Journal of Scientific and Innovative Research 2017; 6(4): 138-141
Available online at: www.jsirjournal.com

Research Article

ISSN 2320-4818
JSIR 2017; 6(4): 138-141

Received: 29-08-201ss7
Accepted: 09-11-2017

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Resource addition to leather industry: Adhesive from chrome shaving dust

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Abstract

Leather industry produces a prodigious amount of wastewater and solid wastage containing a significant amount of hazardous chromium. Chrome Shaving Dust (CSD) is tanned collagenous micro-fine solid particulate impregnated with chromium synthetic fat and oil, tanning agents and dye chemicals. Contrariwise, the adhesive is a material which is used for bonding two or more materials together. This study will reflect the way of eliminating the CSD as a pollutant in leather industry rather it will show its lucrative function by making adhesive which is used in various footwear industries. In such way, it not only saves the environment but also aids to gain marginal profit. The process includes treating the shaving dust with distilled water, magnesium oxide and trypsin enzyme followed by force filtration, heating, evaporating, copolymerization with acrylic resin, polyvinyl alcohol, compounding with polyvinyl acetate, glycerol, Busan bactericide, and Busan fungicide. After that produced adhesive was applied in various parts of footwear to assess its function. The study not only tells about the ethical manufacturing and waste management process but also emphasizes on resource management. This considerably shows the waste generation process and also shows its alternate application in another field rather than polluting environment deliberately. Decaying ecology may get its balance with all natural species by controlling the wastes as well as its implication in an alternative way.

Keywords: Tanning Industry, Chrome Shaving Dust, Adhesive, Bangladesh.

INTRODUCTION

The leather industry is one of the oldest manufacturing sectors in our country. Tanneries in Hazaribagh were started in 1960 by Punjabi what was then Pakistan. The industries grew faster and after the independence of Bangladesh in 1971, became a 'cash cow' to earn foreign currencies. All these tanneries were nationalized under the nationalization decree of 1972 [1]. The principal aim of the leather industry is to transform animal hides/skins into a physically and chemically stable material by subjecting them to chemical and mechanical sequential processes. The leather industry generally uses hides and skins as raw materials, which are the by-products of meat and meat products industry [2]. Bangladesh earns the significant amount of foreign currency by exporting leather goods from its tanning industries. The increasing economic growth in Bangladesh encourages the growth of Leather sector [3]. A recent report revealed that leather and leather products are one of the major external trade sectors which contribute up to 1.39% share of the total export earnings [4]. This sector includes 220 tanneries, 3,500 SMEs and 110 large firms of leather products controlling more than 90% of the export market [5]. The world is very competitive where the basic concern of manufacturing companies is to increase their customers' satisfaction by constantly improving their delivery yet to keep quality at its best level. At the same time, the companies need to keep their costs and prices as low as possible to be able to compete with others by keeping their profitability [6]. Hazaribagh, the largest tanning industrial area of the country situated in the southwestern part of the capital city of Dhaka on the bank of the river Buriganga [7]. However, these industries are discharging and dumping their wastes and effluents without treatment into nearby water bodies [8].

Out of 1000 kg of rawhide, nearly 850 kg is generated as solid wastes in leather processing. Only 150 kg of the raw material is converted into leather. Tannery generates the huge amount of solid waste as follows: fleshing, 50-60; chrome shaving, chrome splits and buffing dust 35-40%; skin trimmings, 5-7; and hair, 2-5%. Solid wastes in leather processing constitute beam house, 80; tanning, 19; finishing, 1% [9].

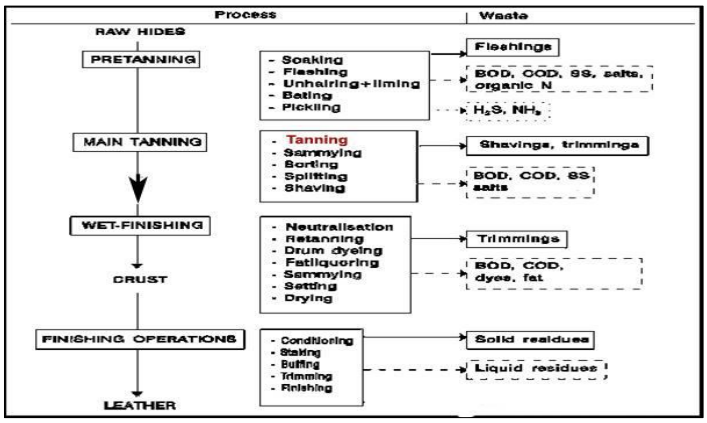

Figure 1: Waste generation from each unit operation of a tannery [10]

The above figure shows the overall process of tanning which are-

a) Pre-tanning (soaking, fleshing, unhairing, liming, bating and pickling are included in this section)
b) Main tanning (tanning, shamming, bolting, splitting, shaving operations cover this section)
c) Wet-finishing (after this crust leather is produced) and
d) Finishing Operation (after this final leather can be got).

