Glove Leather Manufacture From Sheepskins: Influence of Fatliquors and Syntans on the Gloving Properties

by

B. Madhan[1], G. Balaji[1], R. Aravindhan[2], Swarna V Kanth[1], S. Sadulla[1] and J. Raghava Rao[2],*

[1]*Centre for Human and Organizational Resources Development,* [2]*Chemical Laboratory*

Central Leather Research Institute,

Adyar, Chennai-600020, India

Abstract

The post tanning auxiliaries like syntans and fatliquors are known to significantly influence the properties of glove leathers. The right choice of fatliquors and syntans is critical to obtain the leathers with good gloving property. Hence, in the present work an attempt has been made to study systematically the influence of various fatliquors and syntans on the gloving properties of leather made from sheep skins. Combinations of six different types of fatliquors and four syntans have been studied for their influence on the gloving properties *viz.*, run, softness, strength properties and other subjective properties like smoothness and stretch. It is observed that the combination of fatliquors based on sulfited fish oil, sulfochlorinated paraffin wax and lecithin along with glutaraldehyde and polymeric retanning agents result in leathers with better gloving characteristics.

Resumen

Los auxiliares de recurtidos como sintanes y engrasantes son conocidos por su marcada influencia en la producción de cueros de guantes. La correcta elección de engrasantes y sintanes es crítica para obtener cueros con buenas propiedades para guantería. Por lo tanto, en el actual trabajo se ha hecho una tentativa para estudiar sistemáticamente la influencia de varios engrasantes y sintanes en las características para guantería sobre pieles ovinas. Las combinaciones de seis diversos tipos de engrasantes y de cuatro sintanes se han estudiado por su influencia sobre las características aptas para guantería en cuanto a su funcionamiento, v.g caída, blandura, propiedades de resistencia y otras características subjetivas como suavidad y estiramiento. Se observa que la combinación de los engrasantes basados en aceites de pescado sulfitado, lecitinas y ceras de parafinas sulfocloradas junto con glutaraldehido y agentes recurtientes poliméricos da lugar a cueros con mejores características de guantería.

Introduction

Gloves are used to protect the hand or part of the hand against impurities, infections, accidents and hazards. A glove literally means “a cover” for hand with a sheath for each finger, but it is more than that. A good glove should act as a defense against cold and water, maintain the body temperature and leave the hand movable enough to drive a vehicle, to grasp some heavy object lying underneath and to operate a machine etc. Numerous materials are available in the market that can be fabricated into gloves. Leather, a unique and ubiquitous material, is preferred over other synthetics. So far substitutes have remained mainly as supplements. Thermal insulation and visco-elastic properties of leather very well augur for the gloving applications.[1] Manufacture of glove leathers with washable and water resistance property had been demonstrated earlier.[2-5] However, in industrial gloving applications some of the properties such as cut, flame and vibration resistance characteristics need to be incorporated in the leather for its better utility as a material for glove.

The information available on the influence of different post tanning auxiliaries on the gloving properties of glove leather is very limited.[6] The post tanning auxiliaries, especially the use of right choice of fatliquor is important to impart gloving properties like run, softness and tear strength. In addition, the selection of syntan plays a significant role in determining the gloving properties. Hence, an understanding on the influence of various post tanning auxiliaries on the gloving properties would enable the development of glove leathers with high performance characteristics.

One of the important properties for glove leather is “Run”, an elasto-plastic stretch, which is essential to fit snugly to the hand when pulled on and must not stretch on the wear.[7] Run in glove leather is obtained mainly through good fiber splitting followed by fiber lubrication during leather processing. Longer liming, proper bating and ageing after pickling enhances the fiber splitting.[7,8] The lubrication of fibers improves the gloving properties, which is achieved by proper fatliquoring. The selection of fatliquors plays a vital role in determining the extent of gloving properties. Commercially, fish oil, sperm oil and lecithin based fatliquors are employed for the manufacture of gloving leathers.[9,10] Other important properties required in glove leather are good softness and strength (tear).

