THE *Journal* OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

April 2021 Vol. CXVI, No.4 *JALCA* 116(4), 117–144, 2021

Contents

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ISSN: 0002-9726

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Proceedings, Reports, Notices, and News
of the
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THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION (USPS #019-334) is published monthly by The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412. Telephone (806)744-1798 Fax (806)744-1785. Single copy price: $8.50 members, $17.00 non-member. Subscriptions: $185 for hard copy plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers; $185 for ezine only; and $205 for hard copy and ezine plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers.

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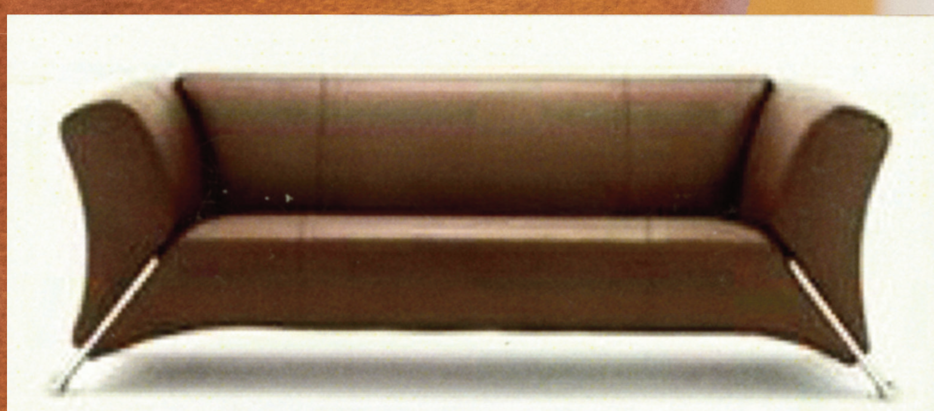

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Chemically Modified Castor Oil for Softening of Leather–A Novel Approach

by
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Abstract

Fatliquoring is an important step of post tanning process of leather manufacturing where incorporation of self-emulsified oil (lubricant) makes the leather soft. There are several methods which introduce polarity into oil and provide the path where reactive species of modified oil can interact with water which leads to form a fatliquor. The aim of this work is to introduce an extra polarity into the fatty acid moiety through chemical modification of castor oil by carbene intermediate. The spectroscopic characterisation such as FTIR, ^{1}H-NMR and ^{13}C-NMR of fatliquor have been carried out. Particle size analysis of fatliquor has also been done. The experimental leathers have been tested for physical strength characterisation such as tensile and tear strength verses control and found to have better properties than control. SEM analysis for morphological study of experimental leather were also carried out which clearly indicates the uniform dispersion of fiber bundles due to the fine distribution of the novel and self-emulsifying fatliquor throughout the matrix.

Introduction

Leather making is a multistep process, which includes tanning, post tanning and finishing steps.[1] In the post tanning process, softening of fibers is an important parameter, which is carried out by the application of fatliquor.[2] Fatliquor is an emulsion prepared by chemical modification of oils or using surfactants/emulsifiers. The proficiency of the fatliquor depends upon its penetration into the pores of the leather fibers.[3,4]

The objective of the chemical modification is to introduce some polarity or functionality into the fatty acid chain of oil. Several oils from synthetic and natural sources such as jatropha oil, castor oil, karanja oil, Neatsfoot oil, flax and soya oil, citrullus colocynthis oil etc., are used for the preparation of fatliquors.[5,6,7,8] With reference to chemical modification of oil, there are only a few known methods which are being carried out for the fatliquor preparation such as transesterification, sulfation, sulphitation, epoxidation and sulfo chlorination.[9,10,11,12] Chemically modified castor oil is used for the lubrication of leather.[13] Turkey red oil is the best example of sulphated castor oil which is commonly used to fatliquor leather.[14] Other methods like transesterification, sulfitation, and epoxidation of castor oil have also been done and explored for the fatliquor preparation. Researchers are always searching for better modification options where cost, time and efforts can be minimised for the making of fatliquors.[15]

The unsaturation which is present in the fatty acids of oils can be exploited for the development of many reactive sites where new opportunities may arise and new products may be formed.[16] Carbene generation and its in-situ reaction with double bonds is another way to explore novel fatliquor preparations. Carbenes are defined as species containing divalent carbon, and they may display either electrophilic or nucleophilic reactivity depending on whether the two unshared electrons on the carbon center are unpaired (triplet carbene) or paired (singlet carbene). When alkenes react with carbenes, three-membered rings are formed. The insertion of a carbene into a π-bond is the most common way for preparing cyclopropanes. The mechanism for a carbene reaction is a concerted process in which all bonds are broken and formed at one time.[17,18]

Carbene can be prepared through many chemical reactions starting from unsaturation.[19] However, oils with multiple double bonds may raise the interest for the development of a variety of fatliquors. Ricinoleic acid present in the castor oil has unsaturation and adjacent polar hydroxyl groups on its backbone. They make it readily available for chemical modification. The uniqueness of castor oil having hydroxyl group in its fatty acid skeleton which is rich in ricinoleic acid (~90%) facilitates the preparation of fatliquor. Consequently, the aim of this study is to add polar moieties to the double bonds which are present in the fatty acid skeleton of castor oil. The di-chloro-carbene polar elements replace double bonds. Furthermore, this new polar group can interact with water which gives water- soluble and/or a preferred self-emulsifying fatliquor.

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Manuscript received November 30, 2020, accepted for publication December 31, 2020.

Materials and Methods

Materials

Castor oil was purchased from Sigma Aldrich. Analytical grade sodium hydroxide, chloroform and sulphuric acid were used for the preparation of fatliquor. All the chemicals used for leather processing were of commercial grade.

Preparation of novel fatliquor

Castor oil (23.3 G./0.025 moles) was put in a reaction flask, and its temperature was increased to 60°C. Chloroform (6 ml./0.025 moles) was added dropwise into the heated castor oil and stirred for about 15 minutes. Subsequently, NaOH pellets (2.6 G./0.025 moles) were first dissolved in distilled H_2O [50 ml.] and this solution was then added into the above reaction mixture. The completion of reaction was confirmed by an in-house water miscibility test. Excess sodium hydroxide in the reaction mixture was neutralized dropwise with sulphuric acid to give the resultant fatliquor a pH = 6.

Characterization

Particle size analysis of fatliquor

The leather matrix has interspaces with small size gaps. It is mandatory for the emulsion to penetrate the fiber structure and fill those spaces. If the particle size of the emulsion matches the pore size of the matrix, proper lubrication can be done. Particle size analysis of our prepared fatliquor has been done by Zeta potential analyser (Zeta sizer 3000, Malvean instruments HSA:2004) in polymer science and technology lab at CSIR-CLRI.

Spectroscopic analysis of fatliquor

The complete analysis of the chemical reaction has been done by spectroscopic analyses including Fourier Transform Infrared (FTIR) and nuclear magnetic resonance (NMR). NMR spectrometer ASCEND-CV series (400 MHz solid state) was used and Perkin Elmer, FTIR spectrophotometer used for FTIR data. The spectroscopic testing has been done at CSIR-CLRI.

Application of novel fatliquor in leather manufacturing

Cow wet blue [5 sides] was acquired from CLRI – Pilot tannery and their thickness adjusted to 1.1 mm. The tanned leathers were cut along the backbone and marked. The left sides were treated with conventional fatliquor (control) whereas the right sides were treated with the novel fatliquor (Experiment). The detailed process recipe is given in Table I.

Scanning Electron Microscopic (SEM) analysis

The resultant crust leather obtained from both control and experimental process was subjected to scanning electron microscopic analysis. All specimens were coated with gold using a Palaron range CA7620- sputtering coater. The Phenom tabletop scanning electron microscope was used to analyse the surface and cross-sectional morphology of the specimens.

Physical strength characteristics and organoleptic properties of leather

We tested the physical strength of the crust. The tests used tensile strength, percent elongation at break,[20] tear strength, grain crack load[21] and distension at grain crack of crust leather obtained from control and experimental processes. The test specimens for physical testing as mentioned above were obtained per IULTCS standard methods and conditioned for 24 hours at 25±1°C and 65±2% RH. The results are shown in Table II. The crust leathers were also evaluated for various organoleptic properties such as softness, grain smoothness, fullness, grain flatness and overall appearance by hand and visual examination by CLRI-experienced tanners. Performance have been rated on a scale of 1-10, where higher points indicate better properties (Table III).