Now in all these operations fleshings, trimmings, shaving dust and solid residues are being discharged which are increasing the BOD, COD, Suspended Solid (SS) etc. values. The environment is under increasing pressures from solid and liquid wastes as by-products from the leather manufacture and tannery effluent create significant pollution unless there has been a form of treatment before discharge. The industry has gained a negative image in the society with respect to its pollution potential and therefore the leather processing activity is facing a serious challenge. Tannery waste management has become a matter of increasing concern as a part of waste management. The following table shows the number of solid wastes generated while processing one ton of wet salted rawhides.

Table 1: Solid wastes (tanned & untanned) generated while processing one ton of wet salted raw hides [11]

Serial No.	Item	Quantity in Kg
01	Raw trimmings	80-120
02	Hairs/wools	40-50
03	Wet limed fleshing	250-300
04	Wet blue trimmings and unused splits	100-110
05	Shavings	90-100
06	Buffing dust	1-2
07	Crust and finished leather trimmings	9-13

The wastes produced in all tanneries through the world are about same in their characteristics. In some cases, wastes are altered to other dimensions to reduce the total amount of wastes. In Bangladesh tanneries are indiscriminately throwing their produced wastes to the rivers, roadsides and here and there, consequently, the putrescible wastes bring about various disasters.

Chrome Shaving Dust (CSD) from chrome tanned leather is one of the solid wastages generated from the leather industry which is hazardous to human health and environment [12]. Now, this tanned collagenous waste can be used to produce the adhesive which is indispensable for the footwear industry. An adhesive is a material that is applied to the surfaces of articles to join them permanently by an adhesive bonding process. An adhesive is a substance capable of forming bonds to each of the two parts when the final object consists of two sections that are bonded together [13]. Preparation of adhesive involves the study of solid wastages that will help to the analysis of the structure and chemical constituents of these wastages.

METHODOLOGY

Raw Materials

The raw material of this project work is low chrome tanned shaving dust. It is a solid waste produced during the shaving operation of wet blue leather. It contains a huge amount of chromium. The Leather sector is such a sector which disposes a large number of wastage materials containing chromium and has a bad effect on the environment. So this was taken as the raw material so that both environments can be kept safe as well as some better output can be gained.

Chemicals

In this case, instead of using analytical or lab grade chemicals, commercial grade chemicals are used. The temperature was strictly maintained in all the steps. The chemicals used in the processing are Magnesium oxide, Trypsin 2000 U/G enzyme, Poly vinyl alcohol, Glycerol, Poly vinyl acetate, Bactericide, Fungicide, Distilled water.

Method

The process of making adhesive from chrome shaving dust possesses some steps. First of all the dust was dried and hydrolyzed to get protein or gelatin. Then it was kept at 4^0C for the preservation. After that protein hydrolyzates were treated with some chemicals to get adhesive. First of all the chrome shaving dust which is the raw material was dried for 30 mints at 100^0C (electrical oven). It removes the moisture and helps to determine the moisture content.100gm of the sample was measured by the electrical analytical balance (Denver Instrument Company AA-160) and soaked with 300% distilled water that was 300 ml. It was kept on the hot plate (Sino chemical co Ltd, 0^0C-300 ^{0}C) under an electrical stirrer (MS 300 HS, has at least 600 rpm) at 60-80^{0}C temperature until the dust got digested (30 min approx.) [14]. After that 3% (3gm) MgO was mixed with 10 ml of distilled water and gradually added to the biker. This was added to control the pH. Now the mixture was rotated for 1 hour at 60-70^{0}C. More time could be needed depending on the digestion of the sample. The pH range for this particular step was 8.5-9.5. After the digestion, the temperature of the mixture was reduced and waited until it became 44-50^{0}C [15]. After that trypsin enzyme (0.1%) was added and the temperature was maintained carefully at high temperature could deactivate the enzyme [16]. Enzyme accelerates the extraction of the protein. The rotation continued up to 30 mints. Then the temperature was allowed to rise up to 80-90^{0}C for the deactivation of the enzyme. It also took 30 mints. The most important and critical part of the whole hydrolysis process was the force filtration. A force filtration unit was used for this step. During this step pressure, butcher funnel, cork all had to be set properly. It took several times for the proper extraction. The remaining shaving cake could be used for two more times. Finally, the protein hydrolyzates were collected and reserved at the refrigerator at 4^0C. In the second stage, reserved protein hydrolyzates were taken out from the refrigerator (Figure 2).This was heated at water bath for at least 3-4 hours for the evaporation of excess water present on it (Figure 3). After that, about 60 ml of protein hydrolyzates were kept at a biker and rotated by a magnetic bar upon a hot plate until the gelatin like protein became water like liquid (Figure