Fatliquors and syntans are known to influence the physical properties of leathers significantly.[11-15] Generally, filling type of syntans and fatliquors containing free oils are avoided in the manufacture of glove leather as they tend to reduce the run in gloving leather. Hence, it is important to select the right choice of fatliquors and syntans to obtain leathers with good gloving property. Hence, in the present work an attempt has been made to study the influence of various fatliquors and syntans on the gloving properties of leather.

* Corresponding Author - e-mail address: clrichem@mailcity.com

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TABLE I

Processing up to wet blue from wet salted sheep for the manufacture of glove leather

Process/chemicals	%	Duration	Remarks
Soaking			Two changes of water at
Water	300	6 hrs	time interval of 3 hrs
Paint liming			
Water	25	12 hrs	Skins were kept overnight and
Lime	10		conventional unhairing was done the
Sodium sulfide	2		next day (over the beam manually)
Reliming			Skins were handled thrice a day and
Water	200	4 days	on the 5th day the skins were
Lime	200		subjected to fleshing followed by scudding operation and washing
			% chemical addition for subsequent processes is based on the fleshed weight.
Deliming			
Water	100		
Ammonium chloride	1	1 hr	pH adjusted to 8.0 – 8.3
Bating			
Microbate R*	1	1 hr	Washing after completion of the process Scudding was done manually
Degreasing			
Water	100		
Lunasol HP*	1	1 ½ hr	Extensive washing was done
Pickling			
Water	100		Acid was given in 3 feeds at 10 min
Salt	10	15 min	interval. pH adjusted to 2.5 – 3.0;
Hydrochloric acid	1	1 hr	50% pickle liquor drained
Chrome tanning			
BCS	8	1 hr	Cross section was checked for penetration
Water	50	30 min	
Basification			The chemicals were given in 3 feeds
Sodium bicarbonate	1		at 15 min interval and pH adjusted
Sodium formate	1	1 ½ hr	to 3.8 – 4.0; Rinse and piled for ageing (1 day), sammed and shaved to 0.6 – 0.7mm; wet back for post tanning

* Textan Chemicals, India

Experimental

Materials and Methods

Wet salted sheepskins of uniform size and weight were taken and processed into wet blue leathers employing the process given in Table I. The post tanning experimental trials were

TABLE II
Fatliquors and retanning agents screened for experiment on glove leather manufacture

Fatliquors/syntans	Name of the product	Nature	Manufacturer
F1	Cutopol TIS	Sulfited fish oil based fatliquor	Dr. Th. Bohme, Germany
F2	Lipoderm liquor SAF	Synthetic based fatliquor	BASF, Germany
F3	Lipoderm liquor FB16	Sulfited natural oil based fatliquor	BASF, Germany
F4	Lipoderm liquor FBSC	Sperm oil based fatliquor	BASF, Germany
F5	Baykanol liquor CCU	Sulfochlorinated paraffin wax	BASF, Germany
F6	Texoil HUN	Lecithin based fatliquor	Salem Oil & Grease Company, USA
S1	Relugan GT 50	Glutaraldehyde based syntan	BASF, Germany
S2	Relugan RE	Acrylic based syntan	BASF, Germany
S3	Tergotan GSI	Polymeric syntan	Clariant Ltd., India
S4	Derugan ND	Styrene maleic anhydride based syntan	Schill+Seilacher, Germany

TABLE III
Experimental trials using various fatliquor/syntan combinations

Experiments	Fatliquor/syntan combinations employed
E1	F1, F2 and F3
E2	F1, F2 and F4
E3	F1, F2 and F5
E4	F1, F2 and F6
E5	F1, F3 and F4
E6	F1, F3 and F5
E7	F1, F3 and F6
E8	F1, F4 and F5
E9	F1, F4 and F6
E10	F1, F5 and F6
R1	S1 and S1
R2	S1 and S2
R3	S1 and S3
R4	S1 and S4

carried out to select suitable fatliquors and retanning agents to obtain glove leather with improved run, softness and strength characteristics.

