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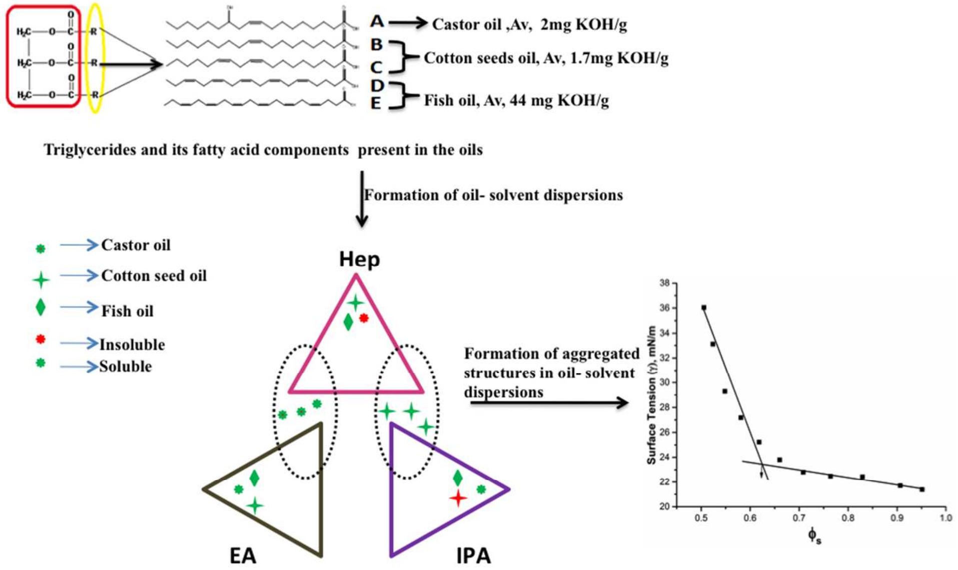

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Emulsifiers-Free Lubrication Process using Natural Oils Dispersions in Non-Aqueous Solvents for Leather

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The current practising method for the lubrication of leather uses emulsions of oils in water (fatliquors) that are prepared using emulsifiers. Precisely, the fatliquoring process is a sum of three processes–surface wetting, oil emulsion spreading and coating of oil on the fibre bundles. This method suffers from drawbacks on account of high water consumption for oil diffusion and discharge of wastewater carrying emulsifiers. This paper reports a new approach of preparing emulsifier free ready-to use oil-solvent dispersions, and their tuning to obtain required softness in leather. The oil and the solvent, both determine the size of the dispersions. The addition of non – aqueous solvent tunes the size of the dispersions, as seen for an e.g. in the case of castor oil in heptane (Hep) and ethyl acetate (EA) mixture at a volume ratio of 0.9:0.1, wherein, size is 4 nm as against 3060 nm in 0.1:0.9 mixtures. The kinematic viscosity (υ) of oil-solvent dispersions was comparable with that of commercial fatliquors. In all cases, the surface tension of oil progressively decreases up to a certain concentration and thereafter, remains almost invariant. This is suggestive of formation of aggregates of solvents. An interesting correlation between the size and lubrication performance was observed. Such of those dispersions with appropriate diameter (10< size <300 nm) and polydispersity index <0.3 had a good diffusion, leading to softer leathers. It is to be noted that to form oil in water emulsions with size in this range, a very large amount of emulsifiers/surfactants, which is invariably equal to or more than that of weight of oil is required. Surface energy of leathers were significantly altered depending on type of oil dispersions, thus in turn influencing the dispersion-leather contact and hence oil spreading on leather surface.

Introduction

The two most important challenges for leather industry are to develop products meeting the fashion/utility demands of consumers and minimizing environmental pollution from its processes. Unique features that make leather non-replaceable in several advanced materials with smart applications are its visco-elasticity, strength, air and water vapour permeability.[1] Consumer desired properties are often achieved through three processes termed as retanning, fatliquoring and dyeing carried out together employing 7-13 L water for every kilogram of leather processed (approximately 26% of the total amount required for leather processing).[2]

Hides or skins, the raw material for leather processing, were highly flexible in a live animal as the inter fibrillar spaces were occupied by water (60% of the total weight of the skin). Leather processing activity results in the removal of this water, leading to collapse and adherence of fibres to each other unless externally lubricated. Improperly lubricated leather would be bony, have poorer strength leading to low value products.[3] The process of fatliquoring is carried out in the form of 8-12% oil in water (o/w) emulsion of the fatliquors to ensure fibre lubrication through the use of oils. A fatliquor is thus described as a multi component homogeneous mixture of oils and emulsifiers. The oil component is drawn from natural and synthetic oils, and emulsifiers are anionic, cationic or non ionic. The emulsifier ensures solubility of oil droplets inside its aggregated structures, and aids the diffusion of o/w emulsion into leather matrix, through optimization of viscosity. Inside the leather matrix, the coating of oil effects separation of fibres and confers desirable physical characteristics.[4] It is important to understand here, that the chemical architecture and the physicochemical characteristics of the oils determine the interface properties and the ultimate effect on the leather. Several studies have addressed the issue of role of emulsifier and oil in a fatliquor and conditions of applications of fatliquors on the physical properties of leather.[5] In the fatliquoring process, about 85-90% uptake of the fatliquor by the leather is achieved, leaving 10-15% unexhausted matter in the waste stream.[6] Conventional fatliquors carry a large amount of emulsifiers to stabilize oils inside the aggregated structures. This is obviously not eco-friendly as waste stream carries emulsifiers, metallic soaps, alkyl phenyl ethoxylates, chlorinated paraffin oils and non-volatile hydrocarbons.[7] Besides, in view of shrinking global water resources, predicted to be 40% by 2030 (assuming the business as usual model), alternate sustainable leather lubrication process with a remarkable minimization of water is demanded.

