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Journal of Cleaner Production 16 (2008) 549–553

Journal of Cleaner Production

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Note from the field

Power ultrasound in fatliquor preparation based on vegetable oil for leather application

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Received 29 September 2005; accepted 20 January 2007

Available online 26 March 2007

Abstract

In recent years, power ultrasound has taken a significant place in chemical and physical activities of the process industries as an effective and non-polluting method of activation. Oil in water emulsions known as fatliquors are used for the lubrication of tanned leather fibres to get softness and also to improve the strength properties. In the present study, ultrasound has been used as a tool for the preparation of fatliquor emulsion for application in leather fatliquoring process. An emulsion is a fine dispersion of one liquid in another liquid. Sulphation is one of the common methods followed to prepare fatliquor emulsion where sulphuric acid is used. In the conventional process, emulsifying agent is also added to increase the stability of oil in water emulsions. The emulsifying agents generally used are chemicals or metal soaps. The potential use of ultrasound in the preparation of stable oil in water emulsions dispensing with sulphation process and with the minimum use of emulsifying agent has been studied and reported in this paper. This process enjoys the benefit of less pollution load in the form of chemical entities. The studies included the effect of process parameters such as ultrasonic output power and amount of oil used. Fatliquor emulsion prepared using ultrasound has been applied in leather fatliquoring process and the strength properties of the leathers were assessed. Emulsion particle size, which is another important parameter for diffusion through leather, has been measured using Laser Diffraction Technique. The stability of the ultrasonically prepared fatliquor emulsion has been found to be good. The results indicate that ultrasound could be effectively utilized in the preparation of non-ionic fatliquor emulsion eliminating sulphuric acid and impart required properties in leather.

Keywords: Power ultrasound; Leather lubrication; Fatliquoring; Fatliquor emulsion preparation; Vegetable oil

1. Introduction

An emulsion is a fine dispersion of one liquid in another liquid with which it is immiscible. Surface-active or other agents that are added to an emulsion to increase its stability by interfacial action is known as emulsifiers or emulsifying agents. In the fatliquoring process, oils/fats are employed as oil in water emulsion known as fatliquor. Fatliquor may be anionic, cationic or non-ionic. Anionic fatliquors are commonly employed for fat binding with chrome-tanned leather, which is cationically charged. Anionic fatliquors are commonly prepared by sulphation, sulphonation or bi-sulphitation of oils/fats. Depending upon the source of the oils/fats used, the fatliquor can be classified as vegetable, synthetic and semi synthetic. Generally, castor oil is used as a source for vegetable based fatliquors. The synthetic fatliquors are usually obtained by sulphochlorination of C_{10}–C_{20} fractions obtained through the Fischer-Tropsch method of paraffin synthesis or from the petroleum industry [1]. Semi-synthetic fatliquors are prepared from both the vegetable and synthetic sources. Characterization and possible use of oil extracted from Seal Hides as leather fatliquor has also been studied [2].

1.1. Ultrasound – application

The application of power ultrasound in process industries has a significant role in the concept of 'clean technology'.

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doi:10.1016/j.jclepro.2007.01.006

Ultrasound is a sound wave with a frequency above the human audible range (16 Hz to 16 kHz). Ultrasound having frequency range of 20 kHz to 100 kHz is termed as power ultrasound [3] and commonly employed for improving the efficiency of physical processes such as cleaning, emulsification, degassing, crystallization, extraction, etc., and for accelerating/performing chemical reactions [4,5]. Ultrasound having frequency range of 1–10 MHz is termed as diagnostic ultrasound and used in medical field and non-destructive testing. The main advantage of physical methods such as use of power ultrasound over chemical means of activation of reactions is that they do not contribute to pollution load in the form of chemical entities. The potential use of ultrasound in process industries such as leather with the aim to improve the quality, improve diffusion rate, reduce process time and pollution load have been investigated extensively [6–12].

