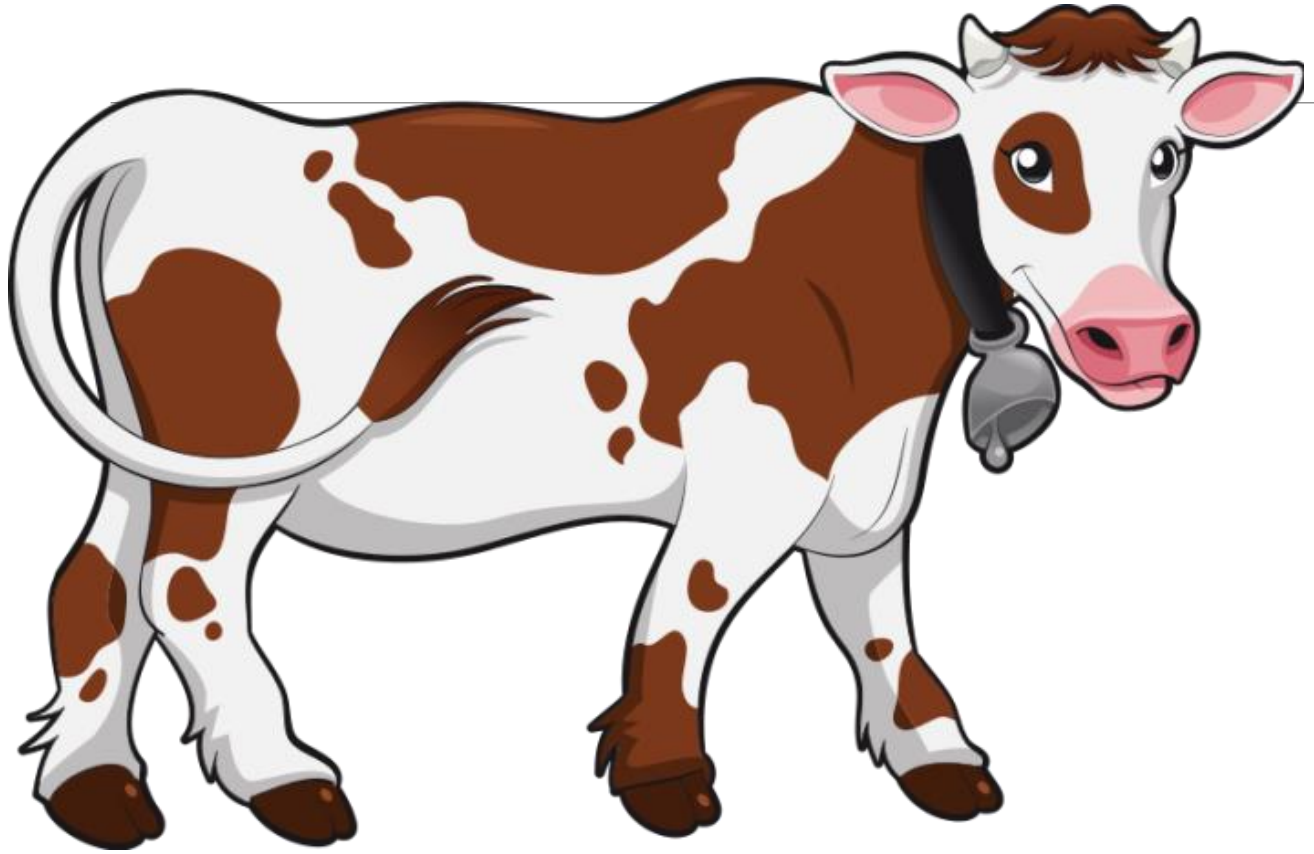
GreenChem UBC

Greening the Tanning Industry

Chip-Chat Wednesday 19th Oct

Sathish,M., Silambarasan, S., Madhanb, B., Rao, J. R.; **Green Chem.**, *2016*, Advance Article