In this study, our aim is to develop emulsifier and water-free lubrication process. In order to obtain a generalized view on applications for which extensions can be drawn to other industries, the oils were chosen from those that find applications in food, pharmaceutics, paints, cosmetics and paper. The non-toxicity and biodegradability of these oils are also well established.[8] Solvents chosen were drawn from the Glaxosmith solvent selection guide primarily based on their polarity, volatility, environmental impact including VOC and LD_{50} values (>5000 mg/kg). They provide zero discharge operation. The recovery of the organic solvents can be enabled by the safe processes of advanced distillation or filtration systems, as practiced in some dry cleaning of textiles.[9] In this study, we report the physico-chemical characteristics oil-solvent dispersions using various methods, and their lubrication effect on leather. The literature reports on the dispersions of oils in non-aqueous solvents are few, and are mainly investigated in aspects of evolving efficient bio-diesel. This study is significant and throws useful leads to evolve sustainable eco-friendly

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technologies for lubrication in leather and various other industries, using oil-solvent dispersions.

EXPERIMENTAL SECTION

Materials. Solvents for the study, viz., ethyl acetate (EA), heptane (Hep) and isopropyl alcohol (IPA), reagents di-iodomethane and decane employed for characterization were of analytical grade (99% purity). Oils-castor oil (CO), cottonseed oil (CSO), and fish oil (FO) were of commercial grade. Leather lubrication trials were carried out on chromium (III) tanned goatskins of Indian origin. Cut pieces were taken from official sampling position for the studies and all chemicals involved for the study were of commercial grade.

Formation of oil-solvent dispersions. Oil-solvent dispersions with volume fraction of oil (Φ_o) in range of about 0.005 to 0.50 were prepared by the simple process of mixing and homogenization in the magnetic stirrer at a speed of 300 - 450 rpm for a period of about 30 min. The solutions remaining transparent and uniform for a period of 5 h (the maximum duration required for penetration of the dispersion into a thick raw material such as a cow hide), as assessed from visual observation were considered stable. The stability was also assessed through determination of size, zeta potential, viscosity and surface tension of the dispersions, after a period of 5 h. Dispersions showing spontaneous layer formation or turbidity leading to layer separation were considered unstable.

Characterization of the oil-solvent dispersions. Hydrodynamic diameter (Z_{ave}) and zeta potential (Z_p) were measured in a quartz cell at 20 ± 0.1 ºC, using a Zetasizer Nano ZS (M/s. Malvern Instruments, UK), equipped with He-Ne gas laser source of wavelength 632.8 nm. The scattering intensity was measured at an angle of 173° and the data analysis performed using CONTIN method to get Z_{ave}, particle size distribution and polydispersity index. Each experiment was repeated three times. Zeta potential measurements were performed using a non-aqueous dip cell, employing built-in M3-PALS (Laser Doppler velocimetry and phase analysis light scattering) technique.

The kinematic viscosity measurements were carried out on oil dispersions at 25 ± 0.1 ºC using calibrated Ubelhode capillary viscometer. Flow time was measured in seconds with a precision of 0.01 sec. All measurements were performed in triplicate. The measurements were performed submerging the viscometer in a constant temperature bath at 25 ± 0.1 ºC. The density measurements were performed on DMA 5000 Anton Paar wherein; the temperature was maintained using built–in thermostat.

Surface tension measurements were performed on oil dispersions 25 ± 0.1 ºC on a GBX 3S tensiometerom (France), using a platinum du Nuoy ring probe, with an accuracy of 0.10 mN/m and calibrated with milli-Q water. The temperature of the solutions was maintained at 25 ± 0.1°C, using a Julabo F12 thermostat. All measurements were repeated three times.

Use of oil dispersion for leather lubrication. A commercially employed standard recipe for lubrication was modified as presented in Table S1 (Supporting Information). The process vessel employed was made of stainless steel as against those that have acrylic process viewers in their front part. Three skins were used for each trial. For leather lubrication studies 80% (w/v) dispersions of oil in solvent were employed. The process water in conventional processes was replaced with 200% (v/w) solvent on the weight of the leather. Tensile strength, percentage elongation at break and grain crack resistance was evaluated by standard protocols in a certified laboratory.[10-13] Leather being a customer centric product, hand evaluation by three experts having over a decade experience in assessing of consumer preferred properties such as softness was adopted to judge the leathers as soft, medium soft and hard.

The contact angle between lubricated leather and water, decane and di-iodomethane was measured using a HO-1AD-CAM-01 contact angle meter supplied by Holmaceopro-mechanotronics Pvt. Ltd. Image J software was used for analysis. The measurements were performed in triplicate at 28 ± 0.1 ºC.

In general practice, oils and fats fixed on to the leather is evaluated by extracting the oils and fats using diethyl ether. As this method is not viable for solvent dispersion of oil, a methodology was devised wherein, solvent left behind after processing was recovered and the oils and fats content evaluated. For this, spent solvent was distilled, residual solvent removed by a rotatory evaporator and the residual mass weight for a given volume of spent solvent determined by drying in an air oven at 80 ºC, until a constant weight was observed. The measurements were carried out in triplicate.

Scanning electron microscopic (SEM) analysis of the grain surface and cross section of leathers were evaluated using a Leica Cambridge Stereoscan 440 SEM after gold coating of the samples using an Edwards E306m sputter coater. An accelerating voltage of 5 KV was employed.

RESULTS AND DISCUSSION

Acid value and saponification value. The acid values of oils, employed in this study, met specifications reported in literature, as can be seen from Table S2 (Supporting Information). However, FO employed had a high acid value of 44 mg KOH/g of oil, indicating presence of free fatty acid, which is roughly 22% on the basis of oleic acid. It needs to be reiterated that the FO sample employed in this study is an ideal system to investigate if organic solvents can influence solubility of fatty acids and triglycerides and also provide for lubrication of leather.

Oil-Solvent dispersions. Oil-solvent dispersions with volume fraction of oil (Φ_o):solvent (Φs) in the range of 0.005:0.994 (±0.001Φs) to 0.490:0.510 (±0.020 Φs) in neat solvents and solvent mixtures were visually assessed. The observations are presented in Table 1.

