

HIGH EXHAUST CHROME TANNING USING NOVEL COPOLYMER FOR ECO-FRIENDLY LEATHER PROCESSING

by

J.KANAGARAJ^{*1}, SANJEEV GUPTA¹, GEETHA BASKAR² AND B.S.R.REDDY²

¹Leather Processing Department;

²Industrial Chemistry Laboratory

Central Leather Research Institute,

ADYAR, CHENNAI 600 020, INDIA

ABSTRACT

The novel nanoparticle dispersion (NPD) of a high molecular weight copolymer in aqueous medium was investigated for its application as an aid to chrome exhaustion. The copolymer chain is made up of two types of monomers, viz. an acrylic ester and an amino acid derivative. The copolymer was synthesized using microemulsion polymerization methods. The monomer from the amino acid derivative provides conditions for microemulsion polymerization reaction in aqueous medium and facilitates formation of NPD of the copolymer in water. The developed NPD exhibits narrow particle size distribution with particle size at 40nm. The NPD is a free flowing liquid with flow characteristics almost similar to water, as shown from its low relative viscosity (η_r) of 1.08 at 25°C. The zeta potential of NPD at -32.9mV demonstrates anionic nature of the copolymer particle and this may be provided from amino acid derived monomer. The NPD was tested in chrome tanning as an exhaustion aid. The NPD was used in chrome tanning experiment in the pilot level scale and the exhaustion and leather properties were found. From elaborate investigations, it is demonstrated that NPD could perform as a high exhaust chrome aid to provide 94% exhaustion of chromium when used during chrome tanning operation. The effect of NPD on the physicochemical characteristics of leather is presented.

RESUMEN

La novedosa dispersión nanoparticulada (NPD) de un copolímero de alto peso molecular en medio acuoso fue investigada por su aplicabilidad como auxiliar de agotamiento del cromo. La cadena del copolímero está compuesta por dos tipos de monómeros v.gr. un ester acrílico y un derivado de un aminoácido. El copolímero fue sintetizado usando métodos de polimerización de microemulsiones. El monómero obtenido del derivado del aminoácido produce las condiciones aptas para la reacción en medio acuoso de

polimerización de la microemulsión y facilita la formación el NPD en agua. El NPD desarrollado exhibe una distribución angosta del tamaño de partícula a los 40nm. El NPD es un líquido de fácil fluidez con características casi similares a las del agua, demostrables por su bajo valor de viscosidad relativa (η_r) de 1,08 a 25°C. El potencial zeta del NPD a -32.9 mV demuestra la naturaleza aniónica de la partícula copolimérica y en esta forma ser proveniente del monómero derivado del aminoácido. El NPD se ensayó en el curtido al cromo como auxiliar de agotamiento. El NPD se utilizó experimentalmente a escala piloto durante la operación del curtido al cromo y el agotamiento y propiedades del cuero fueron determinadas. Por medio de elaboradas investigaciones, se demostró como el NPD podría funcionar como un auxiliar de alto agotamiento proveyendo 94% de agotamiento del cromo cuando se utilice en la operación del curtido al cromo. El efecto sobre las características físicoquímicas del cuero se presenta.

INTRODUCTION

The efficient utilization of chemicals in various unit operations of leather manufacturing process is demanded from the point of view of economic and environmental concerns. Different approaches have been attempted towards this goal. The use of alternate chemicals replacing the existing toxic chemicals employed in the conventional processing offers one of the possible means. But, development of an alternate and potential chemical is very difficult to achieve. For an e.g. in chrome tanning, it could be seen that the complete replacement of the prime material of basic chromium sulfate by an alternate potential chemical has not been realized so far. From the point of view of environmental concerns, an almost complete exhaustion of chromium after chrome tanning operation is demanded. The conventional chrome tanning operation brings about 60-65% exhaustion of chromium. Various chrome exhaust aids were developed to improve the exhaustion levels of chromium. Scholnick *et.al.*¹ developed chrome exhaust aids based on acrylamide and α -carboxy ethyl acrylate derivatives. It is reported that these materials provide crosslinking with

