



"The new 'ion age' – a revolutionary new technology for leather manufacture?"

Andy Abbott^a, Paula Antunes,^b Keib
Mmapatsi^b and **Will Wise**^b

^aDepartment of Chemistry, University of Leicester, Leicester, LE1 7RH, UK

^bInstitute for Creative Leather Technology, University of Northampton,
Northampton, NN2 7AL, UK





Water Water Everywhere

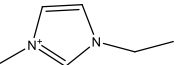
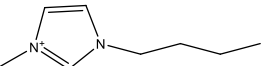
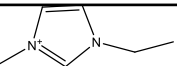
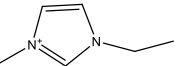
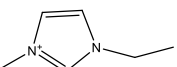
- For > 6000 year leather technology has been water based.
- Effluents are heavily polluting with $\sim 35 \text{ m}^3$ water used per tonne hide produced.¹
- Solutes must be removed before water is returned to the environment.
- Is there an alternative?

1. H. C. S. Ozgunay, S. Colak, M. Mutlu, F. Akyuz, *Pol. J. Env. Stu.* 2007, **16**, 867-873.

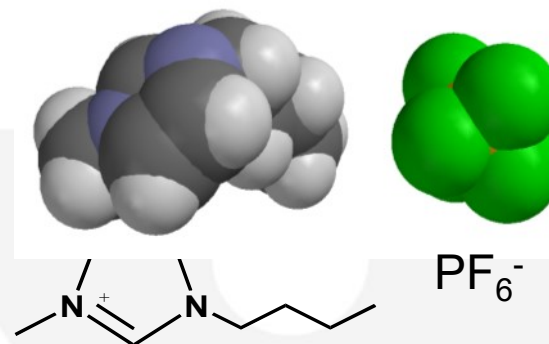


Ionic Liquids

- Salts which are fluid at ambient temperatures.
- Non flammable
- Negligible vapour pressure

Cation	Anion	m.pt. / °C
Na ⁺	Cl ⁻	801
K ⁺	Cl ⁻	772
	Cl ⁻	87
	Cl ⁻	65
	NO ₃ ⁻	38
	AlCl ₄ ⁻	7
	CF ₃ CO ₂ ⁻	-14

Principle is to use large, non-symmetrical ions – lower lattice energy



Expensive – manufacture, registration, environmentally

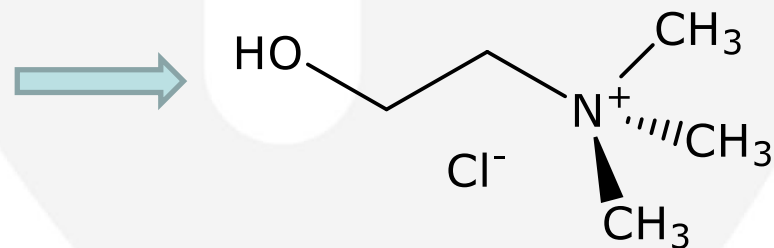


Deep Eutectic Solvents (DES)

- Mixture of a salt and a hydrogen bond donor (HBD)
- Use choline chloride as a non-toxic (vitamin B4 RDA – 550mg) salt.
 - Produced on Mt scale (chicken feed additive) hence costs about 4 Euro/kg
 - Non-toxic and biodegradable



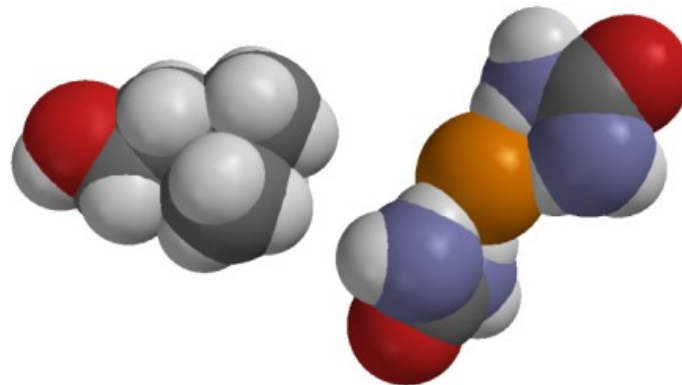
E factor = 0





Deep Eutectic Solvents (DES)

