Journal of Hazardous Materials 37 (1994) 143-151

REDUCTION OF WASTE OF TANNERY INDUSTRY BY RECYCLING OF DAIRY BY PRODUCTS

K. Kolomazník [a], P. Sáha [a], A. Blaha [a], D. Janáčová [a] and D. G. Bailey [b]

[a] Technical University Zlín, Czech Republic.

[b] Eastern Regional Research Center Philadelphia U.S.A.

ABSTRACT

In the tanning process there is a serious problem with waste water containing substantial quantities of ammonium ions. Our project proposes the replacement of incoming ammonium chemicals by ions derived from the magnesite dust which is a waste in the production of firebricks. The system of a magnesium lactate is proposed for deliming and neutralisation for bating. Magnesium lactate is produced from a dairy waste.

INTRODUCTION

In 1972 Czechoslovakia was one of three countries (U.S.A. ,Japan and Czech Republic) in the world which started to produce poromeric leather. This time was published that the discovery and production of poromeric leather substitutes the end the era of hide and skin tanning. Animal skins in the future will serve as base for food only. Further developments showed that this prediction was not correct. On the contrary the demands for products from natural leather materials have constantly increased. The major reason is that the hygienic properties of poromeric materials did not reach the level of natural materials made from leather.

0304-3894/94/$07.00
SSDI 0304-3894(94)00024-B

Tanning process begins with the soaking of hide. Soaking removes the preservative chemical, which is usually sodium chloride. In next step, the unhairing and liming processes, hair is removed by the reduction of keratin proteins by sodium sulphide in strongly alkaline medium of saturated calcium hydroxide (lime). The keratin is dissolved under conditions of the unhairing process while collagen the major component of the hide remains relatively unchanged.

After liming the hides are strongly swollen and contain large quantities of sodium sulphide and calcium hydroxide, which must be eliminated for reasons of further reactions under acid conditions. This is done by washing in water, washing in a solution of deliming chemicals (chemical deliming). Further for bating a pancreatic enzyme is used in Czech Republic, which is a part of the commercial preparation Pepsizin or Pelin, which contains about 80% of ammonium sulphate. Consequently a further source of ammonium ions in waste tanning waters is chemical deliming and bating of white hide. Their share of the total content of ammonium ions in waste water is 40-80% depending on the type of technology. Deliming is done in two stages. In the first stage free calcium is eliminated by washing in clean water. After washing out the free and partially also the bonded calcium, the washing with water must be interrupted and continued by washing in a solution of deliming chemical, because washing in clean would enormously increase the period of the washing process and consumption of washing water. The moment when washing with clean water must be interrupted is determined on the basis of experience, and when using ammonium sulphate due to its low cost, or if the content of ammonium ions need not be watched, this need not be determined exactly. At the present moment when the laws for protection of the environment against pollution are to be implemented strictly, the situation will be fully different. Ammonium sulphate will have to be replaced by a much more costly ecologically safe deliming agent, and for this reason it is necessary at least to estimate qualitatively the period and consummation of water for washing with clean water, and to determine the time when washing in clean water will be replaced by washing in a solution of deliming chemicals.

THEORY

Our new procedure is based on the application of bioreactor engineering. First of all we shall determine the optimal volume of washing liquid, that is necessary for achieving the required degree of washing. The main part of operational costs is the cost of energy consumption by the washing equipment(tanning drum) and the cost of washing water-eventually, of the solution of deliming chemicals.

$$N_t = N_E + N_V = K_E \; P \; t + K_V V_V \qquad (1)$$

It has been proved that for washing, like for soaking, it is possible to use for its quantitative description the diffusion model [1, 2, 3]. This model is required for the determination of the time (t) in the equation (1) at the required quality of the washing process (y).

$$y = \frac{c_{sp} - c_s}{c_{sp}} \qquad (2)$$

Due to the diffusive nature of the washing process the time necessary for attaining the required quality of washing decreases with the increase of water consumption (higher concentration gradient); the cost of electric power consumption decreases, but the cost of water consumption grows. It is apparent from this consideration that the costs function (1) in relation to the consumption of washing liquid has a V_V minimum. Our first effort will thus be t determine this minimum for individual examples of the washing process. For the case of the single decant washing we shall use the following model:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{\partial c_A}{\partial t} \qquad \begin{array}{l} t > 0 \\ 0 < x < b \end{array} \qquad (3)$$

The concentration field of bonded and free components (lime) in white hide.

$$c_A = f(c) \qquad (4)$$

Sorption isotherm of lime for white hide.

$$- D\,S \frac{\partial c}{\partial x}(b,t) = V_V \frac{dc_o}{dt}, \qquad t > 0 \qquad (5)$$