collagen and contribute to improved chrome tanning. Protein hydrolysates from fleshings crosslinked with acrylic acid² and keratin hydrolysates³ have been demonstrated to perform as chrome exhaust aids. It is significant to observe that these chrome exhaust aids consist of reactive amino or carboxyl groups capable of modifying collagen and forming complex with chromium. We have developed a novel copolymer (NPD) capable of forming dispersion in water with particle size distribution at nanometer (10^{-9} meter) range. The copolymer consists of a new monomer derived from an amino acid derivative. From literature⁴⁻⁹, it could be understood that simple or polymerizable surfactants provide conditions for microemulsion polymerization reaction necessary to generate nanoparticle copolymer dispersion. The new amino acid derived monomer, similar to a polymerizable surfactant, provides conditions for microemulsion polymerization reaction and is found useful in generation of nanoparticle dispersion after copolymerization with an acrylate ester. In view of free COOH group, the amino acid derived monomer affords functionalization of the copolymer particle and by virtue of this; the developed NPD is expected to contribute to improved tannage. Furthermore, the new copolymer in NPD, in view of its high molecular weight at 6.04×10^5 Daltons is expected to provide filling effect. In this paper, we present the application of NPD as a chrome exhaust aid in tanning process.

EXPERIMENTAL

Materials

Raw Material

Wet salted cow hides with the weight range of 20-25 kg/piece were taken.

Chemicals

The following chemicals from commercial source were employed in tanning and post tanning operations.

1. Basic chromium sulfate (BCS) from Golden chemicals, Mumbai, India.
2. Retanning agents:
 - a. Relugan® RE, from BASF, Mumbai, India.
 - b. Basyntan® DI, from BASF, Mumbai, India.
 - c. Sellasol® PR from TFL, Chennai, India.
3. Fatliquoring agents:
 - a. Lipoderm® liquor ASN and
 - b. Lipoderm liquor SA, both from BASF, Mumbai, India.
4. Dye: Coloderm® Red SG from Colourtex, Chennai, India.
5. Acrylate Ester Monomer (AEM), viz. butyl acrylate (98% pure) purchased from Aldrich was used.
6. Fleshing Hydrolysate-Acrylate composite was used as control sample to evaluate cost analysis. This product had been developed at Central Leather Research Institute (CLRI), Chennai, India and the findings were published in JALCA2. The product has been selected for control sample because it has similar reactive groups and 90% exhaustion in chrome tanning was observed by 2% application of the product on pelt weight.
7. Monomer derived from amino acid (MND), synthesized at our institute, CLRI, Chennai, India.
8. Potassium per sulfate (98% pure) was obtained from S.d. fine chemicals Ltd. India