Influence of Fatliquors and Syntans on glove leathers

Six fatliquors of different chemical bases, which find extensive usage in commercial practice, were screened for glove leather manufacture. The chosen fatliquors and their chemical base along with the name of the manufacturer are shown in Table II. An offer of 24% of fatliquor (on shaved weight) was used for all the experimental trials. Ten experimental trials (E1 to E10) were carried out varying the combination of fatliquors (F1 to F6) as shown in Table III. Since fish oil is known to impart better run properties, the fatliquor based on sulfited fish oil (F1) was kept constant for all the experiments. The offer of the three fatliquors used for each trial was maintained at 8% each on the shaved weight.

Nine wet blue leathers (processed as mentioned in Table I) of 5 sq. ft (average) were used for the experiments. The wet blue leathers were cut into 2 halves. Each left half was processed separately employing the recipe given in Table IV having fatliquor combination E1. These leathers were used as reference for inter comparison with the respective right halves. The right halves were processed employing the recipe given in Table IV employing the fatliquor combinations E2 to E10. Experiments E1 to E10 were done in duplicates. Retanning system R1 used for all fatliquoring experiments.

The choice of syntan is important for the manufacture of glove leather. Four synthetic retanning agents (S1, S2, S3 and S4) based on gluteraldehyde, acrylic, polymeric and styrene maleic anhydride were screened to identify their suitability in glove leather making. The details of syntans along with manufacturers name are given in Table II. Four experimental trials R1 to R4 were carried out employing four syntans of different combinations as shown in Table III. The offer of each syntan was maintained at 2% on shaved weight so as to maintain the total offer at 4%. The Syntan based on gluteraldehyde is essential for providing better perspiration resistance in gloving leathers; hence an offer of 2% of gluteraldehyde based syntan was maintained constant for all the experiments. Three wet blue leathers (as per Table I) were used for these experiments. Each left half was processed separately employing the process recipe as given in Table IV using the syntan combination R1 (Table III). These left halves were used as reference for the corresponding right halves, which were processed using fatliquor combinations R2, R3 and R4. Experiments R1 to R4 were done in duplicate. Fatliquoring system E1 used for all retanning experiments.

Run Measurement

The run in glove leather was measured by stretching the leather lengthwise and measuring the breadthwise length of the

TABLE IV
Post tanning process for control and experimental glove leathers

Process/chemicals	%*	Duration	Remarks
Neutralization			
Water	150		The chemicals were given in 3 feeds
Sodium formate	1		at 15 min interval. pH
Sodium bicarbonate	1	1 hr	adjusted to 6.0, washed twice
Post tanning			
Water	100		
Syntan S1	2	20 min	
Fatliquoring			
F1	8	30 min	
Combination of two fatliquors from F2 to F6, 8% each	16	1 hr	Exhaustion was checked
Retanning			
Syntan S1 to S4, 2% each	4	30 min	Exhaustion was checked
Fixing			
Formic acid	2	1 hr	Acid was given in 3 feeds at 10 min interval

Wet blue leathers processed as per Table I was used as raw material
* % chemicals based on shaved weight

TABLE V
Softness and %run of leathers treated with various combinations of fatliquors

Sample	Softness		Run	
	Softness value	%Deviation from reference	% Run	%Deviation from reference
E1	5.92±0.02	-	17.86±0.2	-
E2	5.54±0.04	-6.42	16.39±0.2	-8.30
E1	5.83±0.04		18.73±0.3	
E3	5.38±.05	-7.72	21.50±0.4	+14.79
E1	6.02±0.03		23.14±0.3	
E4	5.65±0.03	-6.14	21.94±0.2	-5.19
E1	6.58±0.03		19.71±0.2	
E5	5.16±0.04	-21.58	16.51±0.3	-16.23
E1	6.25±0.03		22.28±0.4	
E6	5.62±0.03	-10.08	25.96±0.3	+16.52
E1	6.23±0.05		23.26±0.3	
E7	6.02±0.03	-3.37	19.61±0.2	-15.69
E1	6.68±0.04		25.46±0.3	
E8	6.34±0.03	-5.09	22.80±0.5	-10.45
E1	6.32±0.02		25.85±0.3	
E9	6.02±0.02	-4.75	32.5±0.5	+25.72
E1	6.42±0.02		26.31±0.6	
E10	6.52±0.03	+1.55	30.86±0.2	+17.29