- Many HBDs are inexpensive (c.a. €1/kg), non-toxic, non-flammable, biodegradable, versatile ($>10^5$ liquids), unusual solvent properties.
- Dissolve a wide range of solutes e.g. salts, polar organics, metal oxides, amino acids, enzymes and surfactants.
- Solvent properties can be markedly changed by altering the HBD





Making DES's is Simple





Concept for Leather Processing

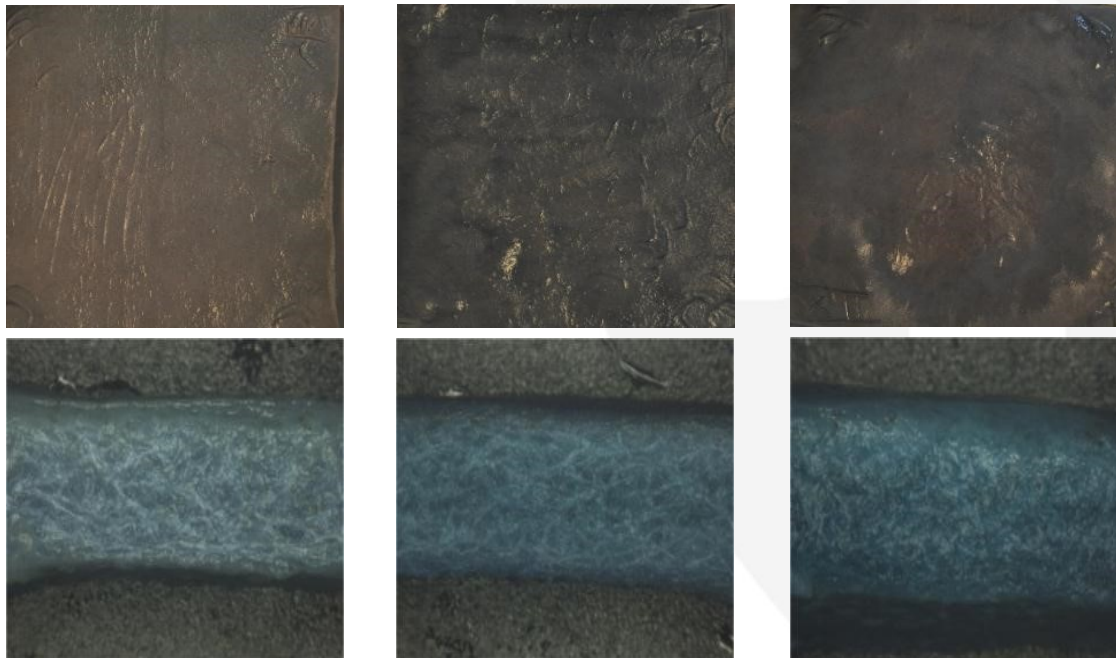
- Make the active ingredient into a liquid rather than dissolving it into a solvent.
- These are “liquid actives” rather than solvents – liquefy the tanning agent through complexation.
- High concentration – negligible loss
- Less aqueous waste





Mineral Tanning

- Can formulate Cr(III) into a number of DES's.
- Good penetration into hide at pH4
- No apparent loss of collagen structure



Chromium Tanning

- Applied as a cream – little wastage
- Mechanically remove excess and reuse

Tanning agent	Cr content %	T_{Shrink} /°C	Thickness /mm	Tensile strength/MPa	Elongation /%
Conventional Cr	3.04	109	3.02	32.6	50.8
ChCl:2 CrCl ₃ .6H ₂ O	2.27	71	2.55	37.7	39.3
2 Urea: 1 CrCl ₃ .6H ₂ O	3.43	80	2.84	27.4	34.9
2 Urea: 1 KCr(SO ₄) ₂ .10H ₂ O	3.52	83	3.10	30.3	42.5