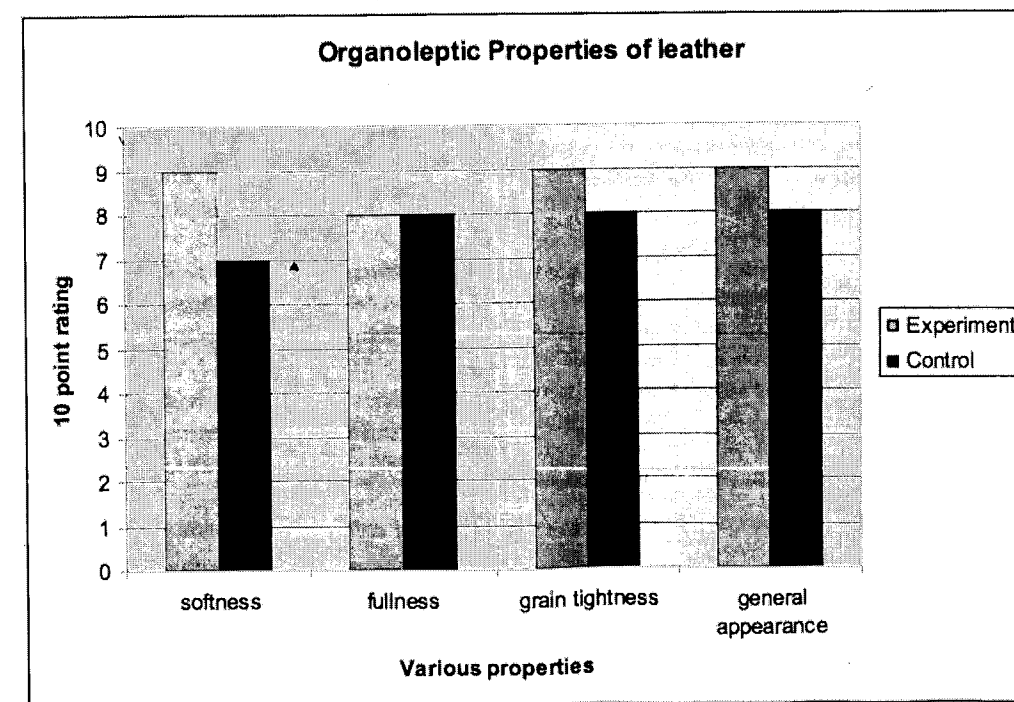


Figure 1: Organoleptic properties of full chrome crust leather, (Experiment 4) 1: softness, 2: fullness, 3: grain tightness, 4: general appearance

* Author for correspondence - Email: tanneryclri@yahoo.com

Manuscript received November 8, 2006 and accepted for publication April 18, 2007

Methods

Preparation of microemulsion of the monomers

The AEM monomer viz. butyl acrylate (66gms) was dispersed in aqueous solution of sodium dodecyl sulfate (SDS) (64gms) and MND (12.5gms) in 600cc of distilled water. The dispersion was kept under continuous stirring for a period of 45 min at ambient temperature to form homogeneous microemulsion.

Copolymerization reaction of microemulsion

The microemulsion prepared as detailed above was transferred into a three necked flask provided with a stirrer, N₂ inlet and thermometer. The microemulsion was degassed and bubbled with inert N₂ gas for duration of 30 min. Potassium persulfate initiator weighing 1% on the weight of the monomers was dissolved into the microemulsion. The microemulsion polymerization reaction was carried out at temperature of 80°C for a period of 8h under N₂ atmosphere. The polymerized microemulsion thus prepared is termed as nanoparticle dispersion (NPD). The copolymer was precipitated from known weight of aliquot of the NPD using methanol as precipitating solvent. The copolymer was washed several times in water to remove SDS and MND. The isolated copolymer was weighed and the yield was calculated based on the weight of the monomers taken for polymerization reaction.

Surface Tension measurements

The surface tension estimation on the NPD was performed on Nima DST9005 tensiometer where platinum Du Nouy ring was used as a probe. Each measurement was made several times to obtain coherent values, allowing a rest time of almost 15min. between the sample addition and surface tension measurement to allow surface adsorption equilibrium to be achieved. The measurement was performed at 25°C.

Physicochemical characteristics of copolymer dispersion

- The particle size and zeta potential measurements were performed on NPD using Malvern zeta sizer model 1000HS/3000HS, UK. Particle analysis was performed at a fixed scattering angle of 90°. The sample of NPD was filtered using 0.45micron filter paper before measurements.
- The molecular weight of the copolymer isolated from dispersion using methanol as precipitating solvent as detailed under the section on copolymerization reaction of microemulsion was taken for GPC analysis (JASCO International Co., Ltd, Japan.). The GPC instrument is fitted with ultrastaygel columns (pore size 10³ -10⁵ Å, also supplied by JASCO International Co.Ltd, Japan) and Refractive Index detector. Tetrahydrofuran solvent was used as an eluting solvent and the flow rate was maintained at 1mL min⁻¹.

Estimation of solid level in NPD

The solid level of NPD was measured from evaporation method. The known weight of NPD was weighed into porcelain basin, evaporated over water bath for a period of 5h followed by drying at temperature of 90°C in the air oven. The solid content in the basin was weighed after cooling. The concordance of the result was reported by repeated heating, cooling and weighing until two consecutive weights are same.

TABLE I
Characteristics of Polymeric Latex

pH	4.0- 4.5
Particle size	40nm
Zeta potential	-32.9 mV
Surface tension (γ), 25°C	27.6mN/m
Relative viscosity (η _r)	1.08
Molecular weight of the polymer (M _n)	6.04x10 ⁵
Mole fraction (m), of AEM : MND in copolymer	0.84:0.16
Polydispersity index (M _w /M _n)	1.42
% Solid level	19.78

TABLE II
Stability Characteristics of Nanoparticle Dispersion

Solutions 3%	Stability
NaCl	No creaming
NaOH	or turbidity
Formic acid	for more than 3hrs
Basic chromium sulfate	

The solid level is expressed as percentage in the weight of NPD taken.

