Potential Danger of Chromium Tanned Wastes

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Abstract: - This contribution deals with the waste from the processes in which raw hide is transformed into leather, as well as with the waste generated during further leather processing and the final waste of leather industry, the worn-out shoes. All this waste, if deposited in the open-air dumps, represents a potential threat to human health, because it contains trivalent chromium (Cr III), which can oxidise to its hexavalent form (Cr VI) under various conditions. The authors discuss the possibilities of spontaneous transformation of Cr III into Cr VI and propose several technologies of the waste treatment to eliminate the health and environmental risks. Chrome-tanned waste, especially the chrome shavings, is processed with the use of modified enzymatic hydrolysis. The chromium cake obtained after filtration has proved to serve as a suitable precipitator of chromium ions from chromium containing spent liquor. Simultaneously, the chromium cake is enriched by those chromium ions and can be re-used in the tanning process. The method has been successfully tested in pilot and industrial scale. It enables us to possess the total control of solid and liquid chrome-tanned waste, which has shown a new approach towards the issue of chromium recycling in the tanning industry. A two-step technology has been proposed for processing leather scraps, for which it is not possible to apply the same method as in the case of chrome shavings. One of the products of this technology is a protein hydrolysate containing a high portion of nitrogen, phosphorus and potassium. This hydrolysate has been already successfully used as a good-quality NPK fertilizer in agriculture. The authors also warn against the classic ways of worn-out shoes treatment, i.e. disposal in the open-air dumps or combustion, which leads to potentially dangerous products. The separate collection of worn-out shoes is recommended and it is assumed that the hybrid hydrolysis technology used for leather scraps could be also successful at solving the problem of old shoes.

Key-Words: - Chrome-tanned waste, hexavalent chromium, chromium recycling, enzymatic hydrolysis, hybrid hydrolysis

1 Introduction

Although the leather industry is environmentally important as a user of by-products of the meat industry, it is perceived as a consumer of resources and producer of pollutants. By processing of one metric ton of raw hide we receive 200 kg of leather final product, 250 kg of non-tanned waste, 200 kg of tanned waste (3 kg of chromium) and 50 000 kg of waste water (5 kg of chromium). Only 20 % of the raw material weight is converted into leather [11].

The most serious problem, which is now of a great importance, is chrome-tanned solid waste. The simplest solution for this waste is its disposal in the open air. But such solution can be potentially dangerous, because uncontrolled processes in chrome waste deposited in that way could produce various soluble compounds. Chromium III (Cr III) and chromium VI (Cr VI) compounds are produced in large quantities and are accessible to most of the population. There is evidence that hexavalent chromium may be carcinogenic [12]. The National Institute for Occupation Safety and Health has classified the chromate and dichromate salts of calcium and magnesium (elements occurring in soil and drinking water) as carcinogenic compounds.

2 Theory

The basic question is a possible oxidation reaction of Cr III to Cr VI. In basic solutions, the oxidation of Cr III to Cr VI by oxidants such as peroxides and hypohalide occurs easily. Such strong oxidation conditions are created in the process of sterilization of drinking water. This is the first threat for human health and lives.

The rain (especially acid rain) can leach Cr III from chromium waste deposited in dumps and then its soluble salts reach sources of drinking water. During the sterilization process by ozone or hypochlorite, Cr III is converted into Cr VI and reacts with magnesium and calcium ions occurring in drinking water to produce carcinogenic magnesium and calcium chromate or dichromate salts.

The other problem is the possibility of oxidation of Cr III into Cr VI under mild conditions in a wide range of pH. In principle, the oxidation can be described by the following reaction schemes:

$$2Cr_2O_3 + 8OH^- + 3O_2 = 4CrO_4^{-} + 4H_2O \qquad (1)$$

in alkali medium and

$$2Cr_2O_3 + 3O_2 + 2H_2O = 2Cr_2O_7^{-} + 4H^+ \qquad (2)$$

in acid medium.

The probability of a spontaneous oxidation of Cr III into Cr VI is realizable, because the values of Gibbs energy of both reactions are negative. The published thermodynamic functions (Gibbs energies of formation) are shown in Table 1 [10].