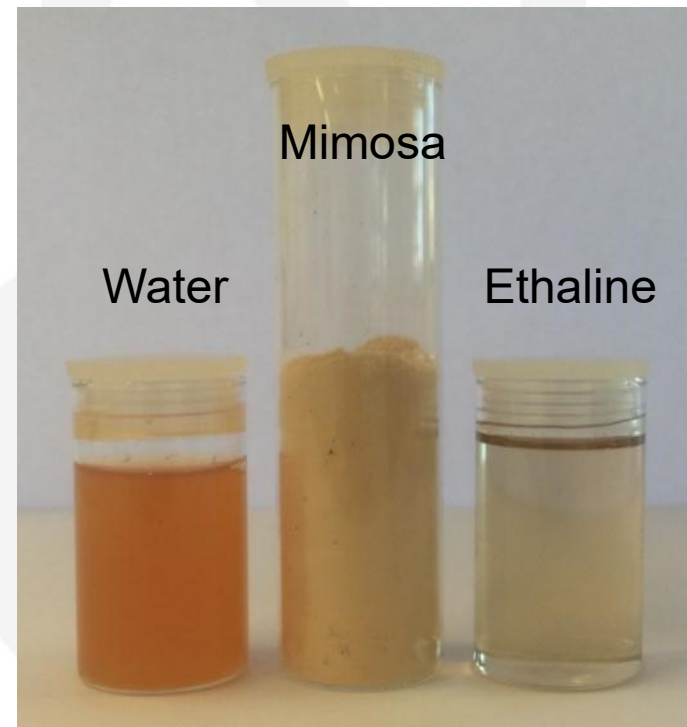
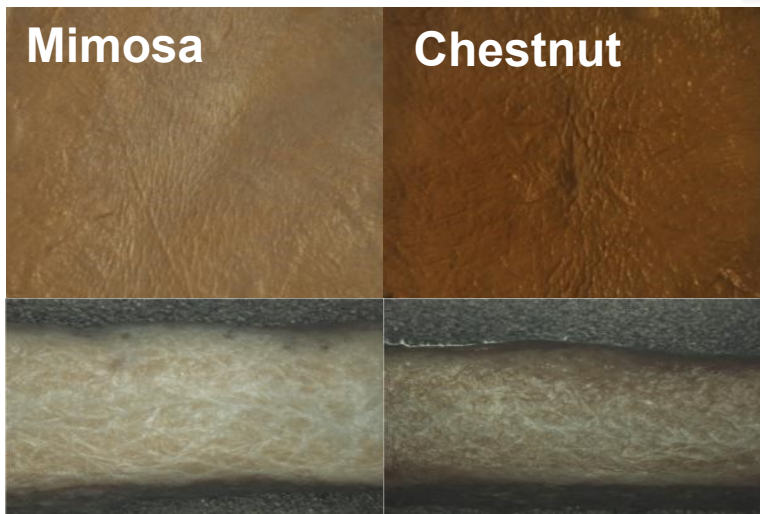
- Similar mechanical properties to aqueous chromium sulfate process
- Not an optimised process – fast penetration - wash with sodium sulphate (86 °C) – raise pH to 8 (96 °C)





Vegetable Tanning

- Vegetable tans dissolve rapidly in DESs forming clear solutions
- Polyhydroxylated species form strong hydrogen bonds with salts
- Hide samples rapidly take on colour



Vegetable Tanning

- Applied as a cream or lab scale pits
- Tensile strength similar to chrome tanned material
- Greater elongation at break

Tanning agent	T_{Shrink} / °C	Thickness / mm	Tensile strength / MPa	Elongation / %
Mimosa	83	2.92	56.6	50.5
Chestnut	78	2.62	43.2	65.7