Table 1. Dispersion of oils in solvents and solvent mixtures

Solvent/Solvent Mixture	Oil*		
	CO	CSO	FO
EA	Soluble	Soluble	Soluble
IPA	Soluble	Spontaneous Separation	Soluble
Hep	Spontaneous Separation	Soluble	Soluble
EA:Hep (0.1:0.9)	Soluble	-	-
EA:Hep (0.9:0.1)	Soluble	-	-
EA:Hep (0.5:0.5)	Soluble	-	-
IPA:Hep (0.1:0.9)	-	Soluble	-
IPA:Hep (0.9:0.1)	-	Soluble	-
IPA:Hep (0.5:0.5)	-	Soluble	-

*Reported for entire range of 1 to 80% w/v oil in solvent at a temperature of 28 ± 1 ºC

In a nutshell, while CO was dispersible in IPA, it remained insoluble in Hep as against CSO, soluble in Hep and insoluble in IPA. Both CO and CSO were dispersible in EA. The presence of large amount of free fatty acid in FO seems to influence its dispersion formation and by this, FO was dispersible in all three solvents. In view of the insolubility of CO in Hep and CSO in IPA, these oils were further investigated in solvents mixtures. Hep and IPA, or Hep and EA are miscible in each other in any ratio, in concurrence with literature reports.[14] The interesting observation from this study is that CO is dispersible in Hep in presence of IPA (i.e. in solvent mixtures having 9 parts of Hep for 1 part of IPA to those having 1 part of Hep for every 9 parts of IPA, by volume). Similarly, CSO was dispersible in IPA in the presence of Hep as can be seen from Table 1.

Dielectric constant (DEC) is not considered as the key parameter to determine dispersion formation. However, DEC serves as a useful guideline parameter to draw information on the interaction among components in the dispersion. DEC thus plays a significant role on the characteristics of dispersion structures. It is known that appropriate matching of DEC between solute and solvent favours mutual interaction and hence the dispersion formation. The chemical architecture of solvent and solute, one of the essential parameters determining DEC thus plays a significant role on the interaction between solute and solvent. The similarity in functional groups favours solubilization process as classically known as "like dissolves like". Based on dielectric constant at 25 ºC, polarity of selected solvents in the increasing order is Hep (DEC =1.92) <EA (DEC= 6.02)< IPA (DEC = 18.2). DEC of CO and CSO has been reported to be around 4.54 and 3.3 respectively.[15] From DEC, it is seen that CO is relatively more polar in comparison to other oils and this is possible due to the presence of ricinoleic acid, which has OH group at 12 position. Different molecular forces, H bonding, dipolar and van der Waals forces underlie the interaction between oils and solvents. The predominance of H bonding interaction is expected in CO- IPA dispersions, and this is obviously ruled out in CSO, in view of fatty acid composition. By the same reason of being non polar, CSO formed good dispersion in the non-polar solvent, Hep. Both oils are dispersible in EA and this might arise due to presence of ester group. The presence of large amounts of fatty acid in FO is expected to lower the DEC in line with understanding of fatty acids exhibiting lower DEC in range of 2.3-2.0. Also, fatty acids are expected to interact with solvents in view of free carboxyl groups. The oil dispersion in ethyl acetate may be promoted due to interaction between COOH of free acid with ester of ethyl acetate, a weak proton acceptor. In IPA, it is evident that H bonding interaction between COOH of fatty acid and OH of IPA must underlie the formation of dispersion. It is known that the polarity of solvents can be modulated in the mixtures, wherein, the DEC of the mixtures is simple additive value contributed from the solvent volume fraction. In fact, this method is popularly employed as a guiding method to prepare industrial formulations.

In this study, dispersion of oils in mixtures of solvents was investigated. Here, the aim was to use Hep for CO and IPA for CSO in the mixtures. The significant observation was that CO was dispersible in Hep:EA mixtures and CSO in Hep:IPA mixtures at volume ratios of 0.9:0.1, 0.5:0.5 and 0.1:0.9. The solvent mixtures of Hep:EA and IPA:Hep at 0.9:0.1 are of great importance. The DEC of Hep:EA mixtures at 0.9:0.1, is 2.31. The minimum enhancement in DEC of Hep by about 18% is sufficient to disperse CO in solvent mixtures consisting of Hep. The reduction in polarity of IPA by about 9% (with respect to DEC), in solvent mixtures favours dispersion of CSO in IPA containing solvent mixtures. In respect of FO, it is interesting to observe that the free fatty acid modifies the DEC and also favours H bonding interaction through COOH, thus leading to dispersion formation in all neat solvents. This observation is significant, especially in the context of evolving new fatliquor formulations in non-aqueous solvents, depending on the requirement to choose between solvent mixtures or fatty derivatives like fatty acids, fatty alcohols or amines to generate oil dispersions.

Size and stability of oil-solvent dispersions. Size distribution analysis of selected oil dispersions is presented in Fig.1.

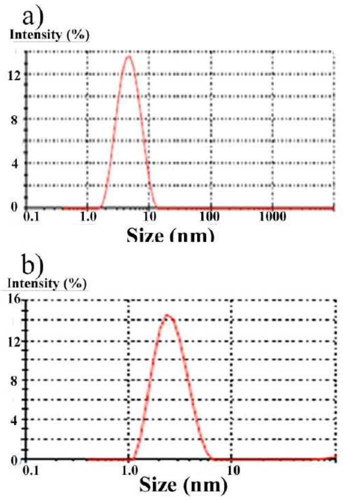

Fig.1 Size distribution for oil-solvent dispersions determined using dynamic light scattering technique for a) CO in Hep:EA (0.9:0.1), b) CSO in Hep:IPA (0.1:0.9). Measurements carried out at 20 ± 0.1 ºC

The measurements were performed on oil-solvent dispersions with Φ_o and Φ_s at 0.047:0.953 (±0.003), close to the composition of the dispersions during application process on leather, and also satisfying the conditions of measurements, by DLS. Z_{ave} values are presented in Table 2.

Table 2. Hydrodynamic diameter (Z_{ave}), polydispersity index (P_d) and zeta potential (Z_p) for dispersions of CO, CSO and FO in EA, IPA, Hep and their mixtures.