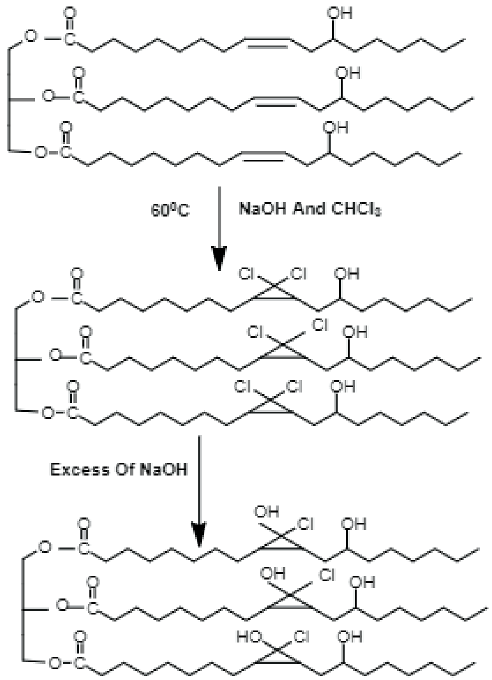
Table I
Process recipe for upper leather making

Process	Materials	Amount (%)	Time	Remarks
Neutralization	Water Neutralizing syntan Sodium bicarbonate + Water	100 0.5 0.2 + 10	30 min 2 × 10 min + 30 min	pH:5.0-5.2, Drained and wash twice
Retanning	Water Melamine syntan + Phenolic syntan + Tara powder	50 5 + 5 + 4	60 min	
Fatliquoring	Water	50	2 × 15 min + 60 min	
Control process	Conventional fatliquor	10		
Experimental process	Novel fatliquor	10		
Fixing	Formic acid + water	2 + 10	3 × 10 min + 60 min	Check exhaustion and pile

Table II

Physical strength characteristics of crust leathers treated with conventional and novel fatliquor

S. No.	Characteristics	Control process	Experimental process
1.	Tensile strength (N/mm²)	19±1	21±1
2.	Elongation at break (%)	56±2.5	41±3
3.	Tear strength (N)	121±2	112±2
4.	Load at grain crack (kg)	37±3	36±2.5
5.	Distension at grain crack (mm)	8.2±0.5	8.6±0.5



Plausible Reaction Scheme 1

Results and Discussions

Preparation of novel fatliquor

Carbenes are highly reactive species and therefore must be produced in-situ. Exploration of carbene chemistry in synthesis of various organic molecules is emerging. However, application of carbene chemistry in the preparation of leather chemicals has not been attempted so far. In the present work, a novel carbene derivative of castor oil has been prepared for softening the leather matrix. Chloroform and NaOH generate carbene which adds to the double bonds in the ricinoleic acid component of castor oil. In a consecutive reaction, the excess hydroxyl ions from NaOH replace chlorine atoms in the intermediate dichloro-cyclopropane to form geminal chlorohydrins. This chlorohydrin is formed by a nucleophilic aliphatic substitution reaction. The overall synthesis of the plausible gem-chlorohydrin product is shown in Reaction Scheme 1. The product on completion of the reaction contains a lot of froth due to the excess NaOH. In order to separate the product from this froth, the contents of the conical flask are emptied into a separating funnel and allowed to settle for an hour. After that the required product can be extracted from the funnel slowly into a beaker. The final pH value of the product was adjusted to pH=6.0. This novel self-emulsifying fatliquor is stable at room temperature.

Particle Size Analysis

The particle size of the experimental fatliquor and the control from Figure 1(a) and 1(b) was (315.9 dnm) and the control (195.3 dnm) respectively. The particles of the experimental emulsion were suitable for their (good) penetration in the fibrils of the leather matrix.

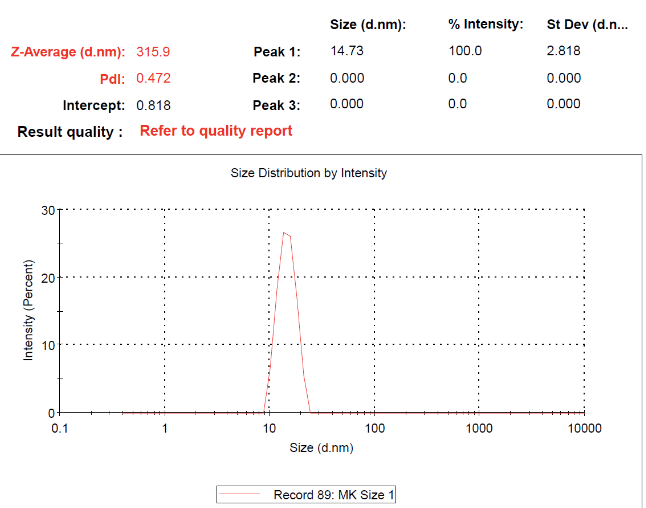


Figure 1a. Particle size distribution of novel fatliquor

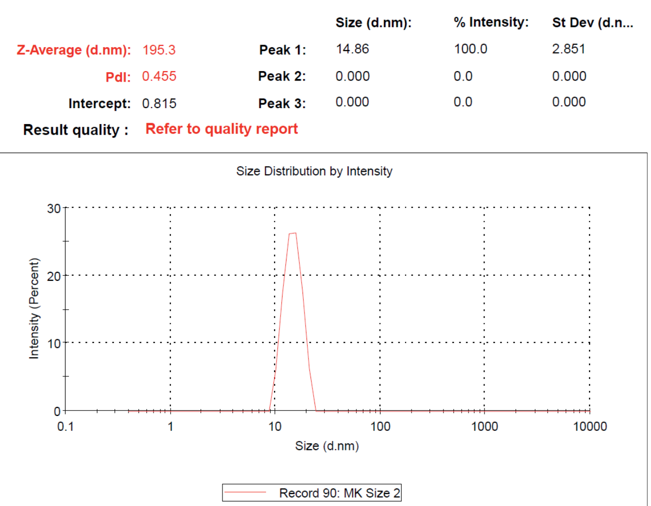


Figure 1b. Particle size distribution of control

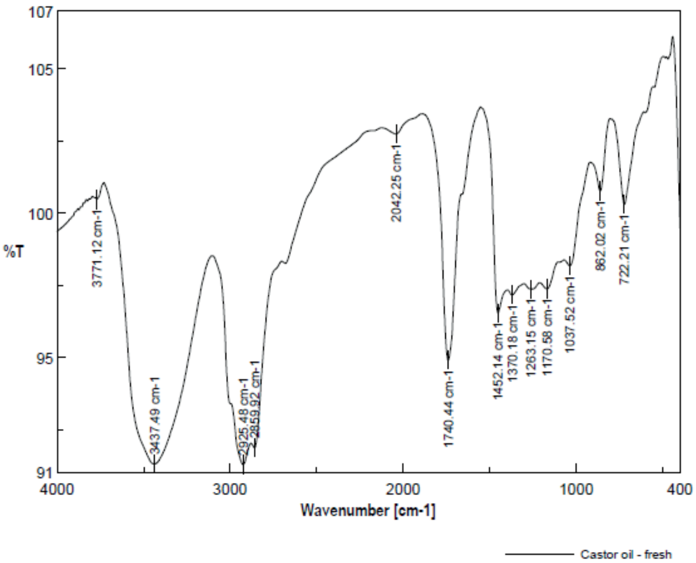


Figure 2a. FTIR spectra of castor oil

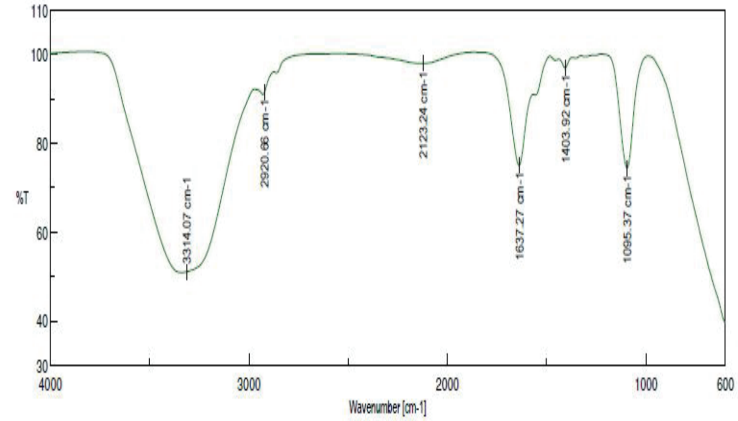


Figure 2b. FTIR spectra of novel fatliquor

FTIR Analysis

The spectroscopic analysis of functionality of fatliquor (control and experimental) have been characterised by FTIR which is shown in the Figure 2(a) and 2(b). The C-H symmetric and asymmetric stretching vibrations of CH_2 groups have been detected at 2923 and 2853 cm^{-1}.

The intense band at 1742 cm^{-1} is due to CO stretching and the absorption bands at 1462 and 1364 cm^{-1} are attributed to CH_2 bending and C-H bending vibration, respectively. The peak at 1655 cm^{-1} represents CH=CH stretching and at 3008 cm^{-1} for =C-H stretching.

Comparing the FTIR of castor oil and the sample, its clearly indicates that the peaks at 3008 cm^{-1} completely vanish in the sample. This peak specifically implies the presence of unsaturation (double bond) in the castor oil. Hence, the attack of carbene onto the double bond of ricinoleic acid thereby removing the unsaturation in the compound. The presence of a peak at 3384 cm^{-1} in castor oil implies the OH group present in ricinoleic acid. The presence of such a big bulge at 3314.07 cm^{-1} implies the presence of intramolecular hydrogen bonding. The presence of a peak at 1095 cm^{-1} corresponds to cyclopropane ring.

NMR

Figure 3(a) and 3(b) shows the ^{1}H-NMR spectra of the castor oil and modified castor oil through carbene intermediate. The δ value at 0.88 ppm corresponds to the terminal methyl group. The δ values from 1.2 to 2.3 shows the signal for the methylene protons associated with long fatty acid chain.

