high exhaustion of the tanning baths.

## CONCLUSIONS

1. Complete elimination of physical volume occupied by these types of chromed collagen wastes (99% of removal) has been show; thus a tremendous environmental problem has been solved; and, consequently, a considerable reduction in the management cost of such a waste has been gained.
2. We have demonstrated that a new dechromation process based on the oxidation with peroxides in alkaline medium, followed by washes, reduces the chromium content from 50.000 ppm (original collagen waste) to 20-90 ppm (on dry weight basis of collagen wastes).
3. Recovery and reuse of the chromium (III) present in chrome-tanned wastes was demonstrated. The chromium (VI) produced with this process is reduced with hydrogen peroxide in acidic medium back to chromium (III) inside of a storage stainless steel stirred tank (high speed kinetic reaction). Finally, adjustment of its basicity to 33° Sch, followed by addition of the necessary amount of solid basic chromium (III) powder salts prepares this bath to the appropriate chromium (III) concentration to be reused into a conventional industrial tanning process.

4. Isolation of industrially reusable bioproducts in Tanneries was shown. Once the majority of chromium was separated from the original chromed-collagen wastes different types of bioproducts could be obtained. Thus, a range of the following chemical leather tannery products were produced: retanning and filling agents, biodegradable film in the finishing operation of certain glazing leathers and delimiting and basifying agents.
5. The CSIC's Process for obtaining collagenic biopolymers out of chrome-tanned wastes can be tailored made for each tannery; therefore diminishing the transport cost from an external communal plant that could treat wastes from different tanneries. According to the economic calculation described in the above Potential Exploitation section, the real cost of 1 Kg of 30% solution of biopolymer obtained is of 0.74 \$ or 0.57 €.

6. Amajor use of these biopolymers is the applications retanning/filling agents in tanneries. Main physical-mechanical properties (tensile strength, tear load, lastometer, etc) have been shown to be either equal, or even higher values, in comparison to the majority of other protein-based retanning products.
7. This present project has introduced a few novelties with respect to previous studied processes. These include: a) grinding the chrome-tanned wastes to a diameter of 1 mm to 5 mm, b) partial retanning of chrome-wastes with formaldehyde to stabilize them, mainly in alkaline medium, so neutral salts can be eliminated; therefore, lowering the residual salt content of the effluents and obtaining better quality of the biopolymers, c) completely elimination of the ion-exchange unit to separate the chromium (VI), showing a great saving for the global installation, d) the authors recommend achieving a 30% solution of biopolymers rather than adding a spray drier unit, which in turn is a significantly equipment cost savings.

## Potential Exploitation

### Global Cost of a Pilot-Plant Installation

#### PRODUCTION

Details	Factor	Kg/day	Concentration %	TM/Year 300 days/year
Chrome wastes		1000		300
Protein yield	0,5	500		150
Chromium oxide yield	0,04	40		12
Ratio wastes:water (dechroming)	10	10000		3000
Ratio wastes:water (hydrolysis)	3	1500		450
Biopolymer solution concentration			33,3	
Chromium oxide solution concentration			0,4	

#### INVESTMENT

Details	euros
Grinder	40000
Dechroming reactor	50000
Hydroextractive centrifuge	40000
Chromium oxide storage tank	20000
Hydrolysis reactor	70000
Biopolymer storage tank	20000
Pumps, valves and others	10000
<b>TOTAL</b>	<b>250000</b>

#### CHEMICALS

Details	Unit/year (e6)	Unit 2	euros/U nit 2	euros/ year	euros/ TM sol biopolymer	euros/Kg biopolymer
<b>DECHROMING</b>						
Hydrogen peroxide	240	m3/year	235	56400,00	125,33	0,13
Sodium carbonate	180	TM/year	220	39600,00	88,00	0,09
Sulphuric acid	30	m3/year	70	2100,00	4,67	0,00
Formaldehyde	3	m3/year	270	810,00	1,80	0,00
<b>WASHES</b>						
Sodium carbonate	60	TM/year	220	13200,00	29,33	0,03
Hydrogen peroxide	60	m3/year	235	14100,00	31,33	0,03
<b>HYDROLISIS</b>						
Sodium hydroxide	3,6	TM/year	390	1404,00	3,12	0,00
Hydrogen peroxide	5,85	m3/year	235	1374,75	3,06	0,00
<b>TOTAL</b>				<b>128988,75</b>	<b>286,64</b>	<b>0,29</b>

#### TOTAL COSTS

Details	Factor	euros/year	total euros/year	euros/TM sol. biopolymer	euros/Kg biopolymer
Chemicals	1	128988,75	128988,75	286,64	0,29
Labour	2	35000,00	70000,00	155,56	0,16
Pay back (10 years)	1	25000,00	25000,00	55,56	0,06
Energy	1	5000,00	5000,00	11,11	0,01
Water	2	10350,00	20700,00	46,00	0,05
Maintenance	1	5000,00	5000,00	11,11	0,01
<b>EURO\$/Kg SOL BIOPOLYMER =</b>					<b>0,57</b>
<b>\$/Kg SOL BIOPOLYMER =</b>					<b>0,74</b>

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