

PRODUCTION AND POTENTIAL USES OF CO-PRODUCTS FROM SOLID TANNERY WASTE

ABSTRACT

The manufacture of high quality leather goods results in an almost equal weight of solid tannery waste. The U.S. leather industry generates more than 50,000 metric tons of shavings and trimmings each year; the world-wide total is about ten times as much. This solid tannery waste consists largely of collagen crosslinked with chromium. Although some shavings are used in the manufacture of leather-board, most at present still go into land disposal. Reduced industrial demand and escalating landfill costs prompted us to look for alternative uses for this waste material. Several years ago, we demonstrated the feasibility of using enzymes as part of a process to detan this chromium-protein complex and isolate inorganic chromium salts and partially hydrolyzed collagen. In this process, the collagen was digested to small peptides useful as constituents of fertilizer or animal feed. A more recently developed two-step process treats the chrome shavings first under mild alkaline conditions to produce a high molecular weight gelable protein fraction for value-added production of gels, adhesives and films. The remaining sludge is then treated with an enzyme as a step in a process to recover the chromium and smaller peptides. A sample of potential uses for the isolated products is included.

INTRODUCTION

The manufacture of high quality leather goods results in an almost equal weight of solid waste material.¹ The U.S. leather industry generates more than 50,000 metric tons of

chrome-tanned trimmings, shavings and buffing dust each year, whereas the world-wide total is about ten times as much. During the past 25 years, some rather innovative methods to treat this waste product have been developed. For example, basic hydrolysis at elevated temperature and/or pressure has been used in many parts of the world for chrome recovery and for the isolation of protein fractions.²⁻⁵ Acid hydrolysis has been used to convert the waste into a chromium-containing hydrolysate usable in the retanning or fatliquoring steps of leather finishing.⁶⁻⁹ Intact trimmings may be used to make small items or patchwork designs. Shavings and buffing dust can form the basis for composite materials such as leather-board. In reality, the demand for these products is greatly exceeded by the supply, so that large amounts of these materials go into land disposal. Environmental concerns and escalating landfill costs have prompted the leather industry to look for ways to convert this waste material, largely collagen crosslinked with chromium, into more valuable co-products.

Research over several years in this laboratory has been designed to aid the US leather industry in the development of alternatives to land disposal for solid tannery waste. The objectives of this work are three-fold: to develop methods for the recovery of valuable components from shavings and trimmings of chrome tanned leather; to separate chromium from the protein matrix; and to isolate chrome-free collagen fragments suitable for use on site in leather finishing, or for sale to the manufacturers of value-added products.

In the earliest stage of this work,^{10,11} digestion of the shavings and trimmings with an alkaline protease allowed chromium to be removed from the protein matrix and recycled into further tanning processes. The resulting protein hydrolysate could be used in fertilizers or animal feeds. The advantage of this first process over previously

available enzyme methods^{12,13} of digesting shavings was that the alkaline proteases functioned better with changes in temperature than enzymes used earlier. More recently the emphasis in our research has been on reducing the amount of enzyme used in the recovery process and increasing the value of the protein product recovered. These goals led to the development of a two-step process,¹⁴ that in the first step yields a gelable protein product and in the second, a protein-free chrome cake. In this process, the chrome-tanned leather waste is treated with alkaline agents for six hours at 70-72° C and then filtered to recover the gelable protein. The chromium-containing sludge that remains is then treated with the bacterial enzyme as in the original process, resulting in a second protein fraction (referred to as protein hydrolysate) and a chrome cake.

The products that result from these two treatments have a variety of possible uses. Chromium may be recycled into the tanning operation or sold to a chemical supplier. Hydrolyzed protein, because of its high nitrogen content, has potential applications as a fertilizer or animal feed additive. The potential industrial uses of the gelable protein include film, gel and glue formulations.