Table 1 Gibbs free energy of reaction components.

Reaction component	**Change of Gibbs free energy ΔG (kJ.mol^{-1})**
Cr_2O_3	-1053.00
OH^-	-157.28
O_2	0.00
CrO_4^{2-}	-727.85
H_2O	-228.61
$Cr_2O_7^{2-}$	-1301.20
H^+	0.00

From the thermodynamic functions we calculate the Gibbs energies for both reactions:

$$\Delta Gf^0 = -4\times727.85 - 4\times228.61 - (-2\times1053 - \\ -8\times157.28) = -461.6\ kJ.mol^{-1} \qquad (3)$$

in alkali medium and

$$Gf^0 = -2\times1301.2 - (-2\times1053 - 2\times228.61) = \\ = -39.18\ kJ.mol^{-1} \qquad (4)$$

in acid medium.

The negative values of both thermodynamic functions prove the possibility of spontaneous oxidation within a wide range of pH. This represents a more serious threat than in the previous case, because we do not know exactly under which conditions Cr III may be converted into Cr VI.

It is estimated that the production of European countries is one million metric tons of chrome-tanned waste containing about 20 000 metric tons of chromium. The annual costs of tanned waste treatment are approximately 5% of the total turnover. That represents nearly 700 millions euros.

3 Results and Discussion

One of the numerous possible solutions of the problem of chrome-tanned waste is its enzymatic dechromation, which has been dealt with in detail in a number of publications [1-8]. We modified the technology, which had been originally developed in USDA – ERRC (US Department of Agriculture – Eastern Regional Research Center) [9]. The modified technology of enzymatic hydrolysis was then employed in a new plant of the TANEX Company, now KORTAN, in Hrádek nad Nisou, with a daily capacity of 3 metric tons of processed chrome shaving.

Chrome-tanned waste in its most usual form of chromium shavings is hydrolyzed under alkali conditions in the presence of a proteolytic enzyme (as catalyst) at the temperature 60-80°C. After termination of the hydrolytic reaction (4-6 hours), the hot reaction blend was filtrated and the filtrate (4-8% of solid phase) is concentrated by a three-step vacuum evaporator up to 40-60% of the dry matter content. The concentrated solution can be dried with the use of a dry sprayer. A white powder is produced. The main operation of the processes in which raw is transformed into leather is the tanning reaction with complex chromium salts. The tanning reaction reaches the equilibrium, i.e. in practice the reaction takes place in the excess of chromium salt. The result is that the waste liquid (spent liquor) contains up to 6000 ppm of chromium ions. The filter cake that is produced by filtration of the reaction blend contains up to 10% of alkali. This fact enables us to use the chromium cake as a precipitator of chromium ions from the spent liquor after the tanning reaction. We used the alkalinity of the chromium cake to remove chromium ions from the spent liquor. We verified this method in pilot and industrial scale tests. We achieved not only the elimination of chromium ions from the spent liquor, but we also enriched the filter cake with chromium from the spent liquor. In other words, we reached the total control of chromium in solid and liquid waste, which has been performed for the first time in the tanning industry. The chromium filter cake contains not only the alkali, but also a non-hydrolyzed protein (40-60%, moisture-free basis). We used this fact for the production of regenerated tanning chromium salts, which are primarily produced by the reduction of sodium dichromate with technical saccharose in a strong acid environment (sulphuric acid). By using of our chromium filter cake, containing the non-hydrolyzed protein, we save the consumption of a relatively expensive technical