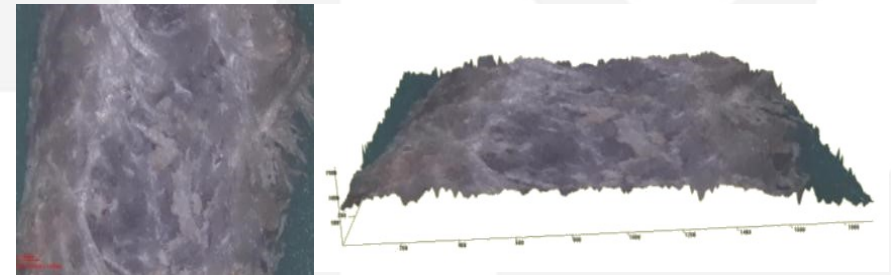
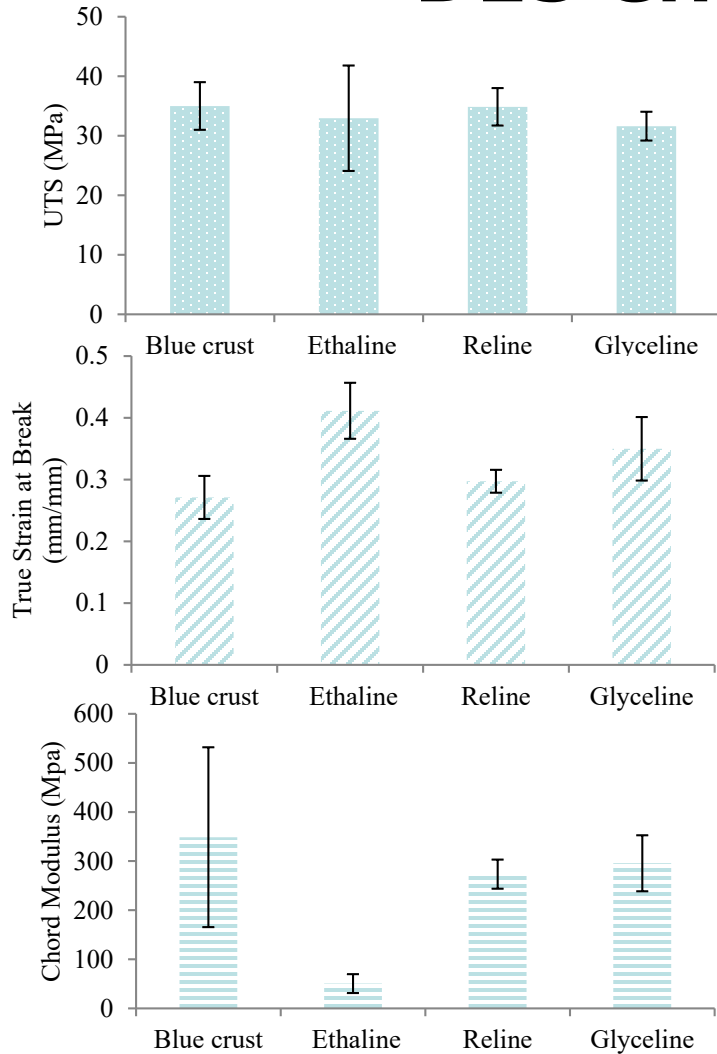
- Decreased processing time
- Decreased effluent





DES effects on leather

- Wet blue immersed in 3 DES.
- Fibrous structure retained despite high ionic strength
- Opens up pore structure