Oil	Solvent/Solvent mixture	Z_{ave} (nm)	P_d	Z_p (mV)
CO	IPA	10	0.11	-11
CO	EA	1406	0.63	-62
CO	Hep:EA (0.9:0.1)	4	0.14	+1
CO	Hep:EA (0.1:0.9)	3060	0.94	-39
CSO	EA	292	0.19	-51
CSO	Hep	174	0.19	+3
CSO	Hep:IPA (0.1:0.9)	3	0.22	+17
CSO	Hep:IPA (0.9:0.1)	88	0.30	-3
FO	EA	63	0.82	-5
FO	IPA	51	0.74	-4
FO	Hep	43	0.41	-1

It infers that most of dispersions from CO and CSO exhibited unimodal distribution of size, more so in the 2-300 nm region. For CO dispersion in IPA, Z_{ave} is about 10 nm with P_d at 0.11, as against that in EA, wherein size is 1406 nm, i.e. about 140 times as that in IPA, with P_d of 0.63. In the solvent mixtures of Hep and EA, it is significant to note that replacement of EA by 90% volume fraction with Hep, results in tremendous reduction in size, by about 350 times, along with concomitant reduction in P_d to 0.14. This means that the size of CO dispersion in Hep:EA mixtures at 0.9:0.1 volume ratio, is about 4 nm with P_d of 0.14. On the contrary, solvent mixtures with larger volume fraction of EA, i.e. EA:Hep at 0.9:0.1, size is almost double as that in EA, with a high P_d value of 0.94. In respect of CSO, P_d in the individual solvents and solvent mixtures with 90% volume fraction of IPA, show very small differences and remain at

0.22±0.03. However, the size also depends on the nature of the solvent. In the presence of EA, size is larger (292nm) in comparison to that in Hep (174 nm). Dispersion of very small size (~3 nm) can be obtained using IPA in solvent mixtures. The size distribution curves of FO in IPA and EA showed a striking difference, with bimodal distribution of major peaks. FO dispersion in Hep showed unimodal distribution of the major peak, almost similar to that observed with CO and CSO dispersions. P_d for FO in all the solvents was high, with maximum being in EA. The bimodal distribution observed with FO in EA and IPA might arise due to difference in the dispersion of the triglycerides and fatty acids in solvent, and the formation of aggregated structures of different sizes and compositions. Interestingly, an almost unimodal distribution for FO in Hep suggests formation of aggregated structures of nearly uniform size distribution. Here, the packing of fatty acid along with triglycerides in the aggregated structures can be anticipated. It is possible that the CO/CSO dispersions also consist of aggregated structures. Additional measurements using tensiometry were performed to understand oil-solvent dispersions structures.

Z_p, a measure of effective charge at the interface, generally is useful to draw information on the stability of dispersions, especially consisting of ionic species. However, in the oil-solvent dispersions, the measurements were performed to draw information on the organization of polar groups from oil and solvent at the interface. It is significant to observe that both CO and CSO dispersions in EA showed high Z_p of -62 and -51 mV (Table 2). The Z_p of oils in Hep neat solvent or solvent mixtures with larger volume fraction was very low in range of 1-3 mV. Dispersions in solvent mixtures with large volume fraction of EA or IPA, result in high –ve and +ve Z_p as observed for CO in Hep:EA (0.1:0.9), -39 mV, and CSO in Hep:IPA (0.1:0.9), +17 mV. FO dispersions showed Z_p of -5 in EA, -4 in IPA and -1 in Hep. The results demonstrate that the polarity of interface in the dispersions is significantly altered depending on the nature of oil and solvent. Quantifiable Z_p in most of the dispersions, despite non-ionic character of oil and solvents, can be explained only on the basis of proton acceptor and donor mechanism, as well documented in literature.[16] Changes in the sign of Z_p depending on nature of solvents have been shown in the case of pigment dispersions in non-aqueous solvents as well.[17] In all cases, in presence of EA, negative Z_p was observed.[18] In line with pigment dispersions, negative Z_p in EA can be explained on the basis of proton acceptor property of EA and positive due to proton donor property of IPA. The Z_{ave} size distribution and Z_p of oil-solvent dispersions measured after 5 h were reproducible within limits of experimental errors in all oil-solvent dispersions. The numbers suggest predominant dependence of Z_p on the solvents. Generally, it is considered that large Z_p value ($\underline{>}$ 30 mV) is desirable for stabilization of dispersions and the magnitude is directly correlated to stability. In the oil-solvent dispersions investigated, the difference in Z_p probably might influence the long-term stability for more than 24 h. It is to be noted for leather applications, minimum stability period is about 1½ h depending on the thickness of the leather.

Viscosity. Viscosity of oil-solvent dispersions is very important especially in the context of controlling diffusion and penetration into leather matrix during fatliquoring process. High viscous oil-solvent dispersions exhibit poor diffusion and penetration characteristics. In the oil-solvent dispersions, kinematic viscosity (υ) provides insight into the intermolecular interaction, and suitability for applications. The measured υ of selected oil-solvent dispersions is presented in Table S3 (Supporting Information). All oil-solvent dispersions, except those in IPA or mixtures with large volume of IPA with Φ_o:Φ_s at about 0.05:0.95, (almost same as that used during application) showed υ in range of 0.62 to 0.96 cSt. For CO-IPA dispersion, υ was measured as 3.49 Cst, FO-IPA, 3.57 and CSO in Hep:IPA (0.1:0.9), 2.37 cSt. For CO dispersion in the solvent mixtures with Φ_o:Φ_s at about 0.05:0.95, υ remained almost same for Hep:EA at volume ratio of 0.1:0.9 as against 16% enhancement for the mixture at 0.9:0.1 in comparison to that in EA. Similarly, in CSO, at same concentration, υ increased by about 16% for Hep:IPA mixtures at 0.9:0.1, and 235% for 0.1:0.9 mixture, in comparison to that in Hep. It is significant to mention here that v reduced tremendously by 76-94%, with change in Φ_s from 0.55 $\underline{+}$ 0.01 to 0.95$\underline{+}$0.01, the former corresponding to the dispersion before, and the later, during the application process. A representative plot of υ vs. Φ_s for CO-IPA dispersions is presented in Fig. 2.