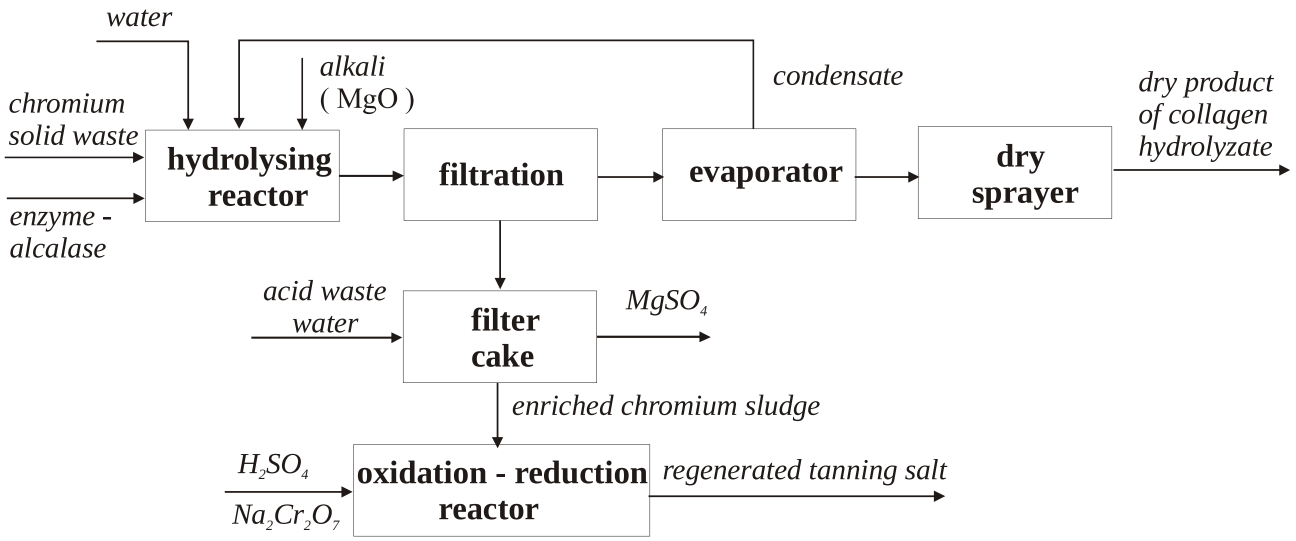

Fig.1 Hydrolysis of chromium tanned waste.

saccharose. The following reactions make clear the above mentioned processes.
Classic preparation of chromium tanning salts:

$$8\ Na_2Cr_2O_7 + 32\ H_2SO_4 + C_{12}H_{22}O_{11} = \\ =8\ Na_2SO_4 + 8\ Cr_2(SO_4)_3 + 43\ H_2O + 12\ CO_2 \qquad (5)$$

Preparation of regenerated tanning salts:

$$5\ Na_2Cr_2O_7 + 24\ H_2SO_4 + 2\ C_3H_5NO + \\ +2\ Cr(OH)_3 + Mg(OH)_2 = 5\ Na_2SO_4 + \\ +6\ Cr_2(SO_4)_3 + 33\ H_2O + 6\ CO_2 + N_2 + \\ + MgSO_4 \qquad (6)$$

Here we mark the non-hydrolyzed protein by the formula C_3H_5NO, which was estimated from the elementary analysis. The reaction is strongly exothermic and it is controlled by dosing of the chromium filter paste into the hot reaction blend of chromium sulphate acid. The whole scheme is shown in Fig.1.

The hydrolysing reactor is dosed with 10 metric tons of water, 90 kg of cyclohexylamine or with corresponding quantity of isopropylamine or diisopropylamine and 60 kg of magnesium oxide. Three metric tons of chrome shavings are gradually added under constant stirring to the above mentioned mixture and the heating is started. In the case of cyclohexylamine, the heating is started after adding 1.5 metric tons. In the case of much more volatile isopropylamine, the heating does not start until the whole batch of shavings, i.e. 3 metric tons, is added. If the hydrolyzed shavings are of larger sizes, we recommend allowing the reaction mixture to stand overnight with occasional stirring and no heat. The hydrolysis is run at the optimum temperature of 70°C and pH = 9. The pH adjustment is made by adding organic bases. After the reaction time of 3 – 5 hours, the hot heterogeneous mixture is filtrated; the filtrate is collected in metering storage tank and repumped into the continuously working three-stage vacuum evaporator. The filter cake is transferred to the reactor, which is situated under the vacuum filter. Three metric tons of water are added, the pH is adjusted to 9; 0.9 kg of proteolytic enzyme (ALCALASE 2, 5LDX of Novo Nordisk, Denmark) is dosed in and the mixture is repeatedly heated under constant stirring for 2 – 3 hours. During the subsequent filtration, the enzymatic hydrolysate and filter cake are obtained. The clear solution of hydrolysate goes to the vacuum evaporator. The filter cake returns to the reactor where it is diluted with water, and the heterogeneous mixture is slowly dosed into a hot solution of sodium dichromate and sulphuric acid in the reactor to produce the tanning salt. Technically, it is possible to say that the solution for chrome-tanned waste, especially chrome shavings, has been found, with the exception of the application of chromium sludge on the market.