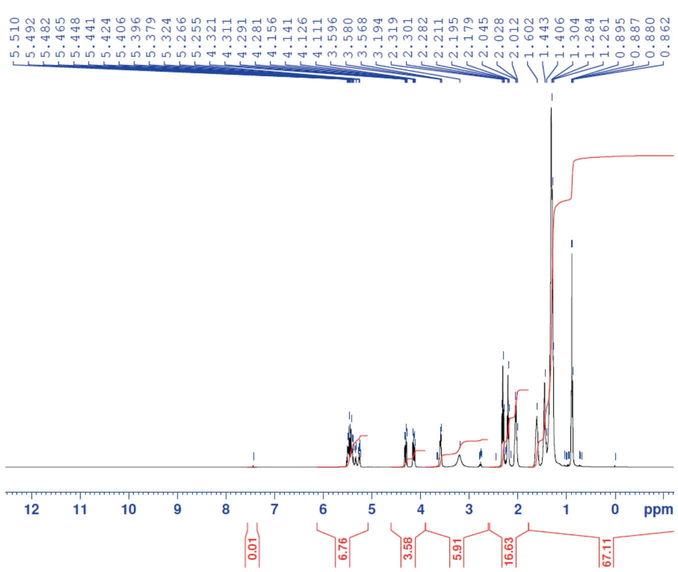


Figure 3a. NMR spectra of castor oil

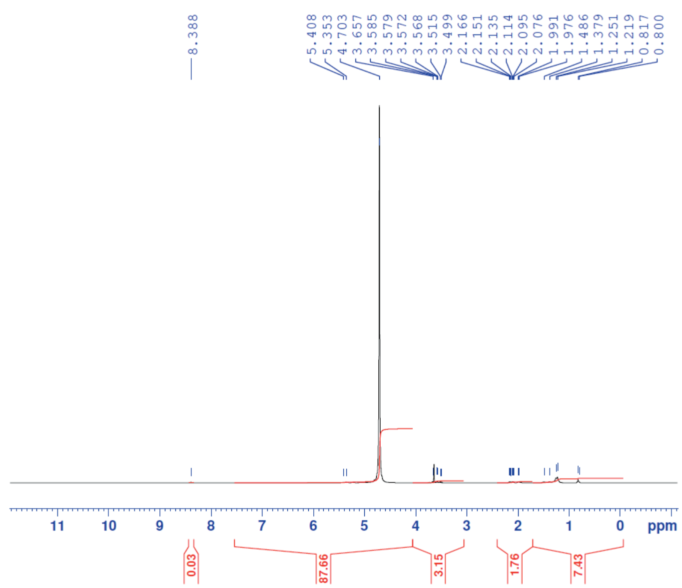


Figure 3b. NMR spectra of novel fatliquor

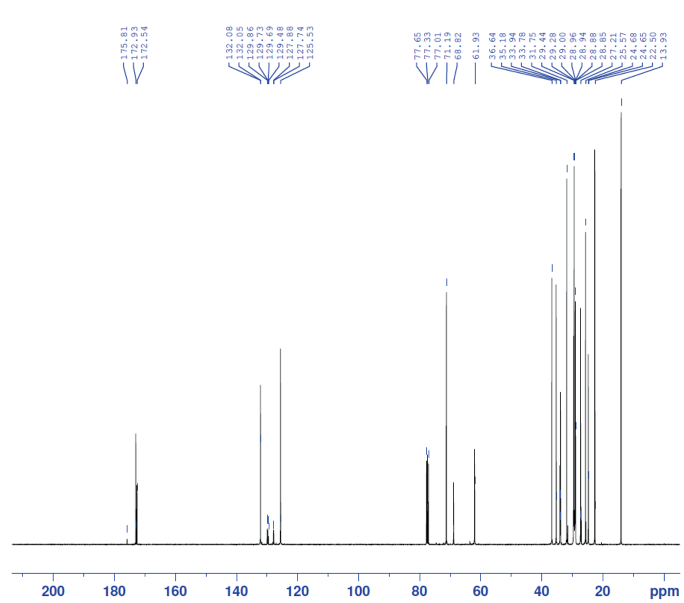


Figure 4a. ^{13}C-NMR spectra of castor oil

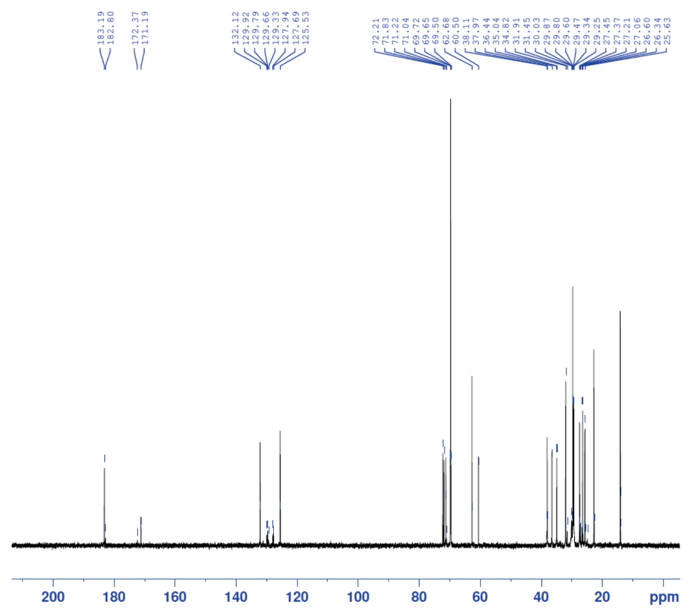


Figure 4b. ^{13}C-NMR spectra of novel fatliquor

Signal at δ 4.1 to 4.3 indicates protons linked with glyceride group. From Figure 3(a) it has been observed that the peaks which are present in the region δ 5.2 to 5.5 of the spectrum of castor oil (fig 3a) indicates the presence of unsaturated protons which are deshielded by the presence of hydroxyl group present in the castor oil. The disappearance of the strong signal in the region δ 5.2 to 5.5 (fig.3 b) indicates the disappearance of the unsaturation.

^{13}C-NMR

^{13}C-NMR spectra of castor oils and experimental fatliquor have recorded in $CDCl_3$ and represented by Figure 4(a) and (b), in the Figure 4(a) the signals at δ 132.08 and δ 125.53 ppm corresponds to unsaturated carbon present at ricinoleic acid which is a major fatty acid component (approx.95%) of castor oil. The peak at δ 71.9 ppm corresponds to carbon atom linked with hydroxyl group and peaks at δ 36.64 and δ 35.19 ppm indicates the carbon atom directly linked with hydroxyl carbon atom. Figure 4 (b) shows all peaks with additional peak at δ 183.19 ppm corresponds to cyclopropane carbon which indicates the conversion of unsaturation present in the castor oil to the three-member cyclic structure.

Physical Strength Characteristics and Organoleptic Properties of Leather

In order to study the effect of the novel fatliquor on leather properties, the matched pair crust leathers of both control and experimental leathers were subjected to various physical strength measurements. The physical strength parameters for control and experimental crust leathers are given in Table II. It is evident from Table II, that there is no significant difference in tensile strength, load at grain crack and distension at grain crack. Whereas tear strength of experimental leather was slightly lower than the control leather. The analysis of bulk properties results reveal that the softness and grain smoothness were (8.5/10) for the experimental leather and (8.0/10) for the control leather, respectively. The overall appearance and other characteristics are on par with control leather.

Table III

Organoleptic property evaluation

S. No.	Characteristics	Control process	Experimental process
1.	Softness	8.0/10	8.5/10
2.	Grain smoothness	8.0/10	8.5/10

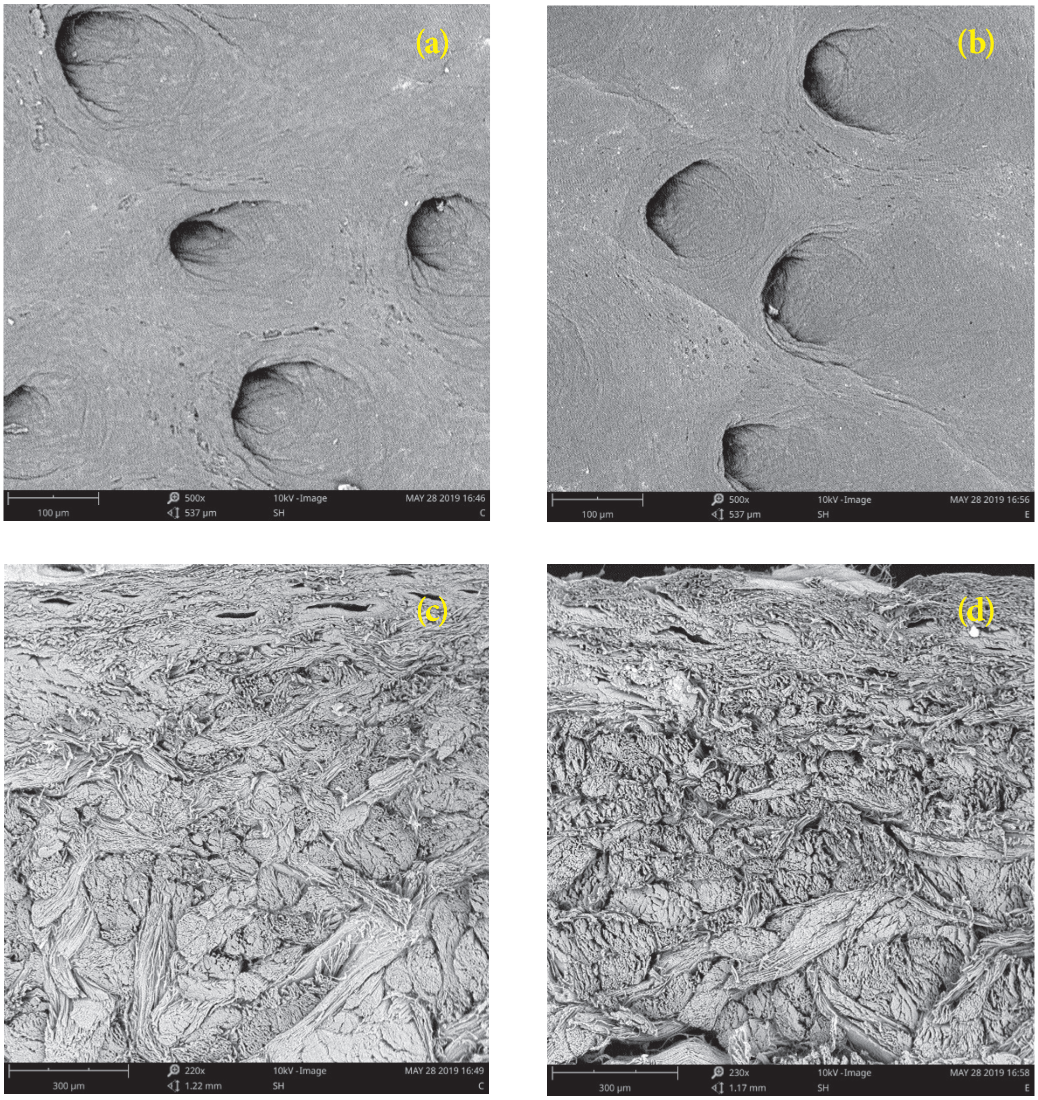


Figure 5. Surface morphology of control and experimental leather **(a)** and **(b)**, respectively. **(c)** and **(d)** cross-sectional view of control and experimental leather, respectively

Scanning Electron Microscopic Analysis

The grain morphology of crust leather from control and experimental process is shown in Figure 4 (a) and (b), respectively. Whereas, Figure. 4 (c) and (d) shows the cross-sectional view of control and experimental process, respectively. It is evident from Figure 4 that the surface characteristics of control and experimental leather are similar. Whereas, it is obvious from cross-sectional micrographs that the fiber splitting of experimental leather is better than control leather. And this clearly indicates the better diffusion and uniform distribution of fatliquor at the fibrillar level.