4). The temperature was maintained at 60-70^{0}C throughout the whole process. Polyvinyl alcohol and poly vinyl acetate were added in different amount for different samples. Here for one sample description has been given. 6% (2.2gm) polyvinyl alcohol was added to the protein hydrolyzates. Polyvinyl alcohol is a chemical with high melting point (200^{0}C) [17] so before adding it to the protein hydrolyzates it was melted by heating at oven with distilled water (1:3) at 200^{0}C. Now the mixture was rotated along with acrylic resin (50%) for 1 hour. Glycerol could be added at any time of the operation for the prevention of burning of the mixture. After one hour 40 ml polyvinyl acetate was added to the mixture and rotated for 1.30-2 hour (Figure 5). The final work was to add bactericide and fungicide to the mixture which would keep adhesive safe from the attack of bacteria and fungus for a long time. After adding each 30 min time was given. Finally, the adhesive was collected and stored for further tests (Figure 6).

Figure 2: Gelatin (peptide & protein)

Figure 3: Evaporating the protein

Figure 4: Glue after evaporation

Figure 5: Stirring chemicals with protein

Figure 6: Prepared adhesive

RESULT

Chrome shaving dust is a waste material in the tanning process which is the raw material for this project. So before starting work, some parameters of CSD like color, moisture content (SLC-113), ash content (SLC-06), chromic oxide content (SLC-08) and pH (SLC-120), protein or nitrogen content (SLC-07) were measured. The color of the sample was bluish and moisture content, ash content, chromic oxide content, and protein or nitrogen content was 18.85%, 7.10% 2.35% and 16.00% respectively (Table-02).

Table 2: Analysis of chrome shaving dust

SL No.	Parameters	Values
01	Color	Bluish
02	Moisture content	18.85%
03	Ash content	7.10%
04	Chromic oxide	2.35%
05	pH	3.72%
06	Protein or Nitrogen content	16.00%

In the first stage, collagen hydrolyzates were extracted from the chrome shaving dust which is the main ingredients in this project. It was light yellow or creamy colored, viscous and sticky, odorless gel type material with pH-8.15 (Table-03).

Table 3: Analysis of collagen hydrolyzates

SL No	Parameters	Values
01	General appearance	Viscous and sticky
02	Color	Light yellow or creamy
03	Odor	Odorless
04	pH	8.15

The solvent based adhesive is mostly used in the Footwear Industry for their strong bonding strength because due to the presence of solvent there drying time is low usually (10-15 minutes) which is very helpful for the faster production. So this project was carried out to produce a solvent based adhesive and there was a strong possibility to get the best outcome. Four samples were prepared in this project by adding poly vinyl alcohol (1%, 2%, 4%, 6%) and ploy vinyl acetate in different (1%, 4%, 6%, 16%) ratio. All the four samples had average stickiness, bonding capability.

Figure 7 shows the graph of the pH value for four samples. pH value of the samples were 8.0, 7.22, 5.98 and 5.23 respectively.