Stability tests:

To 10 cc of aqueous solution of NPD (10%), added individually 1.5 cc of 3% solution of (a) NaCl, (b) basic chromium sulfate (c) NaOH solution and (d) formic acid solution. The stability of the solution was checked from the transparency of solution observed visually. Appearance of turbidity or creaming or layer in the solution indicates the instability of the solution.

Preparation of pickled pelt

The wet salted cow hides were soaked and limed conventionally. After reliming, fleshing and scudding was done manually with the help of knife and the weight of pelt was noted. All chemicals offered were based on pelt weight. Pickling process was carried out conventionally, and the pH was adjusted to 2.8-3.0 before taking for tanning process.

Use of copolymer dispersion, NPD in chrome tanning

Pickled cow pelts were employed for conducting the experiments. The pickled pelts were cut into halves and the left sides of the pelts were used for experiment and the right sides for control. Four sets of experiments were carried out using different concentrations of NPD, based on the pelt weight. In the experiment 1, left side of the pelts were treated with 8% BCS (in 100% float) and agitated in the drum for 120 min. It was followed by addition of 1% NPD and agitated in the

TABLE III
Distribution of Chrome and % Exhaustion of Chrome

Experiments	Chemicals used	Grain layer (%Cr ₂ O ₃)	Middle layer (%Cr ₂ O ₃)	Flesh layer (%Cr ₂ O ₃)	Total chromium (%Cr ₂ O ₃)	% Exhaustion
Tanning 1	BCS 8%+ NPD 1%	4.52 ±0.03	4.40 ±0.06	4.46 ±0.02	4.50±0.04	89
Tanning 2	BCS 8%+ NPD 2%	4.68 ±0.03	4.52 ±0.03	4.63±0.03	4.62±0.02	91
Tanning 3	BCS 8%+ NPD 3%	4.70±0.04	4.57 ±0.04	4.62 ±0.02	4.71±0.05	93
Tanning 4	BCS 8%+ NPD 4%	4.76±0.06	4.63 ±0.02	4.72 ±0.04	4.76±0.04	94
Control (without NPD)	BCS 8%+	3.74 ±0.04	3.68 ±0.03	3.70 ±0.04	3.70±0.03	74

TABLE IV
Emission Factors in Various Tanning Experiments

Experiments	BOD (kg/ton)		COD (kg/ton)		TDS(kg/ton)		TSS (kg/ton)	
	Exp	Cont	Exp	Cont	Exp	Cont	Exp	Cont
BCS 8% + NPD1%	0.82	1.12	1.60	2.24	20.10	28.72	1.20	1.34

drum for 60 min, and then the bath was basified using 1% sodium formate and 0.5% sodium bicarbonate, given in 3 feeds at the interval of 15 min per feed and finally the drum was run for 60 min. Similarly other experiments were carried out on pickled pelts using BCS as above and treated with NPD at the level of 2, 3 and 4% for the experiments 2, 3 and 4, respectively, followed by basification process as described above. After basification (pH of 3.8 - 4.0), the leather samples and the exhaust liquors were analyzed for chromium

Stratigraphic chrome distribution analysis

Samples from the butt¹⁰ of experimental and control wet blue sides were split into three layers with a splitting machine and analyzed layer-wise for chrome content. About 1 g of blue leather in each layer was taken and made into pieces. The cut pieces were taken in a crucible and dried in air oven at 80-100°C for 5-6 hr. After cooling in the desiccator for 30 min, the cut pieces were weighed. Then the dried leather pieces were digested using acid mixture, as provided in detail in the subsequent section. The chrome content in the oxidized mixture is estimated using standard titration procedure.¹¹ The % chromium is expressed on moisture free basis. The total chromium present in the leather was also estimated without splitting the leather into layers and is expressed on moisture free basis using the same procedure as above. The analysis was carried out on five different pieces and the percentage exhaustion of chromium presented was estimated from the chromium taken up by the leather to the total chromium offered.

$$\% \text{ Exhaustion of chromium} = \left[\frac{\text{uptake of chromium by the leather}}{\text{total chromium offered}} \right] \times 100$$

Emission factors in tanning process

The spent liquor from control and experimental leather processing were collected from chrome tanning and analyzed for the pollution loads such as Bio Chemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved

Solids (TDS) and Total Suspended Solids (TSS) of the samples using the standard method.¹² The results are expressed in terms of emission factor i.e. kg of pollution emitted/ ton of the raw material taken.