Fatliquoring emulsion was earlier prepared using natural and sulphated fats and by exposing the mixture to ultrasonic waves for 10–15 min [13]. Fat emulsion of alkyl phenol ethylene oxide condensates and surface-active agents was prepared using ultrasound [14], which lowers the sulphated oil requirement for fatliquoring by 25–30%. Fatliquor emulsion was also successfully prepared quickly and economically using ultrasound [15,16]. In this paper, fatliquor emulsion preparation based on castor oil using ultrasound has been discussed. The use of ultrasound for enhancing the fatliquoring process has also been studied [12]. Due to the growing demand for the good quality leather auxiliary chemicals, newer processing techniques are gaining importance. Although earlier work has been carried out, some of the important aspects have not been addressed so far. The aspects in the present study include, influence of process parameters such as ultrasonic output power, time of emulsion formation, emulsion particle size, stability of the emulsion and suitability of the emulsion for application to leather. Vegetable oil–water emulsion based on castor oil has been studied in this paper. The ultrasonically prepared fatliquor has been employed to leather and their applicability has been studied through the strength properties of fatliquored leather.

1.2. Need for power ultrasound in emulsification process

- Sulphation is the general method followed to prepare fatliquor emulsion based on castor oil where sulphuric acid is used. The use of sulphuric acid in fatliquor preparation reduces the neutral oil component in fatliquor, which is very essential for imparting good feel and better properties to leather.
- Therefore, alternate method, which uses sulphation free process for the preparation of fatliquor, would be beneficial.
- An emulsifying agent is required to increase the stability of oil in water emulsions. The emulsifying agents generally used are chemicals or metal soaps which result in increased pollution.
- The potential use of ultrasound in the preparation of stable oil in water emulsion (as non-ionic vegetable fatliquor) without sulphation process and with minimum use of additional emulsifying agents has been studied in this paper.
- The possible benefits in leather due to the use of the fatliquor so prepared using ultrasound have also been investigated.

1.3. Relevant sonochemistry

The sonochemical activity arises mainly from acoustic cavitation in liquid media, which are nucleation, growth and explosive collapse of microbubbles on a microsecond timescale. The cavitational collapses occurring near a solid surface will generate micro jets and shock waves [17]. Moreover, in the liquid phase surrounding the particles, high micro mixing will increase the heat and mass transfer and even the diffusion of species inside the pores of the solid. The intense agitation and dispersion effect, which is brought on by the effects of cavitation, results in an increase in the number of collisions between the oil droplet and water and hence better emulsification of oil in water.

2. Experimental section

2.1. Experimental set-up

Experiments were carried out using ultrasonic processor VCX 400, 0–400 W, 20 kHz, Sonics & Materials, USA as described [9].

2.2. Materials and methods

Castor oil (*LR grade*, *SD Fine chemicals Ltd*., India) has been used for the emulsion preparation. Ratio of castor oil and water were varied from 50 to 80% keeping the total weight of oil and water as 20 and 40 g. About 4% of non-ionic wetting agent (*Luwet 40*, *Textan chemicals Ltd*.) was used on the basis of castor oil weight in order to aid in the process of emulsification. In order to optimize the ultrasonic output power, ultrasonic power was varied from 60 to 100 W. Time taken for complete oil–water emulsification was noted. Complete emulsification of oil and water was ascertained from the oil–water phase miscibility, formation of milky white emulsion and absence of any separation of two layers.

2.3. Preparation of fatliquor emulsion ‘US LIQ’

Experiment has been carried out for the preparation of fatliquor emulsion ‘US LIQ’ with 80% castor oil for application to leather fatliquoring process. The details of the experiment are as follows:

- Total amount of vegetable oil and water = 80 g,
- Composition of vegetable oil = 80% (64 g),
- Composition of water = 20% (16 g),
- Ultrasound output power = 100 W.

Time taken for complete emulsification was recorded.