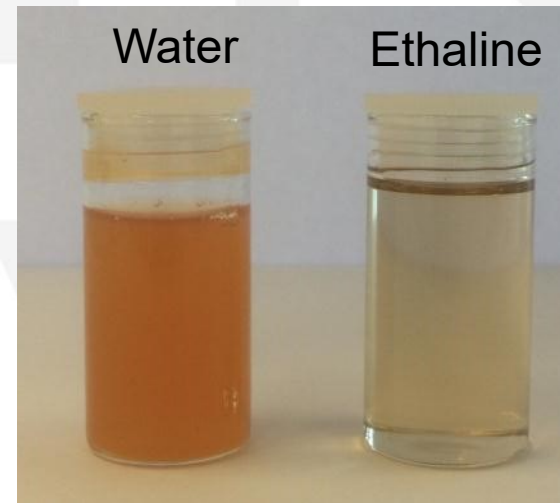
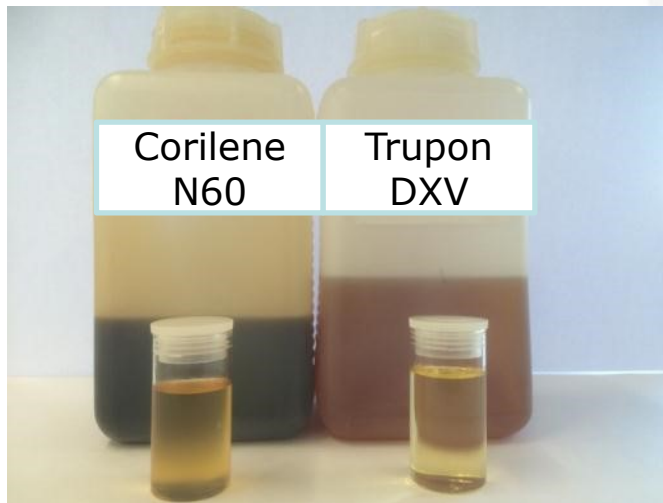
- Little effect on strength
- Ethaline increases strain and decreases chordal modulus
- In-built fatliquoring?





DES for fat liquoring

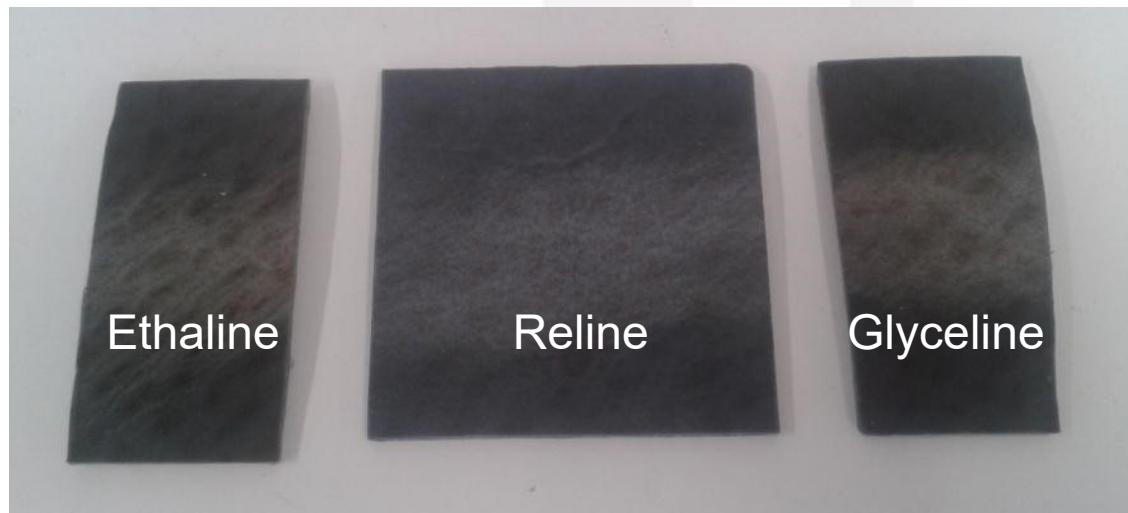
- Fatliquors often have solubility issues in water – often requiring emulsifiers or chemical modification.
- DESs are amphiphilic – they dissolve both polar and non-polar solutes.