TABLE VI
Strength measurements of leathers treated with various combinations of fatliquors

Sample	Tear strength N/mm		Tensile strength N/mm²		% Elongation at break		Load at grain burst Kg		Distention at grain burst mm	
	Average	% Deviation from reference	Average	% Deviation from reference	Average	% Deviation from reference	Load	% Deviation from reference	Distention	% Deviation from reference
E1	15.05±0.3	-	20.45±0.4	-	65.50±0.3	-	18±1	-	10.48±0.2	-
E2	26.10±0.4	+73.42	17.93±0.4	-12.35	50.80±0.3	-22.44	30±2	+66.67	13.43±0.3	+28.15
E1	15.60±0.4		22.84±0.5		71.42±0.4		19±2		10.32±0.4	
E3	28.05±0.3	+79.73	19.15±0.2	-16.15	48.25±0.5	-32.44	28±1	+47.36	12.67±0.4	+22.77
E1	16.04±0.2		23.50±0.3		65.90±0.2		18±1		10.68±0.5	
E4	32.25±0.5	+101.05	15.39±0.4	-34.52	46.80±0.2	-30.08	19±2	+5.56	10.98±0.1	+2.81
E1	33.40±0.4		17.80±0.6		72.65±0.2		20±1		10.38±0.3	
E5	28.90±0.3	-13.47	15.41±0.1	-13.43	41.50±0.2	-42.88	22±1	+10.00	11.84±0.1	+14.07
E1	31.35±0.3		16.98±0.1		73.48±0.2		21±1		11.08±0.1	
E6	30.45±0.5	-2.84	20.65±0.4	+21.61	44.50±0.4	-39.44	18±1	-14.29	13.80±0.4	+24.55
E1	29.07±0.1		18.82±0.4		76.35±0.4		19±1		10.4±0.6	
E7	20.15±0.5	-30.69	18.41±0.2	-2.18	40.00±0.5	-44.85	26±1	+36.84	13.50±0.6	+29.8
E1	19.50±0.2		15.58±0.3		49.20±0.4		22±1		12.84±0.2	
E8	27.70±0.4	+42.05	18.22±0.3	+16.94	55.80±0.4	+13.41	32±1	+45.00	14.20±0.1	+10.59
E1	25.13±0.3		18.06±0.2		54.60±0.4		21±2		12.94±0.1	
E9	30.35±0.4	+20.77	14.58±0.4	-19.27	50.50±0.5	-7.51	20±1	-4.76	12.44±0.3	-3.86
E1	20.63±0.2		17.74±0.5		60.42±0.5		22±1		13.05±0.3	
E10	18.25±0.5	-11.54	16.41±0.5	-7.51	53.85±0.6	-10.87	16±1	-27.27	14.05±0.3	+7.66

TABLE VII
Over all ranking of leathers treated with various combination of fatliquors

Sample	Ranking of softness	Ranking of run	Ranking of strength	Ranking of visual assessment	Cumulative weightage (ranking)*
E1	9	6	7	7	7.25 **(9)**
E2	4	4	9	9	6.50 **(6)**
E3	3	8	8	4	5.75 **(5)**
E4	5	5	4	4	4.50 **(3)**
E5	1	1	2	2	1.50 **(1)**
E6	2	7	6	5	5.00 **(4)**
E7	8	2	5	2	4.25 **(2)**
E8	6	3	10	7	6.50 **(6)**
E9	7	10	2	8	6.75 **(8)**
E10	10	9	3	10	8.00 **(10)**

* Higher the value better is their ranking
Cumulative weigthtage = (Softness x 0.25) + (Run x 0.25) + (Strength x 0.25) + (Visual assessment x 0.25)

leather under stretched condition. This length was taken as the initial length. Then the leather was stretched breadthwise and the stretched breadth wise length was found. The difference between the stretched length and the initial length is a measure of "Run". All run measurements were carried out by four experienced tanners and the average values are presented.