2.4. Emulsion particle size analysis

Emulsion particle size, one of the important parameter which influence properties of an emulsion has been determined using *Shimadzu SALD 1100*, *Laser Diffraction Particle Size Analyzer*. The emulsion particle size has been analyzed for 'USLIQ' as well as for commercial vegetable fatliquor (*Dermalix GRC* Clariant India Ltd.) after suitable dilution of the sample.

2.5. Stability of the fatliquor

The stability of the prepared fatliquor emulsion 'US LIQ' has been studied by observing phase separation (as oil and water) if any takes place with respect to time.

2.6. Leather fatliquoring process

In order to find out the applicability of prepared oil–water emulsions on leather, fatliquoring process has been carried out. Full chrome cow leathers were taken for the fatliquoring experiment. The leathers were cut into two halves through backbone as left and right hand sides for the comparison of the process with and without ultrasound, respectively. The leathers were cut into 6 × 6 cm size samples and then neutralized to the pH of 6.0–6.5 using sodium formate and sodiumbicarbonate. The shaved weight of the leathers was recorded. The effect of amount of fatliquor (*US LIQ*) 2–10% (% based on shaved weight) on fat uptake in leather has been studied. Fatliquoring experiments were carried out with 500% water as float for 2 h in a sample drum (*Ronald Pvt Ltd*., India) with 45 *rpm* having 22 cm diameter × 8.5 cm width. Experiment (A) with 10% ultrasonically prepared fatliquor (*US LIQ*) has been compared with that of partial replacement (B) using 5% commercial synthetic fatliquor (*Dermalix SFL*, Clariant India Ltd.) as well as 5% commercial vegetable fatliquor (*Dermalix GRC* Clariant India Ltd.) and 5% commercial synthetic fatliquor (C).

Fatliquoring experiment (D) was also carried out with 10% 'US LIQ' in presence of ultrasound, 100 W in stationary condition for 2 h and the results were compared.

2.7. Analysis of fat content in leather

Fat content in the leather (*dried leather weight basis*) was determined by following the Soxhlet extraction method using dichloromethane as solvent as per the official method [18] of SLC 4; IUC 4; and BS 1309:4.

The percentage oils/fats in leather

$$= \frac{\text{Oils/fats by Soxhlet method } (g)}{\text{Weight of leather sample taken for Soxhlet analysis } (g)}$$

2.8. Strength properties of the dyed leathers

Strength characteristics of the fatliquored leathers such as tensile strength (*SLP6*; *IUP/6*) and tongue tear strength (*PM 30/Satra*) [19] were tested using an *Instron tensile tester and* grain crack and grain burst (*Satra PM 24*) were tested using *lastometer*. Leather samples for the physical testing were taken parallel to backbone from the leather samples following the IUP/1 procedure for sampling and testing as published [20].

3. Results and discussions

3.1. Effect of ultrasonic output power

The ultrasonic output power has been varied (60–76 W in steps of 4 W) for various castor oil–water ratios (50:50, 60:40, 70:30 and 80:20) and time taken for complete emulsification recorded as shown in Table 1. The total electric power consumption in each case has been calculated (1000 W × h = 1 kWh). The graph drawn between power consumption (kWh) vs. output power (W) for various oil–water ratios for complete emulsification in the case of the total amount of oil and water = 20 g is shown in Fig. 1. Optimal ultrasonic output power for various oil–water ratios is found to be 68 W. Time taken for complete emulsification for optimum ultrasonic power 68 W is given in Table 2. Similarly, on the basis of experiments conducted, emulsification time for different ratios of 40 g oil and water were determined and the results are shown in Table 2.

3.2. Fatliquor emulsion 'US LIQ'

Fatliquor emulsion (*US LIQ*) has been successfully prepared with 80% oil using ultrasound 100 W. Time taken for emulsification for the preparation of '*US LIQ*' is 20 min keeping total amount of oil and water as 80 g.

3.3. Emulsion particle size analysis

The average particle size of ultrasonically prepared fatliquor emulsion and for the commercial vegetable fatliquor emulsion was found to be 3.7 μm and 28.5 μm, respectively. The results indicate that ultrasonication provides finer emulsion particle distribution, which helps in fatliquoring process.