The next kind of leather waste is chrome-tanned scraps produced by shoe-making industry. The direct application of our technology to leather scraps was not successful as a result of the inhibiting effect of the synthetic resin barrier – polyacrylate or polyurethane – against diffused reagents. A very practical result is the value of dimensionless time at which the reagents reach an integral dimension. The value of such integral means the concentration at which the hydrolysis of chromium scrub would run relatively fast. This value of Fourier's criterion (dimensionless time) equals approximately 1. For the values of half thickness of chromium scrub sample d = 2 mm and the estimated diffusion coefficient for alkali in leather D = 10-12 m^2s^{-1} and in synthetic resin D = 10-20 m^2s^{-1}, the reaction times are the following:

$$1=\frac{10^{-12}\tau}{2^2(10^{-3})^2}\Rightarrow \tau=4\times10^{6}s=1111\ hours \qquad (7)$$

for leather and

$$1=\frac{10^{-20}\tau}{(0.5)^2(10^{-3})^2}\Rightarrow \tau=7\times10^{9}\ hours \qquad (8)$$

for resins.

Regardless of the evident very rough estimation of the required reaction times, it is obvious that it is necessary to carry out the destruction of synthetic resin barrier. This we performed with the use of a strong alkali hydrolysis at a relatively high value of pH ~ 12, and further it is necessary to work with defibered (grinded) chromium scrub material – we applied our hybrid technology for NIKE leather scrap.

Chrome-tanned leather scraps with TiO_2 finish treatment came from the NIKE shoe-making plant. Leather scraps were pre-treated by cutting and milling using the cutting mill Pulverisette 19 (Fritsch, GmbH, Idar – Oberstein, Germany) with sieve cassette of 3 mm perforation.

Table 2 shows the leather scraps analysis. The total solid content was determined by heating the samples at 105°C, the nitrogen content by the Kjeldahl method (TNK – Total Kjeldahl Nitrogen), the total ash by burning the sample at 800°C in Muffle furnace, the chromium content was expressed as chromic oxide (Cr_2O_3) according to IUC 8, the titanium content was determined by atomic absorption spectroscopy using GBC GF 3000 instrument (GBC Scientific Equipment Pty Ltd, Dandenong, Victoria, Australia) and the pH value according to the Czech Standard ČSN 79 3878.

Table 2 Leather scraps analysis.

Parameter	Value
Total solid (%)	89.25
N_2 as TNK (%)	11.98
Total ash (%)	9.96
Cr_2O_3 (%)	2.92
pH value	3.90
Ti (%)	2.90

Leather scraps hydrolysis process is based on two steps. The first one is the destruction of synthetic resins (polyurethane or polyacrylate), the second is the enzymatic decomposition process in slightly alkaline environment and under mild reaction conditions – the water bath temperature is 70°C. KOH together with MgO or K_2CO_3 were used as alkaline medium. H_3PO_4 or HNO_3 was used to pH value adjustment after the first step. The technology is shown in Fig.2.