TABLE VIII
Softness and %run of leathers treated with different syntans

Sample	Softness		Run	
	Softness value	%Deviation from reference	% Run	%Deviation from reference
R1	5.32±0.04	-	22.84±0.4	-
R2	5.58±0.02	+4.89	18.7±0.45	-22.13
R1	5.41±0.03		21.54±0.5	
R3	5.88±0.02	+8.68	21.26±0.6	-1.31
R1	5.43±0.06		23.62±0.2	
R4	5.50±0.04	+3.13	22.87±0.3	-3.33

TABLE IX
Strength measurements of leathers treated with different syntans

Sample	Tear strength N/mm		Tensile strength N/mm²		% Elongation at break		Load at grain burst Kg		Distention at grain burst mm	
	Average	% Deviation from reference	Average	% Deviation from reference	Average	% Deviation from reference	Load	% Deviation from reference	Distention	% Deviation from reference
R1	39.95±0.4	-	18.73±0.6	-	56.40±0.2	-	20±1	-	10.84±0.4	-
R2	33.40±0.5	-16.40	17.72±0.3	-5.39	56.60±0.2	+0.3	31±2	+55.00	13.28±0.3	+22.51
R1	42.20±0.5		19.83±0.5		59.12±0.4		21±1		11.07±0.3	
R3	37.40±0.4	-11.37	17.99±0.4	-9.28	58.65±0.4	-0.80	26±1	+23.00	14.31±0.3	+29.27
R1	38.69±0.4		18.35±0.4		62.77±0.3		20±1		11.10±0.3	
R4	30.85±0.4	-20.26	14.51±0.2	-20.93	59.15±0.4	-5.76	22±2	+10.00	12.75±0.2	+14.86

TABLE X
Over all ranking of leathers treated with various combination of fatliquors

Sample	Ranking of softness	Ranking of run	Ranking of strength	Ranking of visual assessment	Cumulative weightage (ranking)*
R1	1	4	2	1	2.00 (2)
R2	3	1	4	3	2.75 (3)
R3	4	3	3	4	3.50 (4)
R4	2	2	1	2	1.75 (1)

* Higher the value better is their ranking
Cumulative weigthtage = (Softness x 0.25) + (Run x 0.25) + (Strength x 0.25) + (Visual assessment x 0.25)

Physical Testing and Hand Evaluation of Leather
The samples from experimental and reference crust leathers for physical testing were obtained as per IUP2 method.[16] Four samples (two parallel to backbone and two perpendicular to the backbone) were used for tensile and tear strength measurements using Instron 3369 Tensometer. Two samples from each trial were taken for the measurement of load at grain burst using STD 104 SATRA test equipment. Specimens were conditioned at 80±4ºF and 65±2% R.H. over a period of 48 hrs. Physical properties such as tensile strength, tear strength, % elongation at break and load at grain bursting were examined as per the standard procedures (IUP6 and IUP8).[17,18] The crust leathers were assessed for softness smoothness and stretch by hand by four experienced tanners. 1-10 point scale was employed for rating the leathers, where high rating indicated better property.

Softness Measurement

Softness of the leather were measured using ST300 Digital leather softness tester. The ST300 D is a means of determining the softness of leather without defacing the sample, as it does not require samples to be cut from the leather prior to testing. The experimental and reference crust leathers were conditioned at 80±4ºF and 65±2% R.H. over a period of 48 hrs. The softness of the samples was noted directly from a digital display after fixing it to the ST300 Digital leather softness tester. This method has now been adopted as the industry standard by IULTCS (IUP 36).[19]

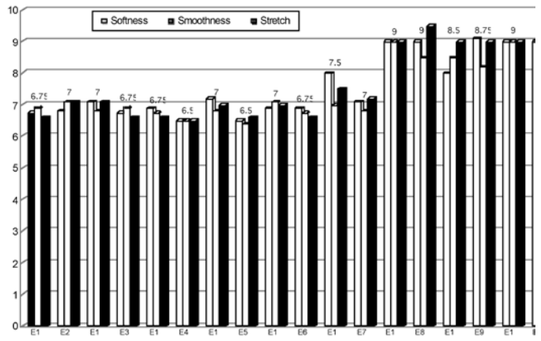

Figure 1: **Visual assessment of leathers treated with various combinations of fatliquors** (values shown in the bar chart are the average rating of softness, smoothness and stretch of a particular sample)