Shrinkage temperature of leather

The shrinkage temperature of leather samples was determined with a Theis shrinkage meter using test samples with dimensions of 20x3mm in a 70/30 glycerol-water solution.¹³ The experiments were repeated for five replications and average value with standard deviation has been reported.

Percent Exhaustion of dye in post tanning process

Known quantity of dye at different concentration levels were prepared by dissolving it in the water. For the different concentration of dye; the respective optical density (OD) measurements were noted in UV spectrophotometer and λ_{max} (maximum absorption of dye at particular wave length) was found out. The OD of spent dye liquor was measured at particular wavelength (λ=577.5) and plotted in the standard graph. From this, % exhaustion of dye was tabulated and estimated.

Organoleptic properties of leather

Experimental and control crust leathers were assessed for softness, fullness, grain tightness, grain flatness and dyeing property by hand and visual examination. The leathers were rated on scale 0-10 points for each functional property by four experienced tanners, and the average value was given. Higher points indicate better property.

Physical strength properties of leather

Conditioned samples of the crust leather (20OC/65% RH/48 hrs) were tested for tensile strength, elongation at break, tear strength and grain crack characteristics using standard method.¹⁴ The physical strength properties of the leather were tested for the five samples (each experiment) and the readings

TABLE V

Shrinkage Temperature for Chrome Tanned Leather

Experiments	Chemicals used	Shrinkage Temperature
Chrome Tanning 1	BCS 8%+ NPD 1%	116 ± 1.0°C
Chrome Tanning 2	BCS 8%+NPD 2%	120 ± 1.3°C
Chrome Tanning 3	BCS 8%+NPD 3%	122 ± 1.4°C
Chrome Tanning 4	BCS 8%+NPD 4%	126 ± 1.2°C
Control (without NPD)	BCS 8%	110 ± 1.0°C

TABLE VI

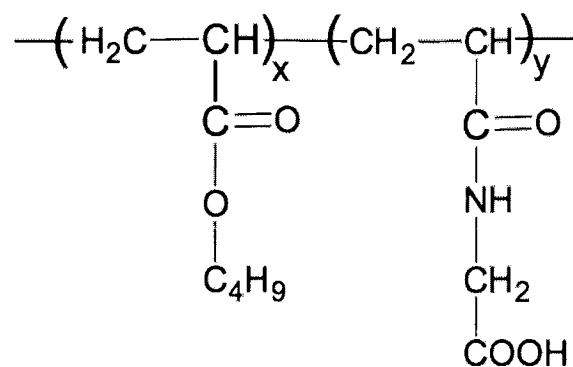
% Dye Exhaustion of the Leather

Experiments	Amount of dye used	% Dye exhaustion
Chrome Tanning 1	1%	95.7
Chrome Tanning 2	2%	96.2
Chrome Tanning 3	3%	96.8
Chrome Tanning 4	4%	97.1
Control (without NPD)	-	94.4

were noted, and the average values were given with standard deviation for accuracy of the result. The physical strength characteristics of experimental leathers were assessed in comparison with control sample.

RESULTS AND DISCUSSION

The molecular structure of the copolymer is presented in scheme 1. The monomer, MND, from amino acid derivative, by virtue of its typical surface-active characteristics, provides conditions for microemulsion polymerization reaction in aqueous medium (distilled water). The NPD was prepared through microemulsion copolymerization reaction between an acrylate ester monomer (AEM, segment a in scheme 1) and the amino acid derivative of a monomer (MND, segment b in scheme 1). The yield of the copolymer was found to be 98% from gravimetric method. The solid level of NPD was measured as 19.78% from evaporation method. The physicochemical characteristics of NPD are presented in Table 1. Estimated on Malvern zeta seizer, it is found that NPD exhibits an average particle size of 40nm. The σ value is indicative of width of particle size distribution curve. The low σ at 0.12 suggests



Scheme 1: Chemical structural representation of the copolymer in NPD, x: AEM, 0.84m, y: MND, 0.16m.