Treatment of Chrome Shavings

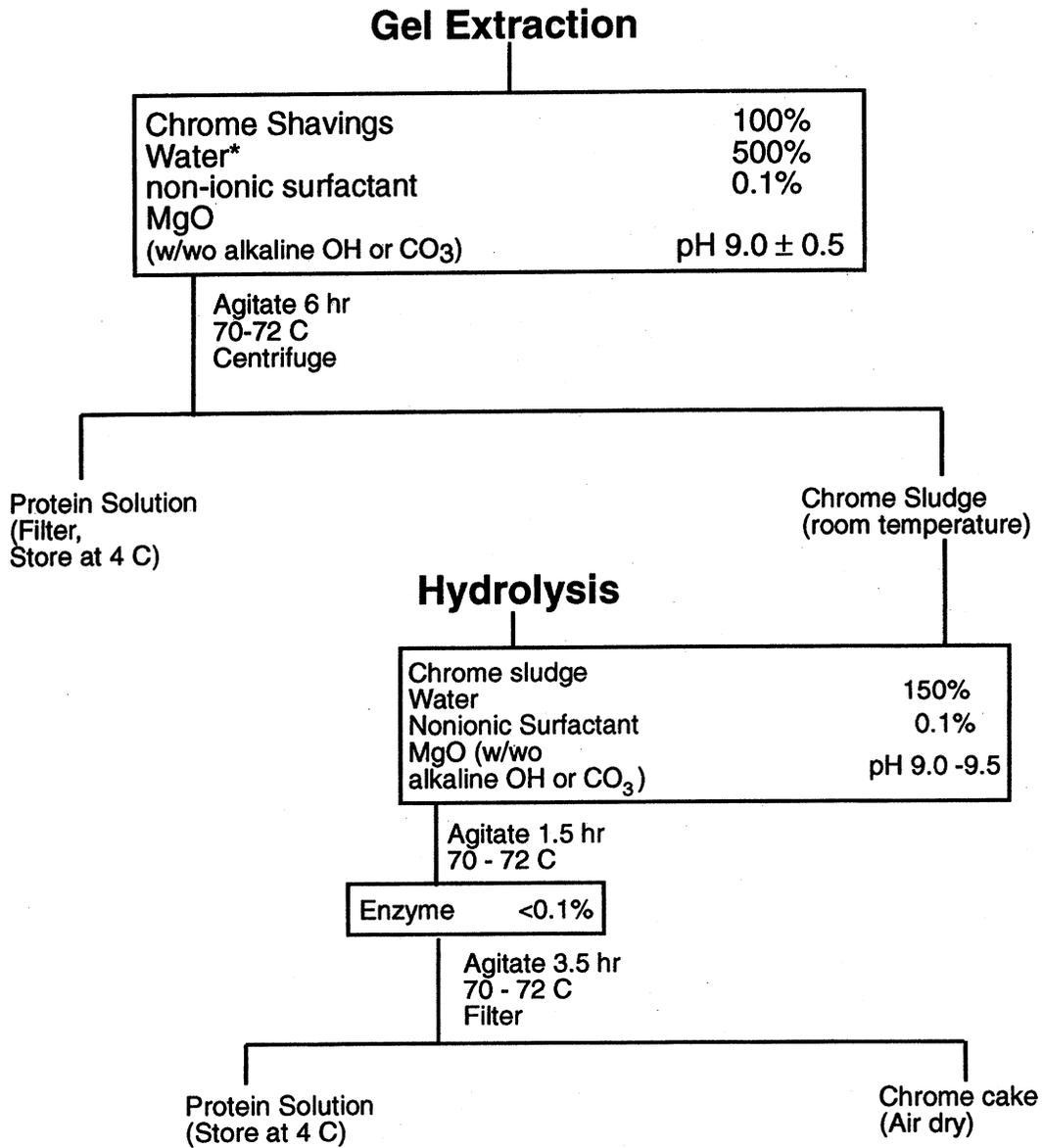
The characteristics of solid chrome-containing tannery waste will depend on the particular tanning process used. For the development of the one-step process we obtained shavings from three different chrome tannages. One sample was from a conventional chrome tannage, one from a high exhaust tannage, and the third from a process yielding slightly more acidic chrome offal (pH 3.6). The average compositions of chrome shavings (Table I) from these three processes were remarkably similar.¹⁵

Figure 1 is a flow diagram for the recovery of gelable and hydrolyzed products from chrome shavings. The shavings were dispersed in water with the aid of a non-ionic surfactant. MgO combined with an alkaline hydroxide or carbonate¹⁶ was added to adjust the pH to 9.0 ± 0.5 and the suspension was agitated at 70-72° C for six hours. The gelable protein solution was isolated by centrifugation and vacuum filtration of hot samples. The sludge remaining on the filter contained chromium and 10 to 20% residual protein. To recover this residual protein, the sludge was resuspended in water with a non-ionic surfactant at 70-72°C, and shaken for 1.5 hours. The mixture was next treated for 3.5 hours with an alkaline protease after adjusting the pH with MgO to the optimum for the enzyme. The solutions were then filtered hot through Whatman #1 filter paper. The chrome cake was air-dried at room temperature and the protein solutions were stored at 4° C.