Conclusion

In the current study, a new approach for the preparation of fatliquor has been reported where, oils with high as well as low number of double bonds can be modified which will be the best part of this work. Any chemical compounds which generate carbene can be used here. The use of castor oil is recommended because of the presence of the polar hydroxyl group which can stabilise the product via hydrogen bonding. This could be a versatile approach for the production of several different kinds of fatliquors.

Acknowledgments

Financial support from CSIR-CLRI, is gratefully acknowledged. The authors thank Dr. J Raghava Rao, Chief Scientist, IPC lab, CSIR-CLRI and Dr. B. Madhan, Senior Principal scientist, CARE, CSIR-CLRI for their encouragement. The authors thank Mr. Rampalli Sai Srivatsa and Mr. Keshav Mahajan from Bitts Pilani. The authors thank Director, CSIR-CLRI for his support. (CLRI Communication number-A/2020/CRE/CLRI/1460).

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Hide Defects of Feedlot Cattle: Assessment of Cattle Management, Breed Type, Sex, Live Market Weight, and Source Factors on Hide Quality

by
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Abstract

Twenty groups of finished feedlot cattle (thirteen steer groups, seven heifer groups) of known origin, breed type, sex and implant status were studied after marketing to determine the type and extent of hide defects as related to days on feed, live market weight, and hot carcass weight. Origin of cattle did not significantly influence the five hide characteristics evaluated (hide defects score, hide vein score, healed scratches, ringworm, and warts). Live weight and sex influenced the weight of the hides ($P < 0.05$), with steers being heavier and having heavier hides. Days on feed increased ($P = 0.06$) the amount of vein damage observed on the hides but was not sex related. Results from this study indicate that under typical commercial cattle feeding practices in Texas, hide defects differ among cattle under the same management and are related to the days on feed in the feedlot, which influences final market weight and degree of finish.

Introduction

The beef cattle industry is the largest single sector of agriculture in the U.S. However, it is not realizing potential profits from feedlot cattle by accepting lower quality hides resulting from routine management and nutrition related factors. Reduction in hide quality decreases the net value of hides which is a silent factor that is involved in arriving at the overall worth of live finished steers and heifers. Live cattle are bought and sold as individual packages without consideration of the type of "wrapper" they may have for use in making different leather products. Furthermore, beef cattle are produced under drastically different management conditions across the nation, that result in the use of different practices which are usually beneficial for the primary purpose intended, but which may negatively influence hide quality. Some of these practices that cause preventable hide defects are branding methods, raising and feeding of un-dehorned cattle, using poor quality and improperly designed fencing and handling equipment, parasite control methods, disease, and days on high concentrate feed in feedlots.

Hides with more defects have greater wastage of leather when fabricated into different products, and also require more labor in cutting and processing. This is a double negative situation which reduces the overall value of finished steers and heifers for producers and increases the cost of leather products. Renewed awareness and attention by cattle owners and managers in improving management and nutrition will impact cattle from the time calves are weaned until they are sold as finished beef. Recognition of these variables will help correct economic inefficiencies that have existed for decades. Benefits to the beef cattle industry would come from higher overall net value of live feedlot cattle per kilogram as compared to other animal species produced for food in the United States.

In an attempt to identify the major concerns of all segments of beef cattle production in the U.S. as related to beef quality, National Beef Audits (NBQA) that were conducted in 1991, 1993, 1995, and 2016 included producers, packers, purveyors, retailers, and restaurateurs.[4,1,3,5,11] These audits found that hide defects was the number one concern for beef packers, and identified excessive fat as the number one concern for beef purveyors, retailers, and restaurateurs. A follow-up NBQA in 2000 collected information to compare the top 10 changes since 1991 for the same segments of the beef industry. In this audit, the producer segment was divided into categories of cow-calf producers, stockers/ backgrounders, and feedlot operators. Results of the 2000 audit showed all categories of producers identified location of injection site as the number one change and identified improved handling as number three to number five. Packers also identified presence of injection site lesions as the number one change but identified hide damage by brands as number ten of the top ten changes. As related to hide quality, purveyors, retailers, and restaurateurs were consistent and identified presence of bruises, and injection site lesions in the top three changes since 1991. These national audit data point to the interest and importance of hide defects and support objectives of this study.

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Technical Note received December 3, 2020, accepted for publication January 10, 2021.

The value of hides to the U.S. beef industry represents 60% of the total by-product sales from cattle and amounts to nearly a billion dollars annually.[2] Thus, reduction in hide defects from better management and nutrition related practices is economically important and improvement appears achievable. Objectives of this study were to determine the type and extent of hide defects in finished steers and heifers as related to source (origin), breed type, sex, days on feed, live market weight, and hot carcass weight.

Experimental

Materials and Methods

Cooperative agreements were arranged with Cactus Feeders, Amarillo, Texas to collect information about groups (pens) of finished steers and heifers marketed from two of their commercial feedlots in the Texas High Plains, and with Tyson / IBP, Amarillo Texas to obtain data on carcass weights, carcass grade and yield, and hide defects of the cattle. A total of 1,844 steers and heifers, representing twenty pens, were involved in this study from March through October 2001. All cattle were fed under the same corporate management and feeding regimen. Carcass information and hide evaluations were collected by qualified personnel at Tyson/ IBP with the assistance of Texas Tech University. Data were then compiled and analyzed by co-authors.

Table I

Information collected about feeder cattle/ feedlot cattle groups used in this study

Source (origin): location within states, or country
Transportation time to feedlots
Breed types within source: domestic;
Brahman influenced; Holsteins
Sex
Number in groups
Feedlot location
Medications administered
Parasite control methods
Vitamins administered
Implant types
Average dry matter intake per day
Average daily gain
Live market weight
Hot carcass weight
Dressing percentage
Quality grade
Yield grade
Type and number of hide defects

Feeder cattle comprised in these twenty pens of finished steers and heifer originated from seven different sources (six states and Mexico). Percentages of the total number of cattle represented by different sources were: Texas - 44%, Mexico – 14%, Oklahoma – 14%, Arkansas – 9%, Mississippi – 8%, Alabama – 7%, and Kentucky – 4%. The length of time in transporting feeder cattle from sources to the feedlots was tabulated using mapquest.com for use in correlating transit time with hide healed scratches and scars.

From the twenty groups of cattle, there were 13 pens of steers (1,174 steers, 64% of total) and 7 pens of heifers (670 heifers, 36% of total). All cattle in all pens were implanted, but the type of implants differed among pens. Three breed types were represented among the twenty pens and types were designated as English and continental crossbred cattle, Brahman influenced, or Holsteins.

All truckloads of finished cattle originating at the two feedlots were met at the packing plant where average live weight was calculated from total pen weight, number of animals in each pen, and individual carcass weights were obtained. Hides were marked with ink at the down-puller in the packing plant and matched with ear tag numbers to correlate hides with the animals they originated from, then hides were followed to the hides department.

Information obtained from the twenty groups of hides consisted of weight score, grade score, vein sore, healed scratches, ringworm, warts, mechanical damage, grub damage, scud damage, light hair stubble, and light draw. Grub damage, scud damage, light hair stubble, and light draw were not statistically analyzed due to their low prevalence in the cattle groups studied. Feedlot derived information about breed type, source of feeder cattle, sex, days on feed, and live weight was used in analysis of hide defect variables, to determine relationships.

Table II

Example of comparative monetary values of main constituent parts of finished cattle[a]

Item	Dollar value, $	Live animal value, %
Live animal value	960.00	–
Carcass value (CV)	903.09	94.1
Carcass parts value[1]		
Loin and ribs (55% of CV)	496.70	51.7
Round (27% of CV)	243.83	25.4
Chuck (14% of CV)	126.43	13.2
Flank and plate (4% of CV)	36.12	3.8
Hide value estimates	40.00/70.00	4.2/7.3

[a]Estimates are based on 545kg (1,200lb) steers, prices for June 9, 2003

[1]Percentages of CV are estimates for medium frame steers, with select quality grade and yield grade of 2.

Table I provides a summary of information collected about the cattle from the originating location of feeder cattle, through their duration in the feedlots, and carcass and hide information at the packaging/hide plant. Some of this information is descriptive in nature and did not offer the opportunity for statistical analysis, while other types of information were analyzed to address objectives of the study. Table II illustrates the comparative dollar value of retail carcass parts from steers and heifers and the dollar spread in hide value. Because carcass values of finished steers and heifers are not related to hide quality, the value for hides may be more or less stable at times when carcass value is fluctuating. Thus, as carcass value decreases, the hide value, as a percentage of live animal value, usually increases. Information presented in Table III describes cattle source, number in groups, breeding, transit time from origin to the feedlots, sex, implant types, medications, injectable vitamins, and feedlot site.