narrow distribution of particle size, which is indicative of uniformity in particle size of the copolymer in NPD. The composition (Table 1) estimated from potentiometric titration method suggests that this copolymer consists of the monomers AEM and MND with mole fraction of 0.84:0.16m. The copolymer in NPD is found to exhibit high molecular weight at 6.04×10^5 . The ratio of number average and weight average molecular weight of the polymer termed as the 'polydispersity index' has been well established to serve as useful parameter in drawing information on molecular weight distribution. The copolymer of NPD developed by us has been found to exhibit narrow polydispersity index at 1.42. The generation of high molecular weight copolymer with narrow polydispersity index has been enabled through microemulsion polymerization method and this primarily establishes the occurrence of polymerization reaction under controlled conditions. The progress of polymerization reaction under uncontrolled conditions would result in polymers with polydispersity index higher than 2.0. It is significant to note that in absence of MND it was not possible to perform microemulsion polymerization reaction with the acrylate monomer AEM. The zeta potential of NPD is estimated to be at -32.9mV. The negative zeta potential of the latex particle demonstrates coverage of the copolymer particle with MND chain and indicative of anionic nature of the copolymer particle. The latex dispersion exhibits free flow properties as shown from a low relative viscosity of 1.08. The dispersion shows surface tension of 27.6mN/m at 25°C. It is well known that water exhibits surface tension of about 72mN/m at 25°C. The lower surface tension of the NPD demonstrates surface-active property of the copolymer chain. The nanoparticle latex does not develop turbidity or creaming in presence of 3% solutions of NaOH, NaCl, formic acid and 3% basic chromium sulfate (Table II) for more than 3hrs. This is indicative of stability of latex for to these salt solutions for more than three hr.

Table III presents distribution of chromium in different layers and % exhaustion of chromium estimated. The distribution of chromium in all the three layers is fairly good for all the experiments. It could be inferred that the addition of NPD in chrome tanning bath brings about significant improvement in up take of chromium. An offer of upto 4% NPD in chrome

TABLE VII

Physical Strength Properties of Full Chrome Upper Leather

Parameters	Chrome tanning experiment by using derivative (Experiment 4)	Chrome tanning (without NPD)
Tensile strength (kg / cm ²)	284±6.0	261±5.0
Extension at break (%)	84±4.0	76±3.0
Tear strength (kg / cm thickness)	92±13	90±4.0
Load at grain crack (kg)	32±1.0	30±1.0
Distension at grain crack (mm)	10±0.4	10±0.3

TABLE VIII
Cost Comparison Chart

Cost details	Cost Comparison Chart	
	Experimental Product	Control Product (Fleshing-Acrylate Composite)
Cost of the product	1.3-1.5 US\$\$	1.7-2.1 US\$\$
Quantity offered on the weight of the leather (4%)/ kg	0.052-0.060 US\$\$	0.068-0.084 US\$\$
Cost involved/1000 kg of leather	52-60 US\$\$	68-84 US\$\$
Cost saved /1000 kg by using NPD	16-24 US\$\$	-

tanning improves the chrome exhaust level of 94% in comparison to conventional chrome tanning. From literature, it could be recognized that availability of additional carboxyl groups of collagen form the basis of improved up take and tanning efficiency of basic chromium sulfate. To cite few e.g. Michael reaction of acrylamide or acrylate derivative has been demonstrated to provide additional carboxyl binding site on collagen during tanning process.¹⁵ Newer materials from fleshing² and keratin hydrolysate employed in tanning³ and glyoxalic acid in pickling and then subsequent tanning⁴ have been shown to provide additional carboxyl sites on collagen effecting increased exhaustion of chrome in chrome tanning operation. Use of Mannich bases,⁵ which may have the ability to complex with the unfixed chrome or to bind with protein substrate through reactive site has been reported to provide chrome exhaustion. It has been also proposed that the improved exhaustion of chrome could be effected through H bonding with Carboxyl groups as observed in investigations using monoethanolamine.^{16,17} It has been found that Acrylamide derivatives react with hide collagen under alkaline condition and cross links irreversibly imparting better shrinkage temperature and chromium to the leather. The reactive groups that are taking place in cross linking are lysine, hydroxyl lysine and arginine.¹⁸