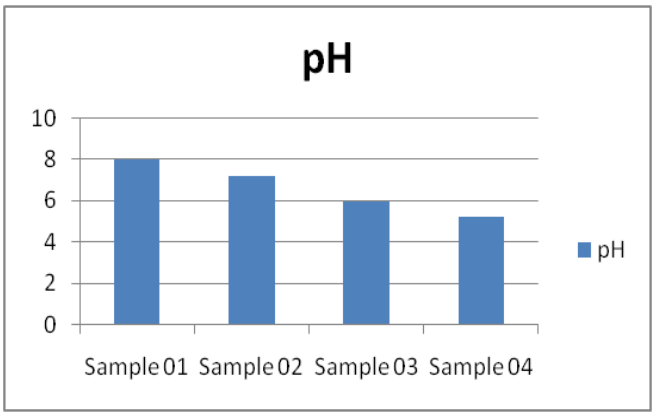

Figure 7: pH of the samples

Figure 8 describes the drying time and pot life of the sample adhesives. Drying time for the 1st two samples were same which was approximately 60 minutes whereas for other two samples were approximately 30 minutes and 40-45 minutes. On the other hand, pot life of the all four samples was same and that was almost 30 days.

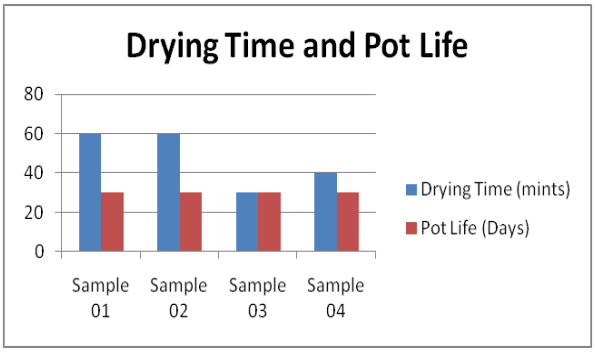

Figure 8: Drying Time and Pot Life

Peel strength was measured after applying the adhesive to leather sample following SATRA TM 416 method. Here it can be seen that the peel strength for the samples was 3.12 N/mm, 3.25 N/mm, 2.95 N/mm and 2.50 N/mm respectively (Figure 9).

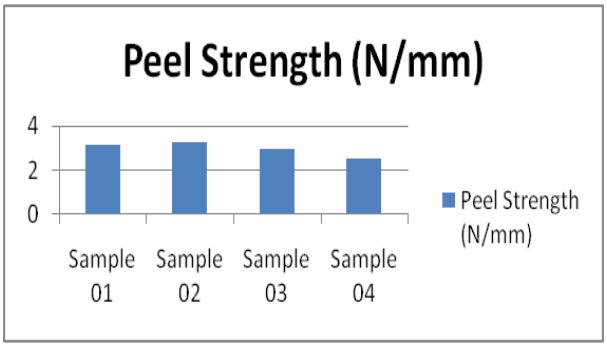

Figure 9: Peel Strength (N/mm) of the samples

Along with these tests, some other tests were carried out like the moisture content and solid content (SLC-114) of the prepared adhesives were measured. The moisture content of the samples was 3.54%, 4.50%, 2.83% and 4.77% respectively. Again the solid content were 97.25%, 94.75%, 98.1% and 95.23% respectively.

DISCUSSION

Adhesive preparation from CSD is almost a new work, so the overall work was hard enough as it was not always possible to add the optimum level of chemicals during the compounding and copolymerization. Due to the limitations of various chemicals, the prepared adhesive may not possess the proper property and so its application in footwear industry is limited to some extent but certainly, its proper application will be available by the controlled compounding and copolymerization. The most dolorous fact is that the bonding capability and stickiness of the adhesive does not meet the requirement. To face this complexity it is wise to use optimum dosages of polyvinyl alcohol and glycerol. This involves trying the experiment many times with various amounts of dosages. Finally, the optimum dosage will be found out. The coagulating problem can be tackled by using glycerol but in that case, the adhesive may lose its sticky property. To solve this problem the addition of various dosages of chemicals from the very first has to be maintained. In a word optimum use of chemicals, time and temperature will yield a successful patent as well as its implementation.

Though some parameters of the prepared adhesive were average but more works can be done on this project in many other ways like extracted collagen hydrolyzates can be further used as poultry feed or to manufacture cosmetics.

CONCLUSION

The most significant topic in any research or project is an independent finding. Every job during the project rotates by centering the aim which may ultimately be the finding if every job is done accurately. The finding of this project work is an adhesive that is a part of resource addition of the leather industry. Although the found adhesive doesn't provide 100% stickiness, it's a totally eco-friendly, solvent-free adhesive which is the foremost demand of today's industries is. The adhesive property of the founded adhesive will certainly increase after more research and subsequent experiments. We will continue to work on that.

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