Results and Discussions

Regression analysis was conducted on five categories of data (hide weight score, hide vein score, healed scratches, ringworm, and warts) to develop prediction equations related to cattle source and sex. Grub damage, scud damage, light hair stubble, and light draw were not statistically analyzed due to their low level of prevalence in the cattle.

Twenty pens of steers and heifers were studied for a total of 1,844 animals. Of this total number of cattle, 46% had butt brands, 26% had side brands, 24% were not branded, and 4% were not graded. (Table IV). Cattle came from seven different sources (six states and Mexico) but source did not affect hide quality variables measured. Likewise,

Table III

Descriptive information about groups of cattle

Group No.	Origin	No. in group	Feed-lot No	Breed type	Travel time, h	Sex	Medications[1]	Injectable vitamins	Parasite contol[2]	Implant type[3]
1	McMahan, TX	107	1	Crossbred	15.23	F	1,2,3,4	A, D	1	1
2	Carthage, TX	104	1	Crossbred	12.67	M	2,3,4,6	None	2	2,3
3	Carnegie, OK	89	1	Okies	8.03	M	3,4,5	A, D	1	–
4	Searcy, AR	80	1	Brangus	13.18	M	2,3,4,5	None	1	–
5	Mexico	82	2	Exotics	–	F	2,3,8	None	1	4,5,6
6	Mexico	87	1	Charolais/Angus	15.38	M	3,4,5	A, D	1	2,3
7	Searcy, AR	87	1	Brangus	13.18	M	3,4,8	A, D	1	2
8	Nazareth, TX	70	1	Holsteins	2.48	M	3,4,8	A, D	1	2,3
9	Lawton, OK	81	1	Okies	4.72	M	3,4,5	A, D	1	2,3
10	Culman, AL	131	1	Charolais/Exotics	20.35	M	3,4,5	A, D	1	2,3
11	Elk City, OK	74	1	Okies	4.72	M	3,4,5	A, D	1	2,3
12	Meridan, MS	70	1	Crossbred	17.70	F	2,3,4,5,6	A, D, E	2	1,4
13	Rosebud, TX	110	1	Okies/Crossbred	11.37	F	3,4,8	A, D	1	1,4
14	Fountain Run, KY	80	1	Okies	19.77	M	3,4	A, D	1	2
15	Howe, TX	91	2	Crossbred	10.82	F	2,3,4,8	None	1	4,6
16	Mexico	92	2	Exotic/Okies	19.77	F	2,3,4	None	1	6
17	Sentobia, MS	82	2	Crossbred	14.02	M	2,3,4	None	1	2,3
18	Lamesa, TX	137	1	Exotics/Okies	–	M	3,4	A, D	1	2
19	Tulia, TX	118	1	Exotics/Okies	–	F	3,4	A, D	1	1
20	Gainesville, TX	72	1	Okies	–	M	2,3,4	None	1	2

[1]Medications administered: 1- Lutalase: 2- Bacterin Pasturella: 3- Vision 7 way; 4- IBRP/Fusion; 5- IBRP/Boost; 6- Micotil; 7- IBRP; 8- IBRP; 9- Covexin 8

[2]Parasite control: 1- Dectomax (injectable); 2- Cydectin (pour on).

[3]Implant type: 1- Tulia, TX; 2- Hereford, TX.

Table IV
Frequency of brands across groups of cattle[a]

Type/ not graded	No. of cattle	Percentage of total cattle
Butt (hip)	854	46%
Side (Colorado)	486	26%
Native (no brand)	434	24%
Hides not graded	70	4%

[a]Multiple brands were found on all cattle from Mexico

breed type was not related to hide quality across twenty pens of cattle. Sex affected hide weight score ($P < 0.01$) with steers having heavier hides. No other hide quality variables were affected by sex.

Performance data as related to days on feed, live market weight, and hot carcass weight are presented in Table IV. Data were collected from cattle fed under the same management, and nutritional regimen. The results indicate duration of time in the feedlot (days on feed) increases vein damage ($P < 0.06$). Live market weight data show that heavier cattle had heavier hides ($P < 0.01$); and that heavier hides had increased amount of healed scratches ($P = 0.04$) (Table V).

Hot carcass weight affected hide weight hide score ($P < 0.01$). Feed intake, daily gain, and feed efficiency are all related to hot carcass weight, and an increase in feed intake results in increased daily gain which improves feed efficiency and increases hot carcass weight. Summaries of carcass data, and hide defects data are presented in Tables VI and VII, respectively.

Table V
Summary of feedlot data

Group No.	Origin	Breed Type	Sex	Live weight, kg	Days on feed	DMI[1], kg	ADG[1], kg	F:G[3], kg
1	McMahan, TX	Crossbred	F	464.40	153	6.86	0.90	3.45
2	Carthage, TX	Crossbred	M	487.98	189	6.07	1.04	2.49
3	Carnegie, OK	Okies	M	490.70	189	6.29	1.15	2.49
4	Searcy, AR	Brangus	M	529.71	176	8.04	1.41	2.59
5	Mexico	Exotics	F	434.01	231	6.28	0.94	3.03
6	Mexico	Charolais/ Angus	M	502.49	214	6.70	1.17	2.59
7	Searcy, AR	Brangus	M	568.71	212	7.76	1.50	2.34
8	Nazareth, TX	Holsteins	M	604.08	184	8.99	1.40	2.91
9	Lawton, OK	Okies	M	551.02	186	7.49	1.40	2.44
10	Cullman, AL	Charolais/ Exotics	M	564.63	162	9.04	1.44	2.85
11	Elk City, AL	Okies	M	542.86	173	8.00	1.46	2.49
12	Meridan, MS	Crossbred	F	515.65	215	6.71	0.93	3.25
13	Rosebud, TX	Okies/ Crossbred	F	480.27	215	6.35	0.99	3.25
14	Fountain Run, KY	Okies	M	578.68	127	8.65	1.37	2.87
15	Howe, TX	Crossbred	F	532.43	133	6.05	1.02	2.70
16	Mexico	Exotics/ Okies	F	468.48	261	8.34	1.59	2.38
17	Senatobia, MS	Crossbred	M	535.60	236	7.19	1.31	2.49
18	Lamesa, TX	Exotics/ Okies	M	614.06	134	1.68	1.68	2.58
19	Tulia, TX	Exotics/ Okies	F	520.63	142	1.49	1.49	2.66
20	Gainesville, TX	Okies	M	592.29	161	1.50	1.50	2.56

[1]DMI: dry matter intake

[2]ADG: average daily gain

[3]F:G = total group DMI ÷ total group gain.

Conclusion

The hides of finished feedlot cattle in the U.S. comprise from 4% to 8% of their market value at live price of $80 per 45.45 kg (Table II). However, producers do not realize a higher value for cattle with higher quality hides. Probable solutions to hide quality concerns of finished feedlot cattle are related to management practices from weaning to final marketing, source of cattle, and type of branding, days on feed in feedlots, and hide processing procedures-and will require input and cooperative efforts of all segments of the beef industry. Data presented in this study provide information that indicate attention is needed to address specific critical points in the overall beef industry and if accomplished, hide quality of finished feedlot cattle can be improved. Furthermore, improvement in hide quality must have a paycheck and/or benefit to all segments of the cattle and leather industries involved. Thus, hide quality should be considered in arriving at the price paid for finished cattle by packers involved and higher quality hides will then enable packers to offer better products to meet demands for selected markets.

Table VI

Summary of carcass data[1]

Group No.	Hot carcass weight, kg	Dressing, %	Prime	Choice	Select	No rolls, %	1	2	3	4
1	292.01	62.88	2	62	33	3	22	60	18	0
2	314.75	64.50	0	24	26	30	39	54	7	0
3	317.24	64.65	0	51	48	1	11	69	20	0
4	338.38	63.88	0	39	52	9	23	50	24	3
5	277.64	63.97	6	68	22	4	21	73	6	0
6	323.91	64.46	2	51	44	3	37	52	11	0
7	397.04	64.54	0	49	46	5	5	34	59	2
8	371.27	61.46	1	70	29	0	28	77	3	0
9	353.98	64.24	2	25	62	14	28	43	26	3
10	355.09	62.89	0	25	61	14	26	43	26	3
11	350.41	64.55	0	20	49	31	30	51	23	0
12	331.41	64.27	4	51	39	6	30	26	41	3
13	313.90	65.36	0	31	63	6	35	50	35	1
14	368.45	63.67	2	37	55	6	41	32	28	5
15	353.90	66.47	2	63	32	2	15	32	26	1
16	299.78	63.99	0	62	36	2	16	47	36	2
17	337.48	63.01	0	39	51	13	16	54	30	0
18	390.05	63.52	1	39	56	4	18	28	50	14
19	329.98	63.38	5	73	22	0	6	30	50	14
20	376.76	63.31	0	54	43	3	14	50	35	1

[1]To read: Quality grades are Prime, Choice, and Select. Yield grades are 1, 2, 3, and 4.