On a dry weight basis, the shavings used in these studies contained about 4% chromic oxide and 80% protein as well as 0.5% calcium, 0.3% magnesium and up to 2% fat. In both processes, the recyclable chrome cake was obtained by enzymatic treatment of either the shavings or the sludge remaining after extraction of the gelable protein. On a dry weight basis, 35% of the chrome cake consisted of fat, calcium, magnesium and organic residues. To remove organic impurities, the air-dried chromecake was dissolved in 10% sulfuric acid (pH <1.0). The acidity of this solution was slowly adjusted to about pH 2 using 0.25N NaOH and the resulting solution was heated at 60° C for several minutes. The nonchrome components were flocculated and could be removed by filtration. Clean chromic oxide (ash content >0.4%) was then precipitated by raising the pH further.

TABLE I
Analysis of Chrome Shavings

	percent	std. dev.
Moisture	52.8	1.2
On a dry weight basis		
Ash	12.6	3.6
Chromic oxide	4.2	0.2
Protein	79.3	1.3
Fat	1.1	0.9
Ca	0.4	0.1
Mg	0.2	0.1



* All quantities are based on weight of chrome shavings

FIGURE 1. — Example of the two step process to treat chromium-containing leather waste.
A variety of alkalinity-inducing agents can be used to extract gelable protein products.

Protein Hydrolysate from the One Step Process

In the original process,^{10,11} a mixture of chrome shavings with lime in water (pH~9) was heated to 50-75° C and agitated for 30 minutes. An alkaline protease (1-12%) was added and the mixture incubated for an additional six hours. The hydrolysate was separated from the chrome cake by vacuum filtration. When 1% enzyme was used, 80% of the material was solubilized. Isolated protein hydrolysates were analyzed for chromium, Total Kjeldahl Nitrogen (TKN), total solids and ash.¹⁵ The results (Table II) are expressed in ppm for the liquid hydrolysate and in wt% on a dry basis. Data for these samples show that the chromium content was less than 1 ppm. Similar chromium levels were found in protein from pilot studies and from industrial scale trials. The TKN, total solids and total ash averaged about 11,000 ppm, 72,000 ppm and 8,000 ppm, respectively. The molecular weight distribution of the hydrolyzed protein was in the 1000-3000 Dalton range.

Gelable and Hydrolyzed Protein from the Two-Step Process

Extraction of gelatin from chromium leather waste has been described in the literature.¹⁷⁻¹⁸ The two-step process^{14,19} illustrated in Figure 1 was developed to isolate in the first step a gelable protein, and in the second step recyclable chromium and a lower molecular weight hydrolyzed protein product. After the gelable protein product was isolated by centrifugation and filtration, the chrome sludge was prepared for enzymatic hydrolysis as in the one-step process.

The characteristics of protein fractions recovered before and after protease treatment are described and compared with those of technical gelatin²⁰ in Table III. The ash content of these protein fractions could be reduced to >1% by treatment with mixed bed ion exchange resins. A range of molecular masses is to be expected for any of the protein products. The fraction of material in different weight ranges can be influenced by the choice of processing techniques.²¹

TABLE II
Analyses of Protein Hydrolysates from the One Step Process

	liquid (ppm)	dry (%)
Chromium	<1	
TKN	11,000	14.4
Total Solids	72,000	
Total Ash	8,000	14.3

Note: Values shown are averages, variability was about 4% except for the total ash, where variability ranged up to 30%.

TABLE III
Characterization of Protein Products

Parameter	gelable protein	hydrolyzed protein	technical gelatin ^a
Total Solids	1.8 - 4.0%	6.0 - 9.5%	
Ash ^b	8.9 - 20.0%	3.3 - 7.7%	0 - 3%
Chromium ^b	0.005 - 0.013%	0.0005 - 0.005%	
MW range	75,000 - >200,000	10,000 - 20,000	100,000 - 500,000
Bloom Value	80-150 g		50 - 300

a See reference 20

b Moisture-Free Basis (MFB)

Further Treatment of the Recovered Products

Two valuable products, the chrome cake and the collagen hydrolysate, are obtained from either process. With the two-step process, an even more valuable gelable protein fraction is obtained. To realize the full value of these products, the producer will need to either identify suitable outlets for the isolated materials or process them further for use in the production of leather or marketing to another industry.