Table 1
Time taken for complete emulsification for various oil–water ratio (with total 20 g) using optimum ultrasonic power 68 W

S. no	% Composition of vegetable oil	% Composition of water	Time taken for emulsification (min)
1	50	50	3
2	60	40	4
3	70	30	4.5
4	80	20	5.5

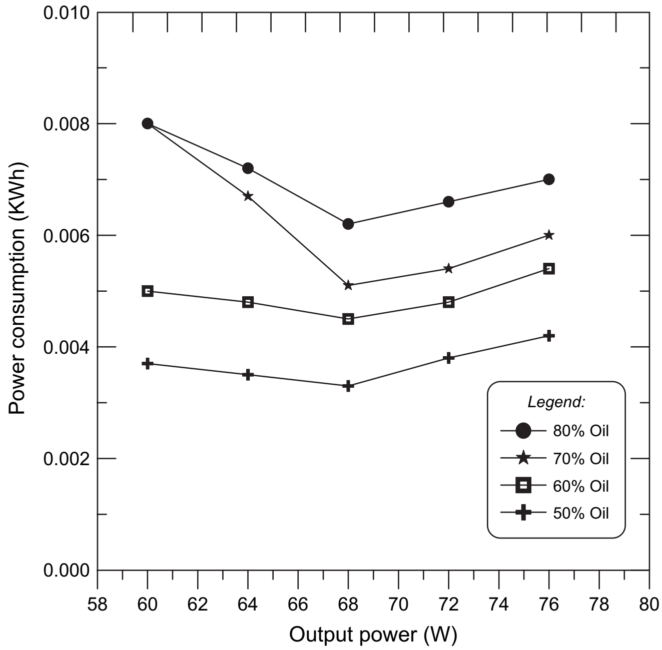

Fig. 1. Power consumption vs. ultrasonic output power for various oil–water ratio (with total 20 g) for complete emulsification.

3.4. Stability of the fatliquor

The ultrasonically prepared fatliquor emulsion 'US LIQ' is stable without any phase separation as oil and water for more than 6 months. It is expected that the fatliquor will have very good shelf life.

3.5. Fatliquor application in leather – effect of amount of fatliquor offer

Fig. 2 shows the effect of amount of fatliquor offer on the % fat uptake in leather. The results indicate that increase in the fat content in leather with increase in the % fatliquor offer from 2 to 10%.

3.6. Comparison of different processes

The fat uptake in leather using 10% ultrasonically prepared fatliquor 'US LIQ' for the process (A) has been compared with that of other processes viz., B, C and D as shown in Fig. 3. The results indicate that fat uptake for different processes are comparable and use of ultrasound in fatliquoring process improves fat uptake by 25%. The reasons for the improvement in fat uptake due to the use of ultrasound in fatliquoring process may be reversible pore-size changes in leather, diffusion rate enhancement and micro-mixing effects.

Table 2
Time taken for complete emulsification for various oil–water ratio (with total 40 g) using optimum ultrasonic power 68 W

S. no	% Composition of vegetable oil	% Composition of water	Time taken for emulsification (min)
1	50	50	6
2	60	40	8
3	70	30	9
4	80	20	10