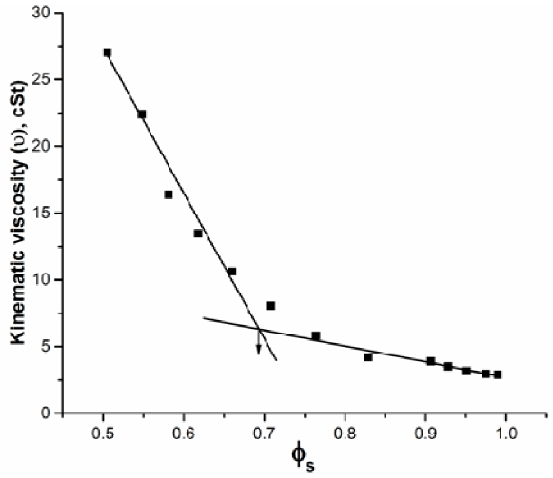

Fig. 2 Kinematic viscosity (υ) of oil-solvent dispersions as a function of volume fraction of solvent (Φ_s) of CO in IPA Temp. 25 ± 0.1 ºC

Interestingly, the oil-solvent dispersions showed a dramatic change in υ with increase in Φ_s of about 0.72± 0.056. This probably is indicative of changes in dispersion structures, which might arise due to various reasons of change in the concentration of aggregated structures and the microstructures of the bulk continuous medium in the dispersions. It is significant to mention here, that commercial vegetable oil based fatliquors at almost similar concentration of 5-weight % in water, (equivalent to oil dispersions with Φ_o:Φ_s at about 0.05:0.95), show υ in range of 1.5-3.0 cSt, depending on the nature of the active matter present. A considerable decrease in viscosity of oils in the oil-solvent dispersions basically occurs due to small viscosity of all solvents <1 cPs (Table S4, Supporting Information), except IPA and its mixture having higher proportion of IPA. In fact, this concept of lowering the viscosity of oils using suitable non-aqueous solvents is extensively investigated in the bio-diesel preparation.[19] The υ of all oil-solvent dispersions meet with requirements for fatliquoring process. Oil-solvent dispersions in fact, offer scope for tuning the viscosity over wide range, through judicious choice of solvent and solvent mixtures, and the compositions, as against the commercial fatliquors requiring appropriate choice of additional chemicals from surfactants and additives.

Surface tension measurements. Surface tension is a useful parameter to draw information on the organization of molecules at the interface and the associated changes in the bulk solutions. The surface tension profiles of CO, CSO and FO in selected solvents are presented in Fig. 3. In most of oil-solvent dispersions, surface tension progressively decreases with Φ_s up to certain concentration, beyond which it shows small variations < 3 mN/m. This profile is almost similar to that observed with surfactants. To elaborate for CO-IPA dispersion, surface tension progressively decreases from about 36 to 24 mN/m with increase in Φ_s up to 0.62 and at $\Phi_s \geq$ 0.62, the point of intersection (CΦ_s) remained almost invariant at 22± 1mN/m (Fig. 3 (a)).

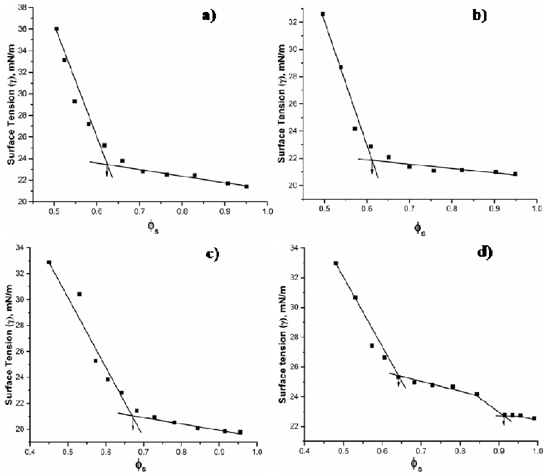

Fig. 3 Surface tension (γ) of oil-solvent dispersions as a function of volume fraction of solvent (Φ_s) from tensiometry measurements of (a) CO in IPA (b) CSO in Hep:IPA (0.1:0.9), (C) FO in Hep and d) FO in EA, Temp. 25 ± 0.1 ºC

Most of the dispersions showed clear inflection point ($C\Phi_s$), as indicated by arrow mark (Fig. 3). This is similar to critical micelle concentration (cmc) observed with surfactants.[20] In the first place, the decrease in surface tension of oil with addition of solvent, suggests that the solvent brings about modifications in the organization of oil molecules adsorbed at the interface. This can happen through adsorption of solvent molecules along with oil at the interface, and formation of aggregates in the bulk phase leading to changes in the microstructures of the oil. It is worth mentioning here, that alcohols especially from propanol onwards are reported to be amphiphilic and form aggregates in alcohol-water mixed solutions.[21, 22] Drawing analogy and based on the surface tension variations, it is reasonable to expect that oil dispersions consist of aggregates of solvent molecules. The size and the number of aggregates are expected to change with increase in Φ_s beyond $C\Phi_s$. It is interesting to observe the oil–solvent dispersions exhibit $C\Phi_s$ which falls in range of 0.64± 0.06. Quite interestingly, for FO-EA dispersions, two break points in surface tension plot (Fig. 3(d)) was observed. We presume that this is suggestive of formation of aggregated structures that vary significantly in size and microstructures. Interestingly, this observation correlates with bimodal distribution observed in size measurements.

Discussion on oil-solvent dispersions. The surface tension profile of oil-solvent dispersions demonstrates the formation of solvent aggregates. Under conditions of the present study, the presence of water in oils and solvents, cannot be ruled out. In presence of small amounts of fatty acids and water, as in case of castor and cottonseed oils, it is reasonable to consider the close resemblance of oil-solvent dispersions to swollen reverse aggregates or in other words, reverse micelles.[23] The microstructures of the dispersions are of course dependent on the composition of the oil-solvent dispersions. At $\Phi_s < C\Phi_s$, it is possible that the solvent organizes at air/oil-solvent dispersion interface and hence changes the microstructures of oil in the bulk phase, similar to that observed with alcohol-water mixtures.[21, 22] This phase is considered similar to oil in solvent dispersions. At $\Phi_s \geq C\Phi_s$, the dispersions predominantly consist of solvent aggregates, similar to reverse micelles, and they are in equilibrium with excess solvent. In respect of solvent mixtures, for e.g. Hep:IPA at different ratios, Hep is expected to act as co-solvent in the reverse micelle structures. Similar aggregated structures of reverse emulsion structures can be anticipated in FO dispersion. Here, in view of large amounts of fatty acids, the difference in the partition of the solvent between the fatty acid and triglycerides is expected to significantly influence the microstructures of the reverse emulsion phase. The difference is especially evident in EA, wherein, bimodal distribution in size and two break points in surface tension profile were observed. The oil-solvent dispersions especially from fish oil consisting of large amount of free fatty acid (~ 22 %) can be considered similar to the surfactant free reverse micro emulsion phase structure established for oleic acid.[24] The difference in the inflection points between surface tension and viscosity curves, amounting to about 10% in Φ_s, must be arising due to sensitivity of the response of the changes in the microstructures to the respective measurements. Based on the size varying over the range of 3 to about 300 nm, the dispersions can be described as reverse emulsions or micro emulsions. Those dispersions especially, CO-EA or CO-Hep:EA (0.1:0.9) can be considered as macro emulsions.