The balancing equation showing the quality of diffusion flow on the surface of the white hide with the speed of accumulation of the same component in the washing bath.

$$c_o(0) = c_{op} \qquad (6)$$

$$c\,(x,0) = f(x) \qquad (7)$$

Initial conditions:

$$\frac{\partial c}{\partial x}(0,t) = 0 \qquad (8)$$

Under the conditions of axial symmetry, maximum concentration of the washing component is in the centre of the white hide. (Need not be always fulfilled).

$$c\,(b,t) = \varepsilon\, c_0 \qquad (9)$$

Condition of perfect mixing of liquid phase. A result of the solution is, among others, the dependence of the quality of washing (y) on time, we subtract the time necessary for determination of the costs function (1), and thus, also its minimum in whose neighbourhood we assume that the process of washing should be controlled. Another question is when to substitute washing of white hide in a solution of deliming agent for washing in clean water. The costs function (1), in general, depends on the bonding strength of the washed - out calcium hydroxide to white hide. The strength of this bond (p) can be defined for a given (y) (or eventually t, and c) by differentiating equation (4):

$$p = \frac{\partial f(c)}{\partial c}. \qquad (10)$$

When the sorption isotherm of lime on white hide can be expressed by Langmuier's equation,

$$c_A = \frac{Ac}{1 + Bc}, \qquad (11)$$

we can see, that at large concentrations of c and thus also of c_A, c is constant, and the derivative p equals zero. The maximum bond strength p is when $c \to 0$; then it approaches A. This means that for low values of y the concentration c_A is great and bond strength, small, and thus, also the costs of washing with clean water are small. With the decreasing concentration of c_A and further washing the bond strength p increases and thus, also, the costs start rapidly increasing. If we washed right from the start in a solution of deliming agent whose unit of volume price is many times greater that of water, then the dependence of washing in clean water at low values of y and under this dependence for higher values of y. The intersection of both of these dependencies then determines (y) and thus, also, the time, when simple deliming will change into chemical deliming.

By chemical deliming the strongly bonded calcium [4] is eliminated in most cases by a neutralising reaction, in which protons from the hydrolysis of the ammonium salt replace it on the carboxyl group of collagen.

Our project is concerned with the utilisation of a deliming system of lactic acid and magnesium lactate. The magnesium salt acts as a buffer and is, at the same time, a good deliming agent. In the quantitative expression of deliming of white hide by application of the general model "non - reactivated nucleus" from the kinetics of heterogeneous reaction we obtain:

$$\frac{\partial c_1}{\partial t} = D_i \frac{\partial^2 c_1}{\partial x^2} - \frac{\partial c_{1A}}{\partial t} \qquad \begin{matrix} t > 0 \\ x_m(t) < x < b \end{matrix} \qquad (12)$$

The concentration field of bonded and free deliming agent in the delimed part of white hide

$$c_{1A} = f(c_1) \qquad (13)$$

sorption isotherm of deliming agent on white hide

$$c_1(x_m,t) = 0 \qquad (14)$$

precondition of very rapid deliming (neutralising) reaction

$$c_{sp}\, n \frac{dx_m}{dt} = - D_l \frac{\partial c_1}{\partial x}(x_m,t) \qquad (15)$$

shift of interface between delimed and non-delimed part of white hide is proportional to the diffusive flow of deliming agent on this interface

$$- D \frac{\partial c_1}{\partial x}(b,t) = V_V \frac{dc_{10}}{dt} \qquad t > 0 \qquad (16)$$

balancing equation expressing the equality of diffusion flow on the surface of white hide with accumulation of deliming agent in the bath of the tanning drum

$$c_1(b,t) = \varepsilon\, c_{10} \qquad (17)$$

Precondition of perfect mixing of liquid phase.

With regard to the low concentration of deliming agent (lactic acid), it is possible to express the sorption isotherm (13) by a linear relation :

$$c_{1A} = K\, c_1 \qquad (18)$$

thus $$\frac{\partial c_{1A}}{\partial t} = K \frac{\partial c_1}{\partial t} ,$$

which by substitution into (12) and after a minor modification we obtain:

$$\frac{\partial c1}{\partial t} = k\frac{\partial^2 c_1}{\partial x^2}, \qquad x_m(t) < x < b, \quad t > 0 \qquad (19)$$