Analyzing the structure of copolymer (scheme 1), it seems that three reactions are possible for the improved uptake of

chromium. The first reaction may be the NPD provides scope for modulating H bonding interactions through interaction of amino acid side chain of NPD with potential functional groups like OH or -NH group of collagen matrix. Such interactions between NPD and collagen matrix are expected to favor complexation with chromium. Secondly, the interaction between polymer particle through COOH group and chromium also should play significant role in influencing the uptake and binding of chromium.¹⁹ However the main reason for the improved uptake of chromium may be due to the carboxyl groups that play main functional group of interaction for this polymer. These carboxylic groups can form a hydrogen bond with side chain groups of polar amino acids like Aspartic acid, Glutamic acid, Lysine and Arginine. All these amino acid residues can act as hydrogen bond donors and acceptors. Since the polymer has carboxyl groups they can form hydrogen bond at multipoint, imparting additional stability to the complex. Also it is possible that hydrophobic interaction and ionic interaction of the collagen also play a major role in imparting stability of NPD with chromium. These interactions may help the chromium to hold tightly with the NPD and favor COO-Cr-NPD-Cr type of cross links. These cross links play critical role in improving the uptake of chromium.²⁰⁻²² The small particle size of NPD at 40nm provides more facile penetration of the polymer particle into the leather matrix. The surface energy of NPD at 27.6mN m⁻¹ indicates surface-active characteristics. By virtue of this, NPD is expected to modulate interfacial energy characteristics promoting uptake of chemicals in the post tanning operation.

Table IV shows the emission factors of pollution load in various experiments. It is seen from the table that by using the copolymer in the chrome tanning experiment, the pollution loads such as BOD, COD, TDS, TSS are reduced to the level of 27%, 29%, 25% and 11% in comparison to the control process. The reduction of pollutants is due to the more uptake of tanning agent and release of less pollutant to the effluent. Also the reactive groups of dicarboxylic acids such as Aspartic acid and Glutamic acid are responsible for the reactivity and more uptake of the auxiliary during the tanning process that paved the way for the reduction of chemical oxidants and relatively bio-chemical oxidants.

Table V presents a comparative account of shrinkage temperature of the wet blue leathers. It is seen from Table V that

addition of NPD in chrome tanning contributes to increase in shrinkage temperature. The higher shrinkage temperature of experimental leathers is indicative of promotion of cross linked structures of collagen matrix and this must have resulted from increased uptake and binding of chromium and NPD with collagen matrix. If the product is used alone, it raises shrinkage of pelt to a limited extent by 6-8°C. Furthermore, NPD on its own does not impart the tanning action. It is found that this product can be used as a tanning aid only.

Organoleptic properties of experimental leathers were evaluated from manual and visual assessment in comparison to control. The results of experiment 4 are presented in Fig. 1. The softness of the experimental leathers (full chrome upper leather) seems to be better than the control samples. The surface-active property of the copolymer chain in NPD contributing to modulation in interfacial energy characteristics might account for the improved softness. Fullness of the full chrome upper leather was generally good in both experimental and control samples. Grain tightness of the experimental leathers seems to be slightly higher than control sample.

The experimental leathers exhibit better dye uptake in comparison to control and it is evident from Table VI. The % exhaustion of dye was increased from 94.4 to 97.1% by the application of NPD to the level of 4%. The reason may be due to the multipoint cross links that forms by the application of NPD in chrome tanning.

Table VII shows the physical strength properties of the full chrome upper leather from experiment 4 (where 4% NPD was added during tanning process). The experimental leather shows comparable tensile strength, distension and load at grain crack characteristics in comparison to control. It is significant to observe that percentage elongation at break and tear strength in experimental leathers are comparable to control samples. It could be inferred that addition of NPD in chrome tanning operation does not alter the strength characteristics of the leather.

The table VIII shows the cost comparison chart for the copolymer developed from amino acid derivative. It is seen from the table that there is considerable amount of cost reduction is achieved (16-24 US\$) by using NPD copolymer in the chrome tanning experiment as compared to control sample of Fleshing-Acrylate sample² (The product has been selected for control sample because it has similar reactive groups and 90% exhaustion in chrome tanning was observed by 2% application of the product on pelt weight).

The potential economic benefit by using the copolymer is that of 90% chrome exhaustion by the application of 2% NPD in chrome tanning. Further, the resultant spent liquor contained much less chrome as well as other pollutants such as BOD, COD, TDS and TSS, and therefore the treatment cost for the waste water is less. In addition to these; the product is very much commercially viable and thus does not pose any safety and handling problem.