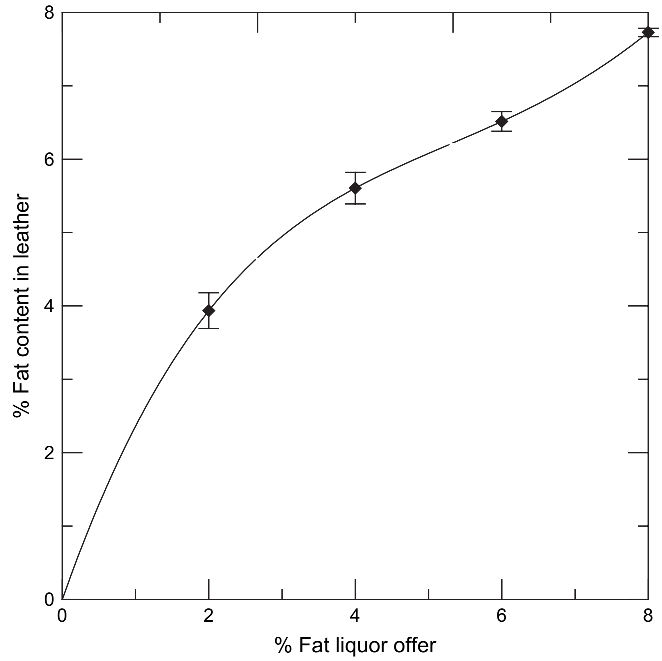

Fig. 2. Effect of amount of fatliquor 'US LIQ' offers on fat uptake in leather.

3.7. Strength property analysis of fatliquored leather

The strength properties of leathers fatliquored by the two processes were compared. Properties like tensile strength, split-tear strength, grain crack and distension were studied. The results of the tests conducted are given in Table 3. From the strength property analysis conducted, it is evident that the leather fatliquored using 'US LIQ' alone (A) has better tear strength, grain crack load and comparable tensile strength compared to leather fatliquored by experiment B. The results also indicate that comparable strength properties with experiment C. The strength property of leather fatliquored with US LIQ alone is well above the quality standards for tensile

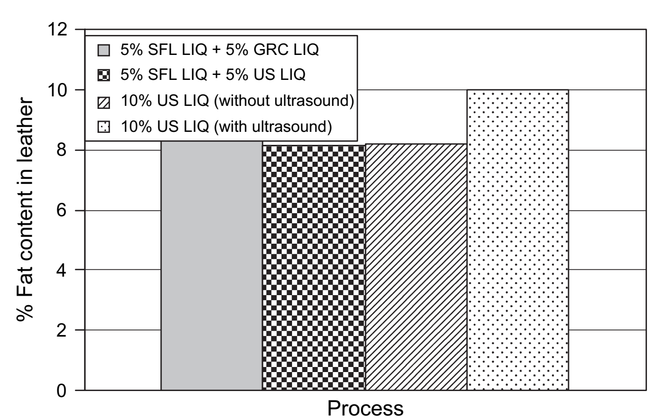

Fig. 3. Comparison of fat uptake in leather for ultrasonically prepared fatliquor with other processes.

Table 3
Strength property analysis of leather fatliquored with different fatliquor combinations

Strength property	Experiments		
	A	B	C
	10% US LIQ	5% US LIQ + 5% SFL	5% SFL + 5% GRC
Tensile strength (kg/cm^2)	293.39	333.08	366.82
Tear strength (kg/cm)	14.18	10.32	22.16
Grain crack load (kg)	8.20	8.14	8.49

strength as specified by Indian Standards Institution (ISI) for upper leathers.

4. Conclusions

The studies indicate that power ultrasound can be used effectively for the preparation of non-ionic vegetable oil fatliquor emulsion with minimum use of surfactant. Leather treated with ultrasonically prepared fatliquor emulsion 'US LIQ' either show better or comparable strength properties as compared to conventional process. Ultrasound also provides finer emulsion particle size distribution and stability, which may help in penetration as well as uniform distribution of fat in fatliquoring process. Therefore, the present study shows potential use of ultrasound in fatliquor emulsion preparation for leather application as a viable Cleaner Production option.

Acknowledgements

Authors thank Dr. T. Ramasami, Secretary, DST, Govt. of India for motivation. Prof. Dr. A. B. Mandal, Acting Director, CLRI, India for encouragement. Authors also thank Dr. N. R. Rajagopal, BITS, Pilani for encouragement, Prof. R. Kumar and Prof. K. S. Gandhi, IISc, Bangalore, for valuable suggestions. Dr. C. Muralidharan, Scientist, CLRI for valuable help. Author (V.S.) is grateful to CSIR, New Delhi, India for support.

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