where

$$k = \frac{D_1}{K+1} \qquad (20)$$

Taking into consideration, that the velocity rate of internal transport of the deliming agent in white hide is the magnitude of the value of the modified effective coefficient (k) it ensues, that at a non-zero setting sorption constant (K), this transport expressed in a very approximate manner is (K +1) times slower. According to our preliminary laboratory tests the value of the sorption constant of lactic acid on white hide is approximately 10 and that apparently the reason why the deliming process takes so long for the greater thickness o white hide. A good deliming agent should have a sorption constant (K) as small as possible. The ideal value of (K) should equal zero i.e. no sorption deliming by the delimed white hide should occur. Such a compound is magnesium lactate, which fulfils also demanding ecological aspects. We shall carry out deliming using magnesium lactate in combination with sulphuric acid, which will transform a part of the magnesium salt to magnesium sulphate and lactic acid, which will rapidly delimed the surface of the white hide and the subsurface layers. The remaining magnesium lactate and created magnesium sulphate, which are not absorbed ($K \rightarrow 0$) will delime the deeper layers and the centre of the white hide. The proposal of the optimal deliming technology will be worked out in co-operation with the staff of ERRC in Philadelphia, who have great experience in the use of magnesium sulphate for deliming of white hide [5, 6, 7]. The result of the new technology of ammonium free deliming will be also the preparation of white hide for bating by the pancreatic enzyme, where instead of ammonium sulphate will be used magnesium sulphate. The linking technologies of pickling and tanning will also be reelaborated in such a manner that the final utility properties of the produced leather will be maintained just the same as in the classical procedure, if not improved.

For practical application of a new technology in tanning it is necessary to have a new deliming agent i.e. cheap magnesium lactate. We wish to fulfil this requirement in such a way that for its raw material we shall utilise waste whey, which is produced in great quantities in the production of cheese. At present, two types of lactic acid are being manufactured in relation to their optical rotation: L(+) - produced by fibrous fungi and by a racemic blend (DL), which are synthesised by bacteria. A joint characteristic of both of the mentioned technologies is the necessity of regulation of pH during the course of fermentation, approximately in the neutral region (pH 5,5 - 6,5) in relation to the utilised producing microorganism. The intent of the process being executed is to ensure the most suitable physiological medium for the production of lactic acid. Two types of neutralising agents are used. They are hydroxides and carbonates. In the matter of the submitted project it is possible to propose preparation of lactic acid from whey combined with the use of natural magnesite, or as the case may be, from products originating from its processing as a neutralising.

SYMBOLS

N_t	total costs	[U.S.dollars]
N_E	electric power costs	[U.S.dollars]
N_V	water consumption costs	[U.S.dollars]
k_E	cost of unit of electric energy	[U.S.dollars $(kWh)^{-1}$]
k_v	cost of unit of washing water	[U.S.dollars m^{-3}]
P	input of electromotor for driving the washing equipment	[kW]
t	duration of washing period	[s, h]
K_v	cost of unit of washing liquid	[U.S. dollars m^{-3}]
V_v	volume of washing liquid	[m^3]
c_{sp}	initial total concentration of washed component in white hide	[kg m^{-3}]
c_s	total concentration of component in white hide in time t	[kg m^{-3}]

c	concentration of unbounded component in white hide	[kg m^{-3}]
c_A	concentration of bonded component in white hide	[kg m^{-3}]
c_0	concentration of component in washing liquid	[kg m^{-3}]
D	effective diffusion coefficient of washed component in white hide	[m^2s^{-1}]
S	total surface of washed white hide	[m^2]
b	half thickness of white hide	[m]
ε	porosity of white hide	[1]
x	co-ordinates of position	[m]
c_1	concentration of deliming agent in white hide	[kg m^{-3}]
c_{1A}	concentration of bonded deliming agent in white hide	[kg m^{-3}]
D_l	effective coefficient of diffusion of deliming agent in white hide	[m^2s^{-1}]
c_{10}	concentration of deliming agent in bath of tanning drum	[kg m^{-3}]
n	stochiometric coefficient of deliming reaction	[1]

REFERENCES

[1] D. O' Brien: J. Am. Leather Chem., 78, (1983) 286.

[2] A. Bláha and K. Kolomazník: J. Soc. Leather Tech. Chem., 73, (1989) 136.

[3] A. Bláha , K. Kolomazník, T. Dederle: J. Soc. Leather Tech. Chem., 73, (1989) 172.

[4] K. Kolomazník and D. G. Bailey: The Modeling of Deliming of the White Hide, 8th Congres of the Leather Industry. Budapest, 1986.

[5] M. M. Taylor, J. Am. Leather Chem., 81, (1986) 4.

[6] M. M. Taylor, J. Am. Leather Chem., 83, (1988) 35.

[7] M. M. Taylor, J. Am. Leather Chem., 81, (1986) 45.