These processes are unique in that chromium is insoluble under the reaction conditions (pH 8.3 to 10.5). Thus, both the possible conversion of Cr(III) to Cr(VI) and the poisoning of the enzyme by chromium are averted. Chromium isolated from these treatments is mainly in the form of Cr(OH)₃. Some portion of this chromium could be combined with fresh chrome in a variety of tannery processes. The chrome cake may be treated chemically²² to give a recyclable chrome product. The chrome sludge resulting from the removal of gelable protein may be treated with H₂SO₄ to produce a chromium-containing hydrolysate for use as a retanning agent.^{6,7} Other uses include addition of recovered chrome to cements and mortars.²³ Other investigators have recovered the chromium by wet air oxidation,²⁴ peroxide treatments,²⁵ and incineration at a variety of temperatures.²⁶⁻²⁸ Some Cr(VI) would be generated in these reactions, requiring a further reduction step.

The collagen hydrolysates recovered from the original process¹¹ or from the treatment of the chrome sludge in step two of the newer process¹⁴ may find use as ingredients in fertilizers and animal feed supplements.^{8,29} The surface active properties of these hydrolysates contribute to their utility in adhesive formulations.³⁰ They have been used to produce fatliquors, surfactants and fillers for leather manufacture.⁹ If the collagen hydrolysate is not separated from the chrome, as perhaps in the treatment of the sludge from the two-step process, the material might have potential as a tanning agent.³¹

Without further processing, the gelable protein fraction recovered in the first step of the two-step process¹⁴ could be freeze-dried to a white solid with a moisture content ranging from 4% – 14% and an ash content of 8.9% – 21%. The physical and chemical characteristics are within the acceptable range for technical gelatins.²⁰ These properties are improved when the ash content is reduced to >3% by the use of an ion exchange resin. This gelable protein fraction has the potential for use in a variety of industries. These industries include, but are not limited to, cosmetics,

adhesives, printing or photography and those manufacturing graft-polymerized products.

Survey of Potential Uses

A brief survey of recent literature on nonfood uses for gelatin might provide the starting point for some other marketing directions. Collagenous protein in the form of films, microemulsions or microcapsules is a basic ingredient in the packaging materials used by a number of industries. The surface active properties of gelatin have contributed to its use in films for the storage of information in a variety of forms.³² Gelatin has been crosslinked with glutaraldehyde to prepare a film that immobilizes an enzyme on to a sensor to monitor a continuous flow process.³³ Films of gelatin grafted with polymethyl methacrylate (MMA) have been used as a matrix for the deposition of MMA that can later be removed from the film by hydrolysis.³⁴

Microemulsions of the oil-in-water or glycerol-in-water type can be set into a stiff, transparent organo-gel by the addition of gelatin to the aqueous component of these systems.³⁵ These organo-gels provide a system for the transport of metal ions from the aqueous to the organic phase. In a study of the effectiveness of gelatin in stabilizing emulsions of dibutyl phthalate and dodecane in water, it was shown that gelatins containing 30% or more of the low-molecular mass range were good stabilizers.³⁶ The stabilizing ability was diminished drastically when the low molecular mass species accounted for less than 30% of the total weight, making partially hydrolyzed gelatin suitable for this use. Collagenous protein fractions in a range of molecular sizes including gelatins and glues have proven effective as ecologically benign corrosion inhibitors.³⁷ Gelatin microspheres crosslinked with glutaraldehyde make excellent delivery vehicles where the combination of controlled release and biodegradability are desirable.³⁸

Gelatins are useful for modifying the behavior of other materials. Glass beads are used as chromatographic supports for the separation of charged particles from a solution. Gelatin coating of the beads modifies the character of the particle adhesion and subsequent removal.³⁹ For other separation applications, a reactive biocompatible gelatin-synthetic polymer conjugate was prepared by grafting styrene monomers onto modified carboxyl groups of gelatin.⁴⁰ Microemulsion-based gels are used as carrier materials for dispersed thermotropic liquid crystals. The viscosity of the carrier material and thus the release of the liquid crystals can be specifically changed by varying the gelatin content.⁴¹

CONCLUSIONS

In conclusion, high quality gelable and hydrolyzed protein products can be isolated from chromium-containing leather waste. The characteristics of the products depend on the composition of the original chromium waste product and on the specific treatment conditions chosen. The composition of the starting material will vary as tanning procedures evolve. The specific treatment conditions chosen for the isolation of protein products will be influenced by market demand for particular characteristics. To develop an economic profile of these processes, a variety of costs, savings and returns must be considered. The cost estimate will be unique for each potential processor. While the costs of the chemicals and equipment will be similar for all, energy and labor costs will be specific to each location. Savings will depend on the costs of current disposal arrangements as well as on the extent to which the recovered products may be used on site. Return on the processes will depend on the quality of products and the development of suitable markets. The cost of the additional separation step to obtain a gelable protein should be more than balanced by the higher value of this product.

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