CONCLUSIONS

The novel nanoparticle copolymer dispersion (NPD) of a copolymer has been demonstrated to perform as an efficient chrome exhaustion aid effecting 94% exhaustion of chrome when incorporated at the level of 4% in chrome tanning bath. The copolymer consists of two types of monomers, the one derived from an amino acid derivative and the other, an acrylate ester. The NPD exhibits narrow particle size distribution and particle size at 40nm. The copolymer exhibits high molecular weight of 6.04×10^5 Daltons with narrow polydispersity index of 1.42. The monomer from amino acid derivative in view of its surface-active characteristics provides controlled conditions resembling nano reactors during microemulsion polymerization methods. Use of NPD in chrome tanning bath has been established to provide better uptake of chromium. The leathers produced using NPD have been found to exhibit comparable organoleptic and strength characteristics in comparison with conventional tanned leather. A better conclusion could be made from the present investigation that eco-friendly leather can be made by using NPD.

ACKNOWLEDGEMENT

The authors thank Dr. T. Ramasami, Director, CLRI for his encouragement and permission to publish this paper. The authors thank Dr. A. B. Mandal for his support in characterization of dispersion. L.J.M. thanks CSIR for financial assistance through senior research fellowship.

REFERENCES

- Scholnick F., Diefendorf EJ., Fearheller SH .*et.al.* *J.Am.Leath.Chem.Ass.* **86**, 193-198, 1991
- Kanagaraj J., Samivelu N., Rafiuddin, M.; *et.al.* *J.Am.Leath.Chem.Ass.* **84**, 71, 2002
- Ramamurthy G., Sehgal PK and Mahendrakumar. *J.Soc.Leath.Tech.Chem* **73**, 168, 1989
- Bhaskar Geetha., Mandal A.B and Ramasami T. *Macromolecules* **26**, 4083, 1993
- Ramirez AG., Lopez RG., Tauer, K.; *Macromolecules*, **7**, 2738, 2004
- Gan LM., Chew CH., I.Lye., *et.al.*; *Polymer*, **34**, 3860, 1993
- Pyrasch M., and B. Tiede, B.; *Colloid polym. Sci.*, **278**, 375, 2000
- Larpernt C., Bernard E.J., Richard, *et.al.*; *Macromolecules*, **30**, 354, 1997
- M.Antonietti., R.Basten, F. Groehn.; *Langmuir*, **10**, 2498, 1994
- Official methods of analysis, *Society of Leather Technol. Chem.*, Herts, 1965
- O'Flaherty. Roddy W.T and Lollar, R.M.; The chemistry and technology of leather, Vol. IV, Krieger publishing company, Malabar, Florida, 1977
- Eaton A.D., Clesceri L.S., and Greenberg A.E., APHA, 1995
- McLaughlin G.D., and Theis E.R.; The chemistry of leather manufacture, Reinhold publishing corporation, New York, 1945; pp. 133
- Bureau of Indian Standards, New Delhi, IS:5914", 2-70, 1971
- Fuchs., Kupfer R., and Mitchell J.W.; *J. Am. Leath. Chem. Ass.*, **88**, 402-409, 1993

- Ramasami T and Ramasami D.; *J.Soc.Leath.Tech.Chem.*, **59**, 149, 1975
- Covington AD.; Chrome management, proceedings of 30th LERIG, JAN 27-30, 1997
- Ying L., Chengdu., Scholnick F; *et.al.*; *J. Am. Leath. Chem. Ass.*, **85**, 78-86, 1990
- Covington AD and Shi B.; *J.Soc.Leath.Tech.Chem.*, **82**,

64-71, 1998

- Kanagaraj J., Sadulla S., Jawahar M ; *et.al.*; *J.Soc.Leather Chem., Ass.*, **89**, 18-26, 2005
- Kanagaraj, J., Sadulla S., Suseela Rajakumar, G; *et.al.*; *J.Soc.Leather Chem., Ass.*, **89**, 250-256, 2005
- Kanagaraj, J., Sadulla S., Prasada Rao, B., *J.Soc.Leather Chem., Ass.*, **90**, 127-130, 2006