Several laboratory experiments have been carried out. The hydrolysis using 1.2 % of KOH as an alkaline medium in the first step (pH = 12 – 14) seems to be the most effective, the second step produces the protein hydrolysate in middle alkali conditions. It leads to a hydrolysate that contains a high portion of nitrogen, phosphorus and potassium. Chromium content in the hydrolysate differs from 300 to 500 ppm (related to moisture-free basis). The hydrolysate is currently successfully used as a fertiliser for cotton-plants in the Socialist Republic of Vietnam, where it is mixed

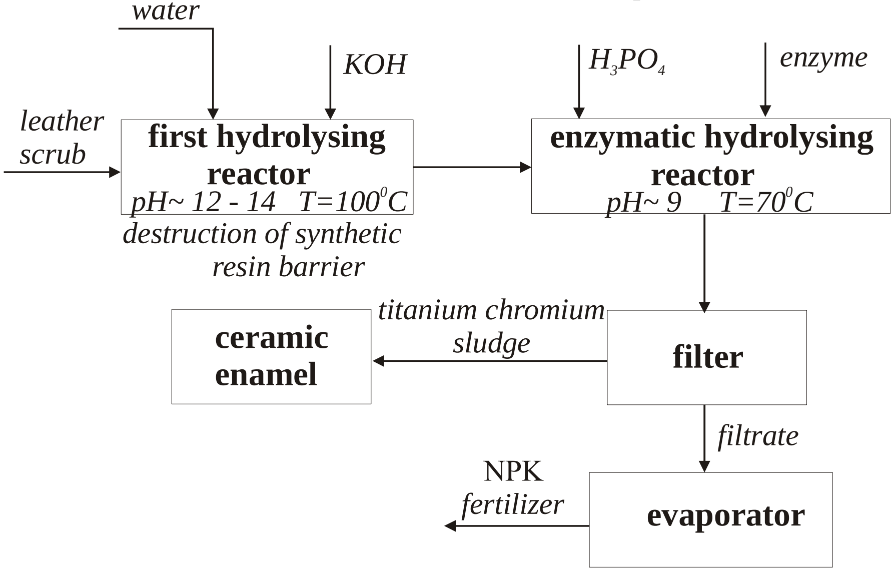

Fig.2 Hybrid hydrolysis of leather scrub.

together with zeolite in order to form stakes that are put under the cotton-crops.

In the fertiliser prepared under the above mentioned conditions, the chromium content is reduced. The fertiliser is an NPK type (N = nitrogen, P = phosphorus, K = potassium) and is very suitable for agriculture purposes. Titanium-chromium sludge has been tested as enamel in Vietnamese ceramics industry.

The final leather waste is represented by those products of the shoe-making industry, which lost its using properties, i.e. old shoes. Such waste has not been treated chemically (hydrolysis) so far and is liquidated in dumps in the open air or burned together with municipal waste. We warn against this way of the waste treatment (especially its disposal in the open air) in the introduction of our paper. The combustion of chrome-tanned waste converts Cr III into Cr VI quantitatively and in addition to that, great quantities of nitrogen oxides are produced.

The combustion is very unsuitable, because its products and the ashes from burnt chromium leather scrub are not under control. We assume that the hybrid hydrolysis technology described before could be successful at solving the problem of old shoes. However, the separate collection of old shoes will be necessary in similar way as it is done with old paper, glass, metals, plastics and PET bottles.

4 Conclusion

In this paper, we point out a potential risk of the waste produced by tanning and leather industry and we have proposed several technologies of its processing. The chromium cake, obtained by enzymatic hydrolysis of chrome shavings, proved to be a suitable precipitator of chromium ions from chromium containing spent liquor. Simultaneously, the chromium cake is enriched by those chromium ions and can be re-used in the tanning process. The method was verified in pilot and industrial scale tests and enables us to possess the total control of solid and liquid waste from the tanning industry. A two-step technology has been proposed for processing leather scraps, for which it is not possible to apply the above mentioned method. One of the products of this technology is a protein hydrolysate containing a high portion of nitrogen, phosphorus and potassium. This hydrolysate has been already successfully used as a good-quality NPK fertilizer in agriculture. We also warn against the classic ways of worn-out shoes treatment, i.e. disposal in the open-air dumps or combustion, which leads to potentially dangerous products. We recommend separate collection of this kind of waste and we assume that the hybrid hydrolysis technology used for leather scraps could be also successful at solving the problem of old shoes.

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