The oil-solvent dispersions, reported for the first time in this study, are considered similar to detergent free reverse emulsions, as reported in detail for Hep/IPA/ water, which carry immense potential for enhancement of enzyme activity.[21, 22] It is pertinent to mention here, that fatty alcohols reverse micro emulsion phase structures favour solubilization of methanol in triglycerides.[25]

Performance evaluation. Selected oil-solvent dispersions were applied on leather and assessed for their performance properties by a team of experts (Table 3).

Table 3. Leather softness assessment by industrial experts in visual/hand evaluation

Oil	Solvent/Solvent mixture	Assessment
CO	IPA	Soft
CO	EA	Hard
CO	Hep:EA (0.9:01)	Medium soft
CO	Hep:EA (0.1:0.9)	Hard
CSO	EA	Medium soft
CSO	Hep	Hard
CSO	Hep:IPA (0.1:0.9)	Medium soft
CSO	Hep:IPA (0.9:0.1)	Hard
FO	EA	Soft
FO	IPA	Soft
FO	Hep	Soft

It can be seen that oil dispersions play a significant role in providing lubrication effect and a very interesting correlation between the physico-chemical characteristics of oil dispersions and performance on leather could be established. Striking influence of nature of oil dispersion on the performance can be seen in CO dispersions. With EA in combinations with Hep at high volume ratio (Hep:EA, 0.1:0.9), leathers that have a papery feel is obtained as against those solvent mixtures with low EA (Hep:EA, 0.9:0.1) where medium soft leathers were obtained. Performance of CSO dispersions in Hep or solvent mixture with high volumes of Hep, such as 0.9:0.1 (Hep:IPA), was poor, i.e. such formulations provided for hard leathers with surface deposition of oil. Interestingly CSO dispersions in EA or those with low volume Hep, such as Hep:IPA (0.1:0.9) resulted in medium soft leathers. In all cases, FO dispersions provided for soft leathers.

The hierarchy of organization of collagen covers a broad scale as fibrils and fibres in scale of 1.5 to 500 nm, and fibre bundles and membrane at 50-500 microns. It is worthwhile to mention here that the pore size distribution determines the diffusion of water droplets as demonstrated in the recent study on the smart leathers.[26] In fatliquoring process, lubrication of leather is dependent on penetration of oil-solvent dispersion and the interfacial processes such as spreading and coating on fibrils. An extensive analysis of lubrication effect and the size of oil-solvent dispersions throw important leads. It infers that hard leather or surface deposition of fat was obtained in respect of dispersions showing $Z_{ave}> 1400$ nm with $P_d > 0.6$, typically as observed with CO in EA or Hep:EA mixture at 0.1:0.9. Dispersions with size < 10 nm and $P_d< 0.3$, resulted in leather with good softness, as in CO in IPA or CSO in Hep:IPA (0.1:0.9) mixtures. The dispersions with size between 10 and 300 nm, with $P_d< 0.3$, result in medium soft leathers. An exception was observed in respect of CSO in Hep or Hep:IPA (0.9:0.1) mixture as it yielded hard leather and showed surface deposition. We believe that low Z_p values at about +3 mV and -3 mV might account for the surface deposition. In respect of CO in Hep:EA (0.9:0.1), although Z_p is low, in view of size <10 nm, penetration is facilitated and hence excellent lubrication effect. Through and through penetration across the leather matrix and hence good lubrication was observed for FO in IPA or EA showing bimodal distribution, with size at two different scales of about 35 nm and 0.6 to 1.4 μm, and in Hep with size <100 nm. The surface tension and kinematic viscosity parameters of 5% oil- solvent dispersions, about 0.95:0.05, Φ_s:Φ_o, (during application process) are comparable to commercial fatliquors applied in aqueous medium and therefore, establish the suitability of oil-dispersions for the lubrication process. The surface tension or viscosity parameters do not seem to influence the lubrication aspects, similar to that observed with commercial fatliquors. Elaborate investigations on these aspects are required to understand the actual mechanism of lubrication process in aqueous and non-aqueous media. It can be understood that in the oil-solvent dispersions, demonstrated to consist of reverse emulsion phase structures, the interaction between the solvent and the oil primarily brings about changes in organization and packing characteristics of the oil. Essentially, three important interfacial processes, viz., wetting, spreading and coating dictate the process of lubrication inside the leather matrix. Both chemical architecture and the interaction of oil with the solvent influence the interfacial process significantly. Influence of chemical architecture on the packing characteristics can be seen in the examples of monolayer films of stearic acid and oleic acid at the interface.[27] Considering that the solvents alter packing characteristics and consequently the molar volume, it is reasonable to presume that solvents act as plasticizers and control the spreading and coating of oils on the leather fibres and thereby influence lubrication properties.[28] The plasticizing effect of oils in rubber is well known. It is to be mentioned here that the drying of the lubricated leather as controlled by evaporation rate of the solvents also plays a significant role on the lubrication effect. Especially in solvent mixtures, azeotropic boiling point and composition of azeotropic mixtures both are expected to play a predominant role in the coating of oil film over the collagen fibres.

Lubricated leathers were evaluated for their physical strength, results of which are presented in Table 4. The leathers exhibited tensile strength in range of 13-19 N/mm^2 and tear strength 33-58 N/mm. These values are within the range required. Similarly, grain crack strength or distension at grain crack falls within the required range of 10-38 and 7-11 mm respectively. The results suggest that oil in solvent dispersions studied as a part of this work provide required strength characteristics, and do not deteriorate the organization of fibre structures. It is to be noted that all lubricated leathers exhibited required strength characteristics, irrespective of lubricating effect. This may have arisen due to various reasons of heterogeneity of the skin structures from the same species.