RESULTS AND DISCUSSION

Effect of Fatliquors on Gloving Properties

Six fatliquors of different chemical base, which find usage in commercial glove leather manufacture, have been screened to find its suitability for making better glove leather. Generally fish oil based fatliquor is essential for glove leathers as it possesses very good lubricating property.[9] Hence, in this study sulfited fish oil based fatliquor (TIS) has been offered at a fixed amount of 8% (on shaved weight) for all experiments. Various experimental trials have been carried out by varying the combination of other five fatliquors as mentioned in Table III. The leathers generally exhibit significant variations from skin to skin due to structural differences in each skin. In order to compare skin to skin with high degree of objectiveness, all left halves were processed separately (Table IV) using the fatliquor combination of experimental trail E1. This has been used as reference. The corresponding nine right halves have been processed using experimental trials (E2 to E10).

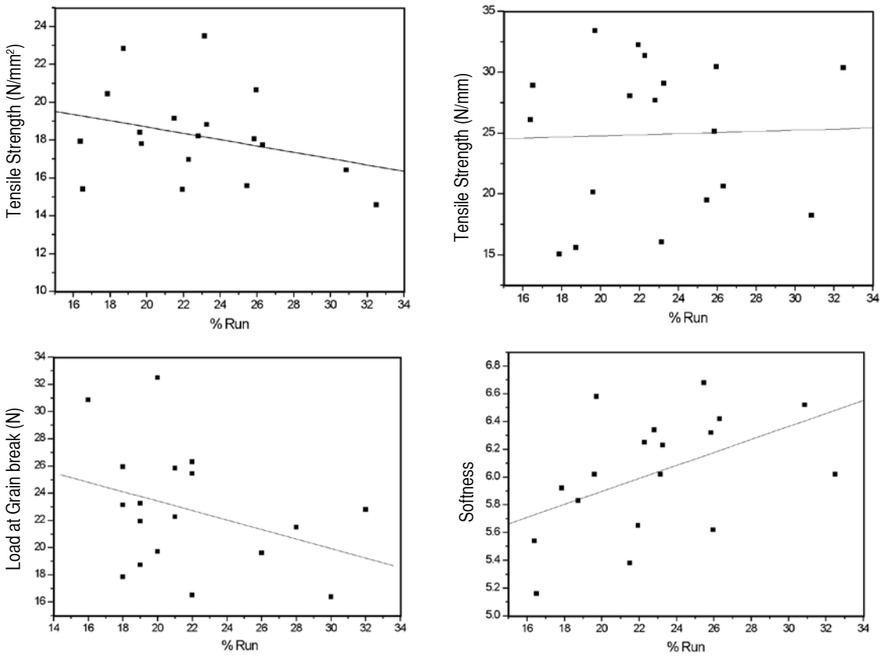

Figure 2: Semi quantitative correlation plot between % run vs Tensile strength and % run vs softness for leathers treated with various combinations of fatliquors

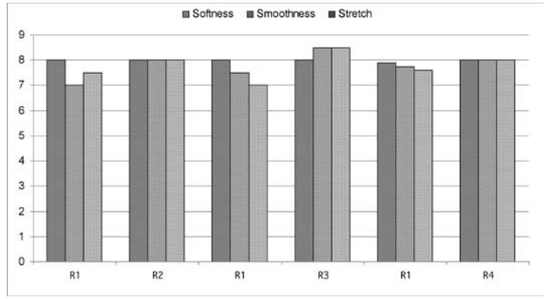

Figure 3: Visual assessment of leathers treated with various combinations of syntans (values shown in the bar chart are the average rating of softness, smoothness and stretch of a particular sample)