DES for fat liquoring

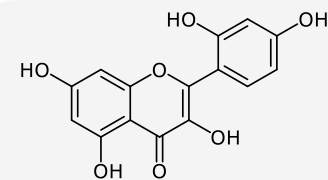
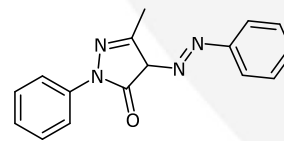
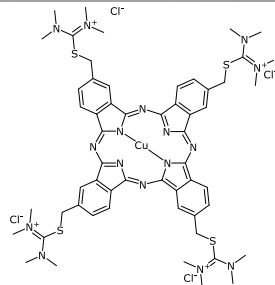
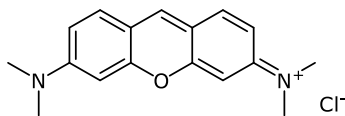
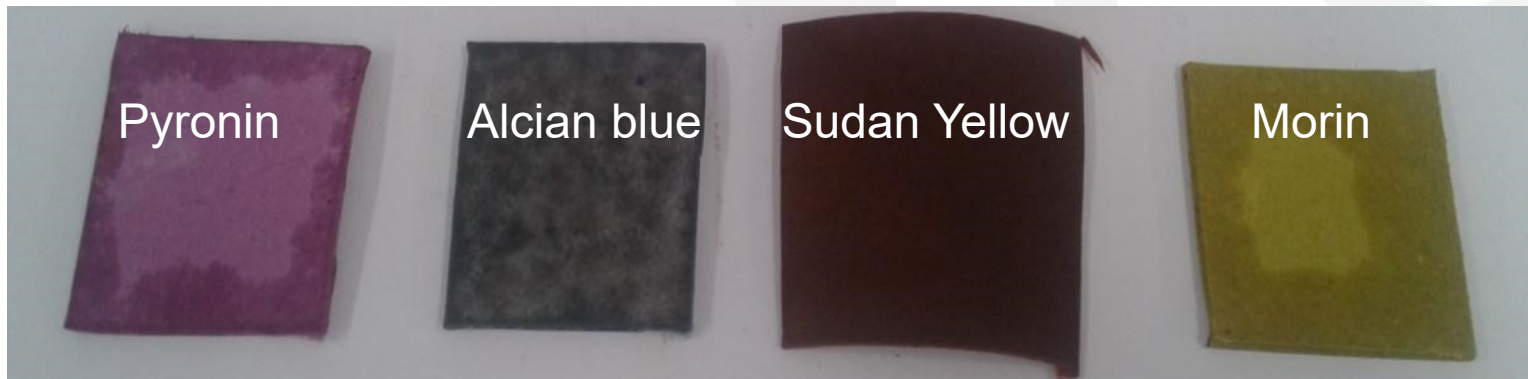
- Ethaline, Reline and Glyceline were used with Trupon DVX (2 wt%).
- A mobile phase was present within the leather.
- Ethaline 200/ Trupon samples were scuff proof.





DES for dyeing

- Conventional water soluble dyes penetrate slowly
- Water insoluble dyes were investigated.
- Sudan yellow, Alcian blue, Pyronin and Morin were easily dissolved and penetrated quickly.





Particulate incorporation

- Because the DES opens the pore structure is it possible to incorporate particulates into the structure?
- Graphite penetrates well into the leather
- Colloidal dispersion of graphite is very stable
- Potentially we can make black suede
- Particles do not wash out
- Ability to make leather conducting?

Graphite and
Water

Graphite and
Ethaline





Conclusions

- These are very early results.
- DES can be used to tan.
- Ethaline imparts interesting, new properties into crusted blue leather.
- DES can be used to transport liquids and particulates into leather.
- Leather thus can be dyed, fat liquored and potentially retanned using DES.
- Newest results show all three post-tanning steps are possible in one pot.





Further Information

- Andrew P. Abbott, Omaymah Alaysuy, A. Paula M. Antunes, Andrew C. Douglas, Jeffry Guthrie-Strachan, and William R. Wise; *ACS Sustainable Chem. Eng.*; **2015**; 3 (6); 1241–1247
- Contact: will.wise@northampton.ac.uk