Table VII
Summary of hide defects data

	Hide weight[1]					Veins[2]				
Group No.	BH	HTS	XHTS	Healed scratches	Ringworm	G1	G2	G3	G4	Warts
1	68	23	0	68	13	0	11	14	66	0
2	12	90	0	75	14	27	40	15	20	0
3	31	45	11	49	10	18	25	13	31	0
4	15	50	12	67	14	2	9	19	47	4
5	67	10	0	51	1	0	11	6	60	0
6	11	76	0	51	1	0	11	6	60	0
7	10	77	0	49	7	11	16	19	41	1
8	16	52	0	12	7	0	14	2	52	1
9	12	61	0	13	3	0	9	12	52	1
10	8	102	21	32	6	19	76	13	23	2
11	12	57	0	19	2	0	11	14	44	0
12	47	20	0	34	5	0	7	13	47	2
13	74	36	0	35	4	9	12	23	66	1
14	0	56	0	9	1	25	4	12	15	0
15	65	26	0	33	2	21	34	17	19	1
16	60	32	0	55	3	0	4	26	62	1
17	17	49	16	42	1	0	0	21	61	2
18	0	97	72	97	1	19	32	35	51	1
19	79	47	0	47	2	30	57	15	16	1
20	0	24	26	24	1	5	12	19	36	0

[1]BH = branded heifers; HTS = heavy Texas steers; XHTS = extra heavy Texas steers

[2]G1 = no visible veins; G2 = visible veins over 1 to 10% of hide; G3 = visible veins over 10 to 25% of hide; G4 = visible veins over 25% of hide

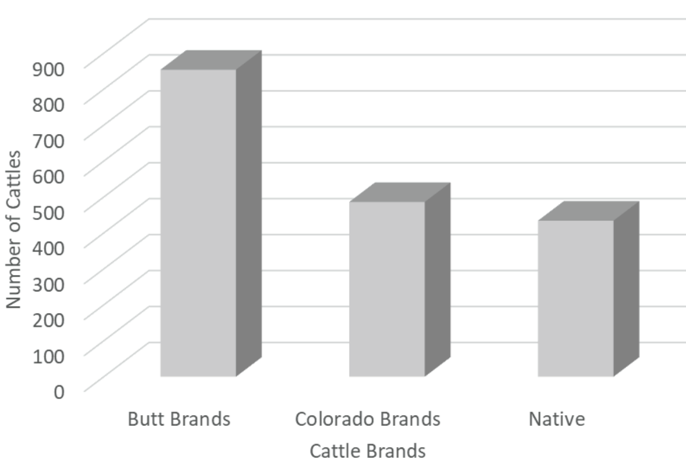

Figure 1. Total Distribution of Brands.

Butt Brands = Hip Brands
Colorado Brands = Side Brands
Native = No Brands

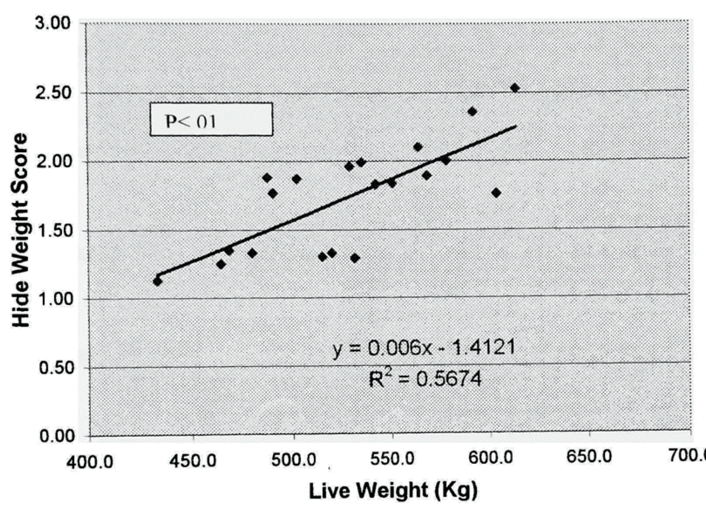

Figure 2. Effect of Live Weight on Hide Weight Score.

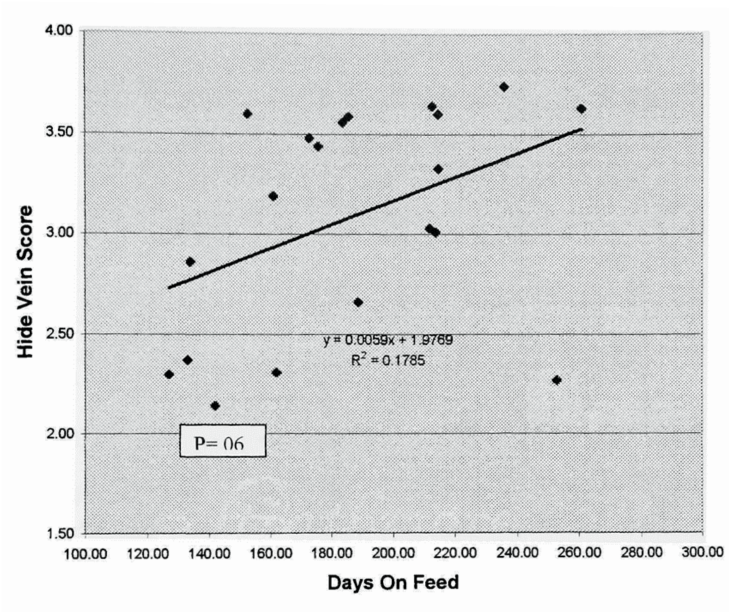

Figure 3. Effect of Days on Feed on Hide Vein Score.

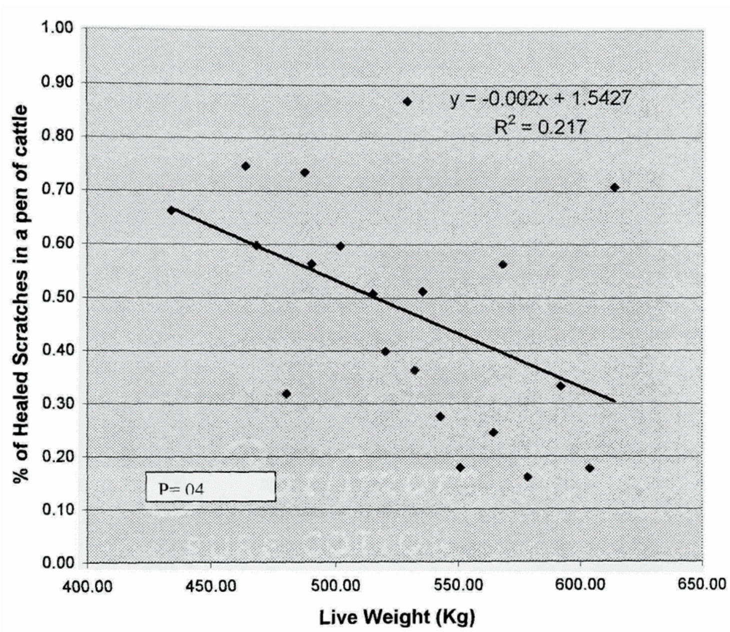

Figure 4. Effect of Live Weight on Healed Scratches.

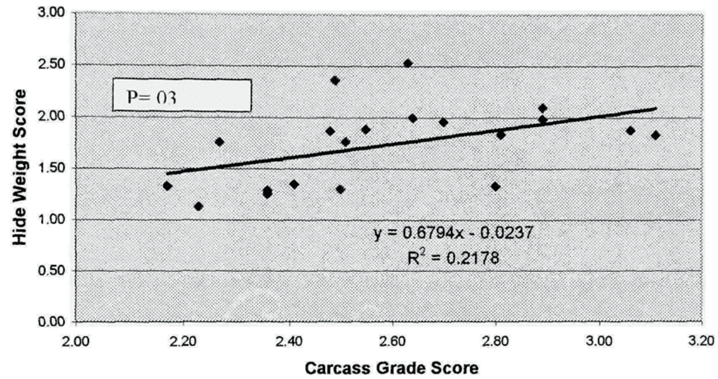

Figure 5. Effect of Carcass Grade Score on Hide Weight Score.

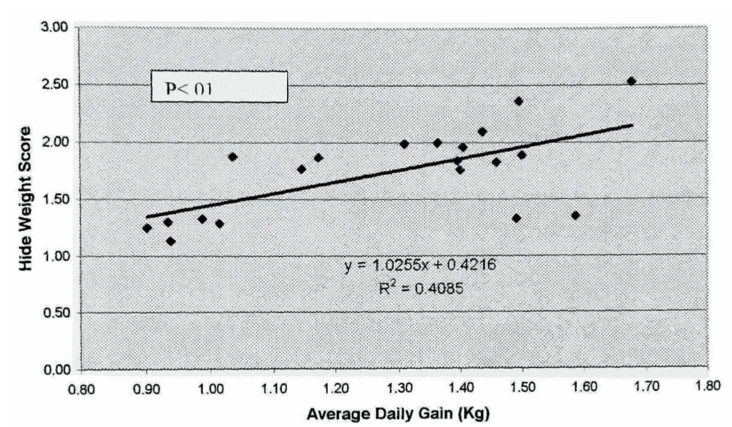

Figure 6. Effect of Average Daily Gain on Hide Weight Score.

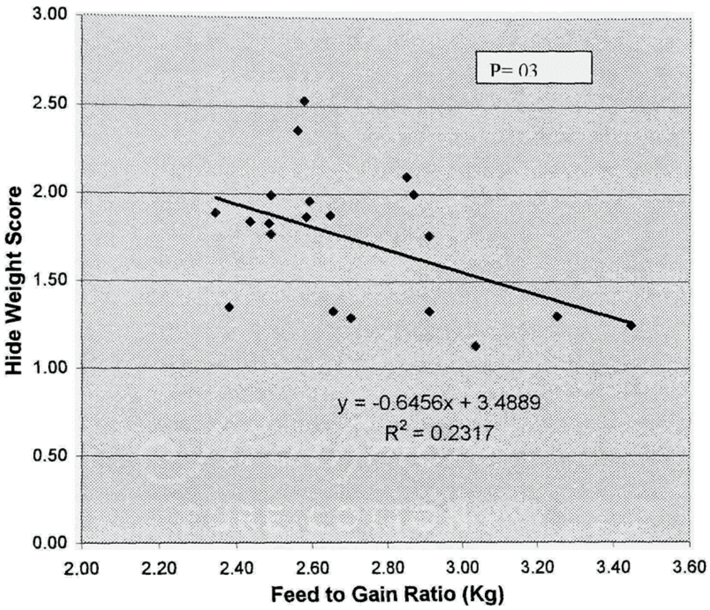

Figure 7. Effect of Feed-to-Gain Ratio on Hide Weight Score.