Table 4. Strength characteristics of leathers lubricated with oil – solvent dispersions.

Oil	Solvent	Tear strength (N/mm)	Tensile strength (N/mm^2)	Load at grain crack (kg)	Distension at grain crack (mm)
CO	IPA	45	17	24	10
CO	Hep:EA (0.9:0.1)	43	15	10	7
CO	Hep:EA (0.1:0.9)	33	15	24	11
CSO	EA	41	15	16	9
CSO	Hep:EA (0.9:0.1)	58	16	14	8
FO	EA	41	16	22	11
FO	IPA	56	19	38	11
FO	Hep	40	16	20	11

The oil left in the float after aided diffusion was measured and percentage uptake by leather evaluated (Table 5).

Table 5. Uptake of oils from the solvent bath carrying oil-solvent dispersions after fatliquoring of leather

Oil	Solvent/Solvent mixture	Uptake by leather (%)
CO	IPA	81
CO	Hep:EA (0.9:0.1)	75
CO	Hep:EA (0.1:0.9)	69
CSO	EA	78
CSO	Hep:IPA (0.9:0.1)	67
FO	EA	84
FO	IPA	86
FO	Hep	85

It was observed that FO and CO in IPA showed about 80% uptake. About 75±3% uptake was obtained with CO in Hep:EA (0.9:0.1) mixture and for CSO in EA. Uptake levels were lower at around 65-70% for dispersions of CO in Hep:EA (0.1:0.9) and CSO in Hep:IPA (0.9:0.1). In the first place, the uptake, especially in FO and selected CO and CSO is comparable with conventional fatliquoring process in aqueous medium. Quite significantly, it infers that there is a correlation between the uptake levels and organoleptic properties. Considering that physico-chemical characteristics of oil dispersions influence the lubrication effects as discussed in detail in previous session, it follows that size and Z_p characteristics of the oil dispersions determines uptake of oils by leather. The results on exhaustion are in agreement with lubrication. To elaborate, oil uptake > 80% resulted in soft leather (e.g. FO dispersions), ~ 75%, medium soft (CO in Hep:EA, 0.9:0.1) and ~ 67%, hard leather or surface deposition (e.g. CSO in Hep:IPA (0.9:0.1)).

The SEM images of oil-solvent dispersion lubricated leather are presented in Fig. 4. A simple comparison of the features of leather treated with EA (without oil (control)) and the oil dispersions at the same magnification scale, throw explicit difference. The oil dispersions treated leather showed features of fibre bundles as against the control (Fig. 4a). CO in IPA (Fig. 4b) and FO in Hep (Fig. 4d) clearly demonstrated features of fibre bundles. On the contrary, SEM of leather from CSO in Hep:IPA (0.9:0.1) showed non-uniform features, though fibre bundles were visible. It infers that well lubricated and soft leather showed features of fibre bundles as against the hard leather and the control. As against the grain features discussed above, the cross-sectional view (Fig. 4e-f) of leathers lubricated with CO in EA (hard) and CSO in Hep:IPA (0.1:0.9) provided information on the fibre packing. It is interesting to observe that the medium soft leather from CSO in Hep:IPA (0.1:0.9), showed feature of good fibre splitting as against CO in EA that was hard. It is known that lubrication of the fibres is effected by coating of oil resulting in a reduction in the cohesion between the fibres, and thus fibre density. SEM image of leather lubricated with CSO in Hep:IPA (0.9:0.1) is classic of good lubrication as against CO in EA, in accordance with the assessment of the lubricated leathers by experts.

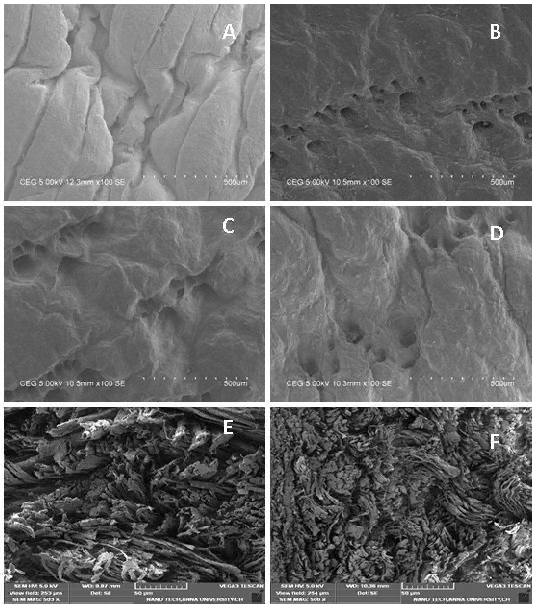

Fig. 4 SEM images of leather lubricated with oil-solvent dispersions. a) Grain surface - EA alone, b) grain surface- CO in IPA, c) grain surface-CSO in Hep:IPA (0.9:0.1), d) grain surface - FO in Hep, e) cross sectional view–CSO in Hep:IPA (0.1:0.9) and f) cross sectional view-CO in EA.

Surface energy characteristics. The leather treated with different oil dispersions was evaluated for surface energy characteristics to understand the effect of oil dispersions. For this, modified Young equation as detailed below was employed.[29]

$\gamma_{lv}(1+\cos\theta) = 2[(\gamma_s^d \times \gamma_l^d)^{1/2} + (\gamma_s^p \times \gamma_l^p)^{1/2}]$ ……………….Eqn.1

Where γ_{lv} was surface tension of liquid, γ_l^d was dispersion component of the surface tension of liquid, γ_l^p the polar component of the surface tension of liquid. Surface energy (γ_{sv}) of leather was calculated from

$\gamma_{sv} = \gamma_s^p + \gamma_s^d$ ………………… Eqn. 2

Where, γ_s^p is the polar component of the surface energy of leather, γ_s^d is the dispersion component of surface energy of the leather.