The run and softness data for leathers processed using different combination of fatliquor are shown in Table V. The visual assessment data (softness, smoothness and stretch) of the leathers are depicted in Figure 1. The table and figure displays the parameters of different combination of fatliquors E2 to E10 along with its deviation from the respective matched pair values used as reference (E1). The fatliquor combination employed in E10 resulted in leathers with good softness compared to other combinations. However, the presence of sperm oil based fatliquor (E9) resulted in leathers with high run value. It is observed from Figure 1 that the visual assessment data is in accordance with the objective evaluation data of glove leathers. It is also observed that fatliquor based on lecithin is common in experimental trial E9 and E10 and hence the presence of lecithin based fatliquor is perceived to contribute softness and smoothness.

The strength characteristics of experimental trials along with respective control leathers are given in Table VI. Tear strength is yet another important property required in glove leather. Leathers from the experimental trials E2, E3 and E4 exhibited better tear strength properties as compared to all other experimental trials. This could be attributed to the presence of the synthetic fatliquor SAF. However, the experimental trial E4, which contains lecithin based fatliquor, is found to exhibit leathers with highest tear strength. The correlations between different physical properties have been evaluated using the physical property data obtained for various fatliquoring experiments. The semi quantitative correlation between run Vs tensile strength, tear strength, softness and load at grain bursting are shown in Figures 2a-d. From the Figure 2a and b it is observed that there seems to be no significant correlation between the run and the strength properties, as the regression coefficient value (R^2) is less than 0.1. However, there exists a significant correlation between the run Vs softness and load at grain break as seen from Figures 2c and d where the regression coefficient value (R^2) is more than 0.2.

The various physical properties obtained in this study are ranked and the cumulative ranking for softness, %run, strength and subjective properties giving equal weighting for all the values are given in Table VII. From the table, it is observed that the experiment E8, having a combination of fatliquors based on sperm oil and sulfochlorinated wax had resulted in better strength characteristics followed by E2 and E3. It is also observed that the experimental trial E10, which has a combination of HUN (lecithin based fatliquor) and CCU (sulfochlorinated wax based fatliquor) exhibited overall better ranking of all the parameters. In addition the experimental leathers processed with HUN, CCU and TIS resulted in better gloving properties as compared to the corresponding reference leathers. Hence, the usage of 8% each of HUN, CCU and TIS fatliquors has been considered as an optimized fatliquoring combination for the manufacture of glove leathers with better gloving properties. In order to improve the strength characteristics, an offer of synthetic fatliquor in small amounts may be considered.

Effect of Retanning Agents on Gloving Properties

Synthetic tanning agents based on four different chemical natures have been screened for glove leather manufacture. Glutaraldehyde based syntan provides good perspiration resistance, which is an essential property of glove leather.[3,4] Hence 2% of glutaraldehyde based syntan (GT 50) has been offered for all experiments. The run and softness data for the leathers processed using different syntan combinations are shown in Table VIII. The visual assessment data is shown in Figure 3. It is observed from the table that the leathers obtained from the retanning system R3 resulted in better softness and run properties. The visual assessment data matches with the objective evaluation of the leather processed with R3 system. Hence, it can be inferred that the presence of polymeric syntan imparts better softness and run properties.

The strength characteristics of all the experimental leathers along with corresponding reference leathers are given in Table IX. The overall ranking for the properties viz., softness, run, strength and visual assessment are tabulated in Table X. It is observed that employing a syntan combination of R3 (2% GSI and 2% GT50) results in better gloving properties.

CONCLUSIONS

The present study indicates that a combination of sulfited fish oil, sulfochlorinated paraffin wax and lecithin based fatliquors at an offer of 8% each (shaved weight) along with glutaraldehyde and polymeric syntan at an offer of 2% each is suitable for making glove leather with better gloving characteristics. A small addition of synthetic fatliquor could improve the strength characteristics of the gloving leathers. The semi quantitative correlation between run and other physical properties indicated significant correlation for softness and load at grain crack. This study provides a systematic approach for the selection of suitable post tanning auxiliaries for the manufacture of glove leathers with required properties.