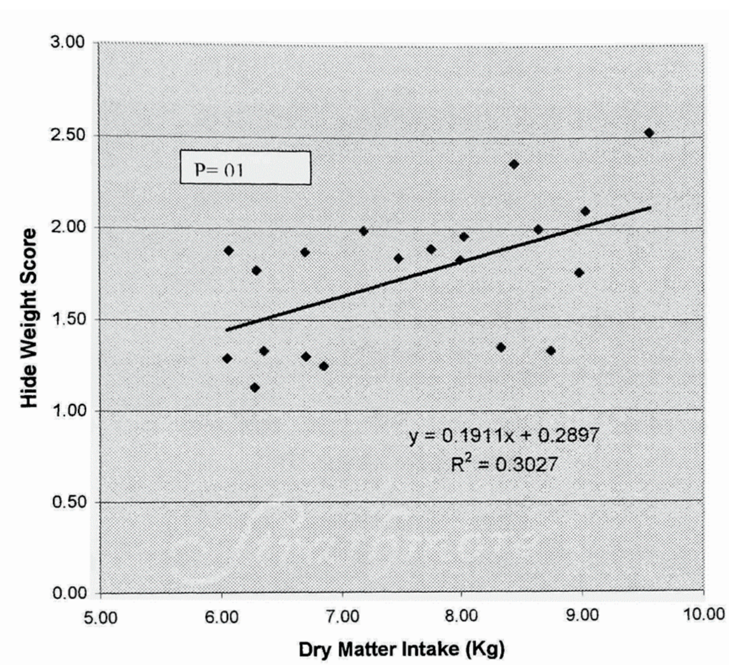

Figure 8. Effect of Dry Matter Intake on Hide Weight Score.

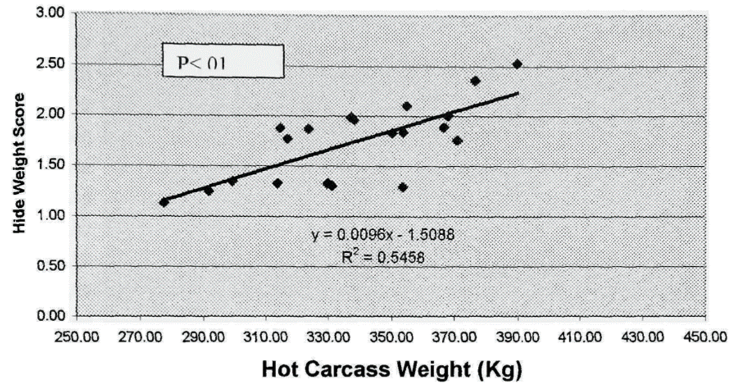

Figure 9. Effect of Hot Carcass Weight on Hide Weight.

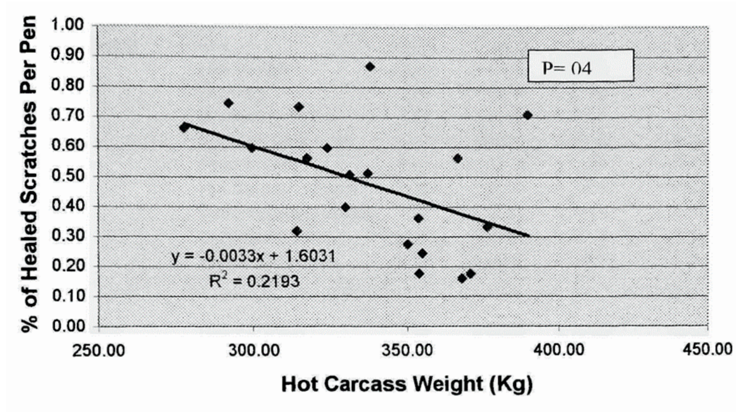

Figure 10. Effect of Hot Carcass Weight on the Amount of Healed Scratches.

Acknowledgments

This study was conducted in cooperation with Cactus Feeders, Amarillo, Texas and Tyson / IBP, Amarillo, Texas. We would like to thank them for providing access to their facilities for acquiring data. Dr. D.C. Shelly at the Texas Tech Leather Institute for his inspiring creative thought and industry application discussions.

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Evaluation of Dye Fixatives – A Comparative Study

by

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Abstract

Dyeing is the important unit process in leather manufacturing, which adds value to the leather. Although formic acid is used for fixing of dyes in leather processing, difficulties do arise in fixation of certain dye stuffs. Further high quantities of formic acid used do create health issues and adds to high cost of production. Compounds such as formic acid, acetic acid, mixture of organic acids and quaternary ammonium compounds have been found to function as dye fixatives. The efficacy of these compounds to function as dye fixatives for various dye stuffs and substances either alone or along with formic acid has been studied in detail in this work. The physical and color characteristics of leather and spent liquor analysis have been carried out.

Introduction

In leather making dyeing is one of most important process because it gives aesthetic look to the leather. Dyeing is necessary to satisfy the sophisticated tastes of the modern person and should keep abreast of the changing fashion trends in color. The final appearance and value of leather is decisively influenced by the color characteristics. Dyeing assumed much greater significance in modern leather finishing particularly with increase in demand for leather for lifestyle products.[1] Conventionally, the following dyes are used in leather processing - acid dyes, direct dyes, metal complex dyes, basic dyes, natural dyes and reactive dyes. The characteristics of dyestuffs have great impact on the color of leather.[2] The main characteristics of dyestuffs can be described as:

- Shade build-up properties and saturation limit
- Affinity of the dyestuff
- The migration power of a dyestuff
- Fastness and other properties

Dyeing parameters such as dye concentration, temperature, float, initial pH, penetration, fixation time and fixing agent, fixation pH are not the same for all cases and all these have effect on the color of the leather.[3,4] Unlike textile dyeing, one deals with a three dimensional matrix in leather dyeing and hence the problems become more complex.[5]

Around the turn of the 20th century, mineral acids were being replaced by less destructive weak acids in the leather dyeing process.[6,7] Formic acid is one such weak acid and has been a popular choice for the dyeing process. Formic acid is traditionally used by the tanning industry during the retan, dyeing and fatliquor processes in order to lower the pH, for the uptake of dyes (particularly acid dyes and anionic dyes) during the dyeing process.[8] Weak acids have also been selected over mineral acids due to greater dye levelness and penetration. Unfortunately, like mineral acids, workers in the tanning industry must handle concentrated formic acid with extreme care since it is a relatively corrosive liquid and exudes noxious vapors. Other limitations of formic acid as a fixative are its inability to provide the same level of fastness and exhaustion for all types of dyes and its cost.[9]

A safe alternative to formic acid in the dyeing process would be highly desired if the alternative not only demonstrated to be an equally efficient but also cost effective replacement. Lots of research has been taken up to evaluate various auxiliaries for dye fixing.[10-16] In this study an attempt has been made to study the efficacy of different dye fixing agents in order to find their usefulness in leather dyeing.

Experimental

Commercial dyestuffs have been purchased from Clariant (India) Ltd for the study. Commercial grade chemicals are used as fixing agents. The main objective of this study is to analyze different dye fixing agents in order to find their efficacy. Experiments were performed using following fixing agents.

Table I
Types of fixing agents

Experiments	Chemicals used
Expt 1	Formic acid
Expt 2	Benzyl triethyl ammonium Chloride
Expt 3	Tetra butyl ammonium bromide
Expt 4	Acetic acid
Expt 5	Formic acid and Acetic acid mixture (in 1:1 ratio)

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Manuscript received December 11, 2020, accepted for publication January 11, 2021.

Preparation of Leather Samples

Chrome tanned goat skins were neutralized, fatliquored, retanned and dried. The crust leathers were rehydrated uniformly and taken for dyeing experiments. The dyeing process is given in Annexure.

Exhaustion Studies

The leathers are dyed with 5% (on the crust weight) of all type of dyes and fixing was done with all the fixing agents (5% on the crust weight) except acetic acid which was used at 7% level (based on preliminary studies to match the exhaustion behavior of formic acid). The spent liquor was analyzed through Spectrophotometer for exhaustion levels. Optical Density (OD) values for different dyes were taken and calibration curves were prepared.