The surface energy (γ_{sv}) of lubricated leathers calculated from static contact angle measurements is presented in Table 6. The polar (γ_s^p) and dispersion (γ_s^d) components of γ_{sv} computed from eqn.1 are also presented. Here, two sets of liquids, water and decane, and water and di-iodomethane were employed for contact angle measurements. The contact angle of decane is almost zero in all leather samples. This means that the γ_s^d remains same, which is calculated to be 27.5 mN/m. The contribution of γ_s^p and γ_s^d to γ_{sv} throws very interesting results. From the set of liquids, water and decane, γ_s^d is > 92% in majority of cases, suggesting comparatively non-polar leather surface. However, in respect of CO in Hep:EA (0.1:0.9) and CSO in EA, γ_s^d is 75±2%, and γ_s^p is larger at 25 ±0.2%, in comparison to other leathers, such as those lubricated with CO in Hep:EA (0.9:0.1) or CSO in Hep:IPA (0.9:0.1) and FO in IPA. It is significant to note that there is an excellent agreement of results on γ_s^d or γ_{sv} with those from other set of liquids, viz., and water and methyl iodide.

Table 6. Surface Energy (γ_{sv}) (mN/m), contribution in % of polar (γ_s^p) and dispersion (γ_s^d) components to γ_{sv} from static contact angle of two sets of liquids, a) water and decane and b) water diiodomethane.

Oil	Solvent	Water – Decane contribution (%) to γ_{sv} of		γ_{sv} (mN/m)	Water – diiodomethane contribution (%) to γ_{sv} of		γ_{sv} (mN/m)
		γ_s^p	γ_s^d		γ_s^p	γ_s^d	
CO	IPA	55	45	60.9	29	71	71.5
CO	Hep:EA (0.9:0.1)	6	94	29.3	5	95	30.8
CO	Hep:EA (0.1:0.9)	23	77	35.6	27	73	33.9
CSO	EA	27	73	37.5	25	74	38.0
CSO	Hep:IPA (0.9:0.1)	8	92	30.2	6	94	32.9
FO	IPA	4	96	28.7	2	98	32.8
FO	Hep	4	96	28.6	5	95	34.1

Here, variation in γ_s^p contribution and γ_{sv} is less than 6% (in comparison to values obtained using water and decane). In respect of FO treated leathers, the variation in γ_{sv} is about 15%. This might be due to different nature of the dispersion structures, consisting of fatty acid. A definite influence of the polarity of solvent on the γ_s^p can be recognized. For an example, γ_s^p of leather from CO in Hep:EA (0.9:0.1) is almost negligible, as against the 0.1:0.9 mixture, wherein, γ_s^p was 23 %. Correlating this with Z_p of dispersions and also the polarity of solvents, it is reasonable to conclude that the dispersions with low Z_p result in less polar leather surface, or in other words, more non-polar characteristics. In line with this, it is significant to note that all FO treated leathers were predominantly non-polar. The surface energy characteristic of leathers lubricated with CO in IPA was very different, wherein, contribution from the γ_s^p and γ_s^d components was very close at 45 and 55%. In this case, the γ_{sv} was 60.9 mN/m. The numbers suggest more polar characteristic of the leather and this can be anticipated considering larger polarity of IPA. The role of H bonding interaction between IPA and ricinoleic acid in the dispersion that controls the physico-chemical characteristics also cannot be ruled out. It is significant to observe a large mismatch of γ_s^p in leather lubricated with CO in IPA dispersion. The contribution of γ_s^p from water and decane has been calculated to be 55 as against 29% with water and methyl iodide. A close examination of the contact angle reveals that the difference is mainly due to zero contact angle of methyl iodide. Based on the concepts of spreading of a liquid on the solid substrate, it is understood that spontaneous spreading of a liquid on the solid substrate is promoted when the surface tension of the liquid, γ_{lv} is less than γ_{sv}. By this, it infers spontaneous spreading. Zero contact angle for methyl iodide on the leather lubricated with CO in IPA is anticipated, in view of γ_{lv} of methyl iodide (50.8 mN/m) being less than γ_{sv} (60.9mN/m), and this is in line with observed results. It is to be noted that γ_{sv},γ_s^p and γ_s^d cannot be related to functional properties of the leathers and this might arise due to the fact that surface energy from contact angle measurements is related to the topmost layer of the leather matrix, and the expert assessment on the organoleptic properties, across the leather matrix from grain through cross-section to flesh. A definite correlation of the tuning of surface energy and the polar component through choice of solvent and oil has been demonstrated.

CONCLUSION

A new methodology to replace the use of emulsifiers and water in the lubrication step (fatliquoring) of leathers is reported. From the investigations comprising three different types of oils and solvents, it has been concluded that the oil-solvent dispersion formation can be modulated through appropriate matching of the dielectric constant of the oil with that of the solvent or solvent mixture. The oil-solvent dispersions showed optimum size distribution and υ that match with the conventional fatliquors. It is important to mention here that a large amount of emulsifiers is required to meet with the optimum size and υ parameters in the commercial fatliquors. The oil-solvent dispersions are considered to consist of solvent aggregates from surface tension measurements. The oil and solvent characteristics determined the size distribution of the aggregates. The presence of large amounts of free fatty acid as in case of FO, leads to bimodal distribution in IPA and EA. Such of those dispersions with a diameter between 10 and 300 nm and polydispersity index less than 0.3 had good diffusion into the leather and result in medium soft to soft leather. In essence, for given oil, by tuning the properties of oil-solvent dispersion, a range of leathers that were papery, hard, medium soft or soft is produced. An interesting correlation between polar component of surface energy of leather and the solvent is established.

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AUTHOR INFORMATION

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ABBREVIATIONS

CO-Castor oil, cPs- Centipoise, CSO-Cotton seed oil, DEC- Dielectric constant, EA-Ethyl acetate, FO-Fish oil, Hep-Hepatne, HLB-Hydrophilic-lipophilic balance, IPA-Iso propyl alcohol, KOH-Potassium hydroxide, LD-Lethal dose, O/W- Oil in Water, P_d-Polydispersity index, SEM- Scanning electron microscopy, K-Specific conductivity, V-Volume, W-Weight, Z_{ave}- Hydrodynamic diameter, Z_p-Zeta potential, Φ_o- volume fraction of oil, Φ_s-volume fraction of solvent, $C\Phi_s$-point of intersection, υ -kinematic viscosity, γ- Surface tension, γ_l^d - dispersion component of the surface tension of the liquid, γ_l^p -polar component of the surface tension of liquid, γ_{lv} -surface tension of liquid, γ_s^d -dispersion component of surface energy of the leather, γ_s^p -polar component of the surface energy of leather, γ_{sv}-surface energy