Color Value of Dyed Crust Leathers

Quantification of the color values of conventional and experimental dyed crust leathers were made by reflectance measurements. This assessment is more accurate and it signify hues (h*), Chromaticity (C*) and actual color difference (DE). In this assessment, color values can be determined by using Gardner's tristimulus colorimeter and measured in terms of 'L', 'a', 'b'. The values indicate, the greater the **b** value more yellow and lesser the **b** value greater the blueness. Greater the **L** value, greater its brightness and lesser the **L** value, lesser the brightness or more darkness, lesser the **a** value, greater is the greenness and greater the **a** value more of redness of samples. From the color value of our experimental leather color difference was calculated on basis of comparison with the Experiment – 1 as standard.

$$E = \sqrt{(L_s - L_{T1})^2 + (a_s - a_{T1})^2 + (b_s - b_{T1})^2}$$

L_s, a_s, b_s – standard color

L_{T1}, a_{T1}, b_{T1} – Experimental color values

Plotting of graph

$$\text{Chromaticity} = \sqrt{a^2 + b^2}$$

Color Fastness

Wet rubbing, dry rubbing and light fastness tests were done to ascertain the fastness of dyed leathers fixed by different chemicals.[17]

Physical Testing of Leathers

Testing is a very important part of the leather manufacturing process. When trying to improve the quality of leathers, testing is necessary in order to ascertain the functional properties. Hence tensile strength, elongation at break, tear strength, fastness of color to wet and dry rubbing have been analyzed according to standard procedures.[18,19]

Results and Discussion

Exhaustion of Dyes

The dye spent liquor was analyzed and described in Table II. It is observed that formic acid is consistent in exhaustion levels with each class of dyestuffs. Use of acid mixture resulted in better exhaustion when compared with acetic acid with all dye stuffs. Benzyl triethyl ammonium Chloride and Tetra butyl ammonium bromide yielded moderate with acid, direct, metal complex 1:1 and poor with metal complex 1:2 dye stuffs. Better exhaustion of dyes also results in effective dye removal in the effluents.[20-22]

Table II

Spent Liquor Exhaustion

S.No	Dyes	Expt-1	Expt-2	Expt-3	Expt-4	Expt-5
1	Acid dye	97±2%	90±2%	87±2%	92±2%	97±2%
2	Direct dye	97±2%	89.±2%	85±2%	92±2%	97±2%
3	Metal complex 1:1	96±2%	84±2%	80±2%	90±2%	96±2%
4	Metal complex 1:2	96±2%	78±2%	71±2%	87±2%	96±2%

Table III
Acid Dyes

S.No	Sample	L*	a*	b*	c*	h	DE_{CIE}	DE_{CME}
1	Expt-1	37.549	7.805	15.892	17.705	296.156	–	–
2	Expt-2	33.456	8.034	15.978	18.456	298.493	3.782	2.256
3	Expt-3	33.167	8.734	15.988	18.652	298.794	3.812	2.351
4	Expt-4	38.516	7.334	15.671	17.416	296.123	2.814	1.658
5	Expt-5	36.730	8.523	15.985	18.115	298.066	3.887	2.173

Table IV
Direct Dyes

S.No	Sample	L*	a*	b*	c*	h	DE_{CIE}	DE_{CME}
1	Expt-1	43.280	2.528	6.931	7.378	249.958	–	–
2	Expt-2	40.076	3.392	8.749	9.621	248.042	4.095	2.454
3	Expt-3	40.022	3.738	8.894	9.822	248.981	4.395	2.765
4	Expt-4	45.471	2.836	7.598	7.829	249.089	3.095	2.015
5	Expt-5	44.476	3.632	8.590	9.326	247.082	4.295	2.665

Table V
Metal Complex Dyes 1:1

S.No	Sample	L*	a*	b*	c*	h	DE_{CIE}	DE_{CME}
1	Expt-1	63.280	18.741	50.447	53.815	69.620	–	–
2	Expt-2	60.456	20.345	52.789	55.897	69.484	2.456	0.984
3	Expt-3	60.176	20.045	52.397	56.126	69.184	2.563	1.045
4	Expt-4	65.677	18.156	46.447	50.818	69.326	2.063	0.945
5	Expt-5	63.771	19.101	51.884	55.288	69.789	2.115	0.840

Table VI
Metal Complex Dyes 1:2

S.No	Sample	L*	a*	b*	c*	h	DE_{CIE}	DE_{CME}
1	Expt-1	70.988	1.377	37.030	37.055	87.870	–	–
2	Expt-2	67.647	2.045	41.214	41.476	86.644	3.365	1.494
3	Expt-3	66.491	2.141	41.146	41.765	86.471	3.568	1.584
4	Expt-4	71.677	1.745	36.214	36.476	86.142	3.252	1.894
5	Expt-5	70.323	2.470	40.414	40.489	86.503	3.168	1.719

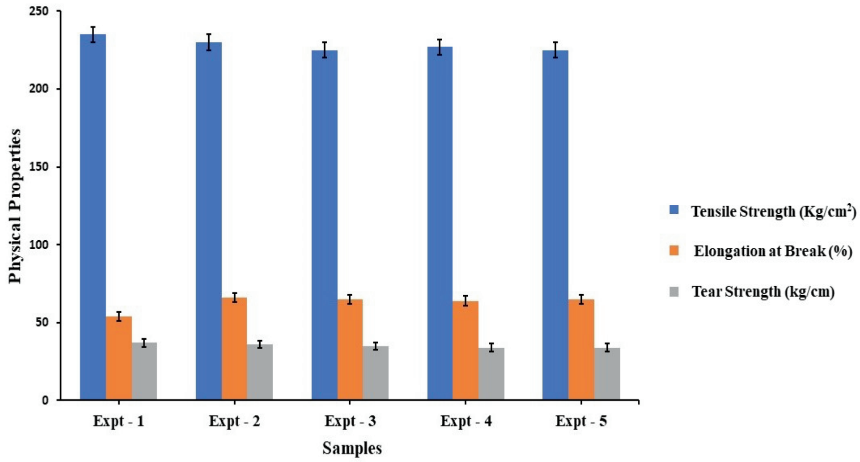

Figure 1. Physical Properties of Leathers

Color Value of dyed crust leathers

From the Tables III-VI it was observed that there are no significant changes in the hue for all the dye fixing agents. Quaternary ammonium compounds treated leathers gave slightly darker shade. There is not much improvement in the shade of acid mixture treated leather.

Physical Strength Characteristics of Leathers

The physical testing values of crust leathers are listed in Figure 1. In order to assess the strength characteristics of experimental leathers acid dyestuff was chosen. It was observed that there are no significant changes in strength characteristics for dye fixing agents.

Fastness Properties of Leather

The fastness property values for leathers of four different fixing agents with direct dye are listed in Table VII. From the results it could be inferred that acid mixture gives results similar to formic acid. Quaternary ammonium compounds yielded better wet and dry fastness. Acetic acid gives moderate fastness properties. Light fastness for TBAB treated leathers was moderate.

Table VII

Fastness Properties of Leather (Direct Dye)

S.No	Fastness Properties	Expt 1	Expt 2	Expt 3	Expt 4	Expt 5
1	Dry rub	#4	#4-5	#4-5	#4-5	#4-5
2	Wet rub	4	4	4-5	4-5	4
3	Light	6-7	6	5-6	6	6-7

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

Table VIII

Fastness Properties of Leather (Acid Dye)

S.No	Fastness Properties	Expt 1	Expt 2	Expt 3	Expt 4	Expt 5
1	Dry rub	#4	#4	#4-5	#4-5	#4-5
2	Wet rub	4	4	4-5	4-5	4
3	Light	6-7	6	4-5	5-6	6-7

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

The fastness property readings of acid dye treated leathers are listed in Table VIII. The results show fastness properties of acid mixture and formic acid treated leathers were more or less same. Quaternary ammonium compounds give better fastness than other agents. Acetic acid gives only moderate fastness properties when compared to other agents. TBAB treated leathers have only moderate light fastness.

The fastness property readings for metal complex dye 1:1 are listed in the Table IX. From the results it is inferred that acid mixture gives good results as formic acid when used for fixing of dyed leathers. Quaternary ammonium compounds give better wet and dry fastness but moderate light fastness. Acetic acid gives moderate fastness properties.

Table IX

Fastness Properties of Leather (Metal-Complex Dye 1:1)

S.No	Fastness Properties	Expt 1	Expt 2	Expt 3	Expt 4	Expt 5
1	Dry rub	#4-5	#4-5	#4-5	#4-5	#4-5
2	Wet rub	4	4	4	4-5	4
3	Light	6-7	5-6	6	5-6	6

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

Table X
Fastness Properties of Leather (Metal-Complex Dye 1:2)

S.No	Fastness properties	Expt 1	Expt 2	Expt 3	Expt 4	Expt 5
1	Dry rub	#4-5	#4-5	#4-5	#4-5	#4-5
2	Wet rub	4-5	4-5	4-5	4-5	4-5
3	Light	6-7	6	5-6	5	6-7

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

The fastness property values for metal complex dye 1:2 are listed in the Table X. The leathers fixed with acid mixture and formic acid yielded same results. Quaternary ammonium compounds give better wet and dry fastness but moderate light fastness. Acetic acid gives moderate fastness Properties.

Conclusions

Extensive studies were carried out to ascertain the ability to fix different dye stuffs with different fixing agents in comparison with formic acid. The results indicate that acid mixture could replace formic acid as dye fixative based on color properties and exhaustion levels. While quaternary ammonium compounds give better fastness properties, the exhaustion levels were found to be much lower compared to formic acid.

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Annexure

Dyeing Experiments

The experimental procedure given below was followed for all types of dyestuffs and fixing agents (acid dyes, direct dyes, 1:1 metal complex dyes and 1:2 metal complex dyes). Full chrome goat crust leathers were chosen for the experiments. All quantities are based on crust weight.

Wetting back

Water	150%		
Wetting agent	0.5%		
NH_3	0.2%	Run for 1 hr then left overnight	
Next Day			

Washing

Water	100%	15 min	
Drain			

Dyeing

Hot Water	300%	@50°C	
Synthetic fatliquor	2%	30 min	
Dyestuffs	5%	30 min	
Synthetic fatliquor	2%		
Semi-synthetic fatliquor	2.5%	- 60 min	Checked exhaustion

Fixing

Fixing Agents	5%	- 5 × 5 min + 30 min pH 3.8-4.0

Leathers were rinsed in water and aged for 8 hrs. Then hooked to dry, staked, toggled and assessed for fixing efficiency.

Lifelines

Bindia Sahu, see JALCA 114, 359, 2019.

M. Sathish, see JALCA 110(11), 379, 2015.

G. C. Jayakumar, see JALCA 106, 68, 2011.

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