Tanning Leather

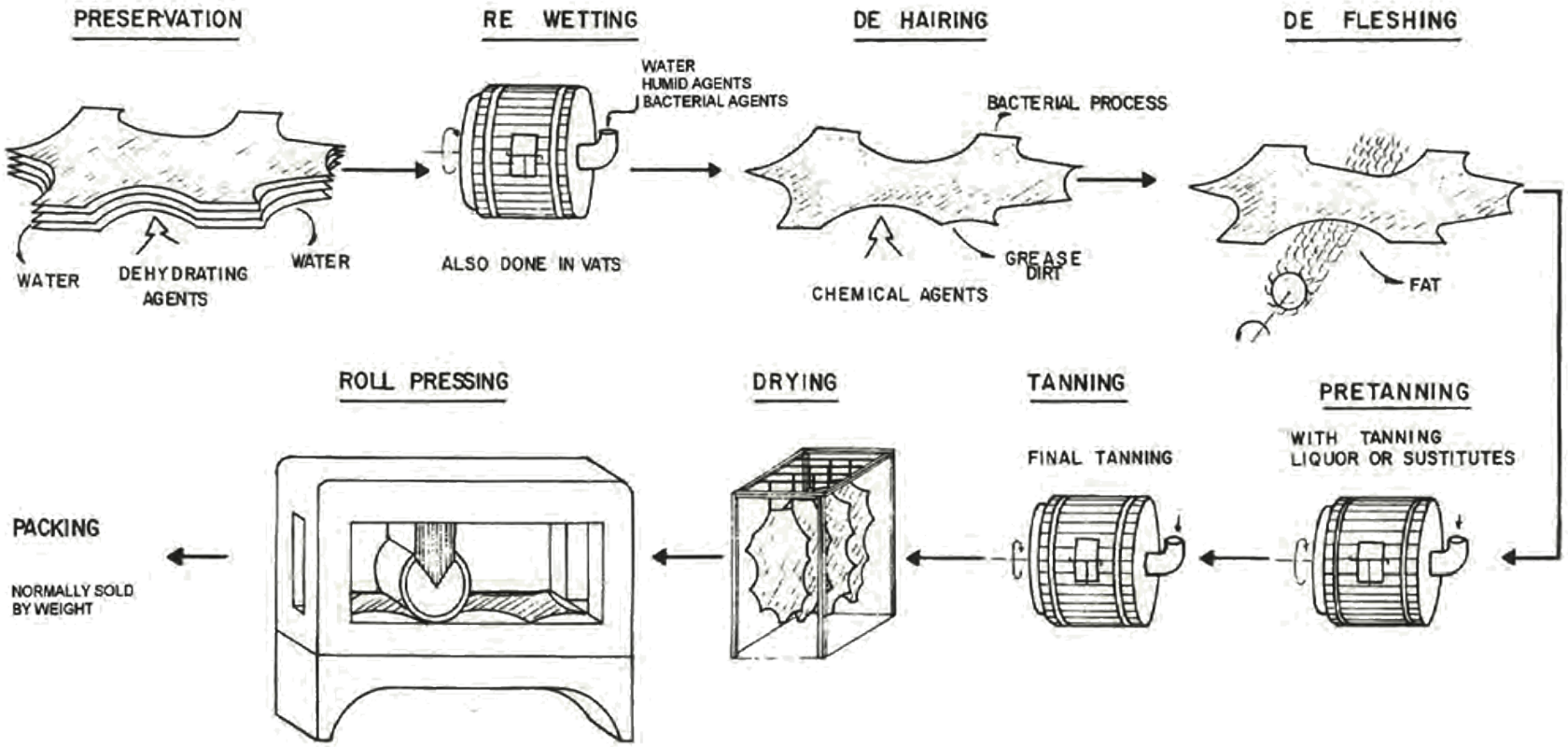


Altering protein structure of the skin

- Live skin is soft, flexible, very tough with the ability to allow water vapour to pass out, but it will not allow water
- Tanning retains the skin's natural properties, to stabilise its structure and chemically processes it so it will no longer be subject to putrefaction
- Skin is made up of many bundles of interwoven protein fibres which are able to move in relation to one another when the skin is alive
- When skin dies, these fibres tend to shrivel and stick together
- Tanning permanently fix the fibres apart by chemical treatment, and to lubricates them so they can move in relation to one another

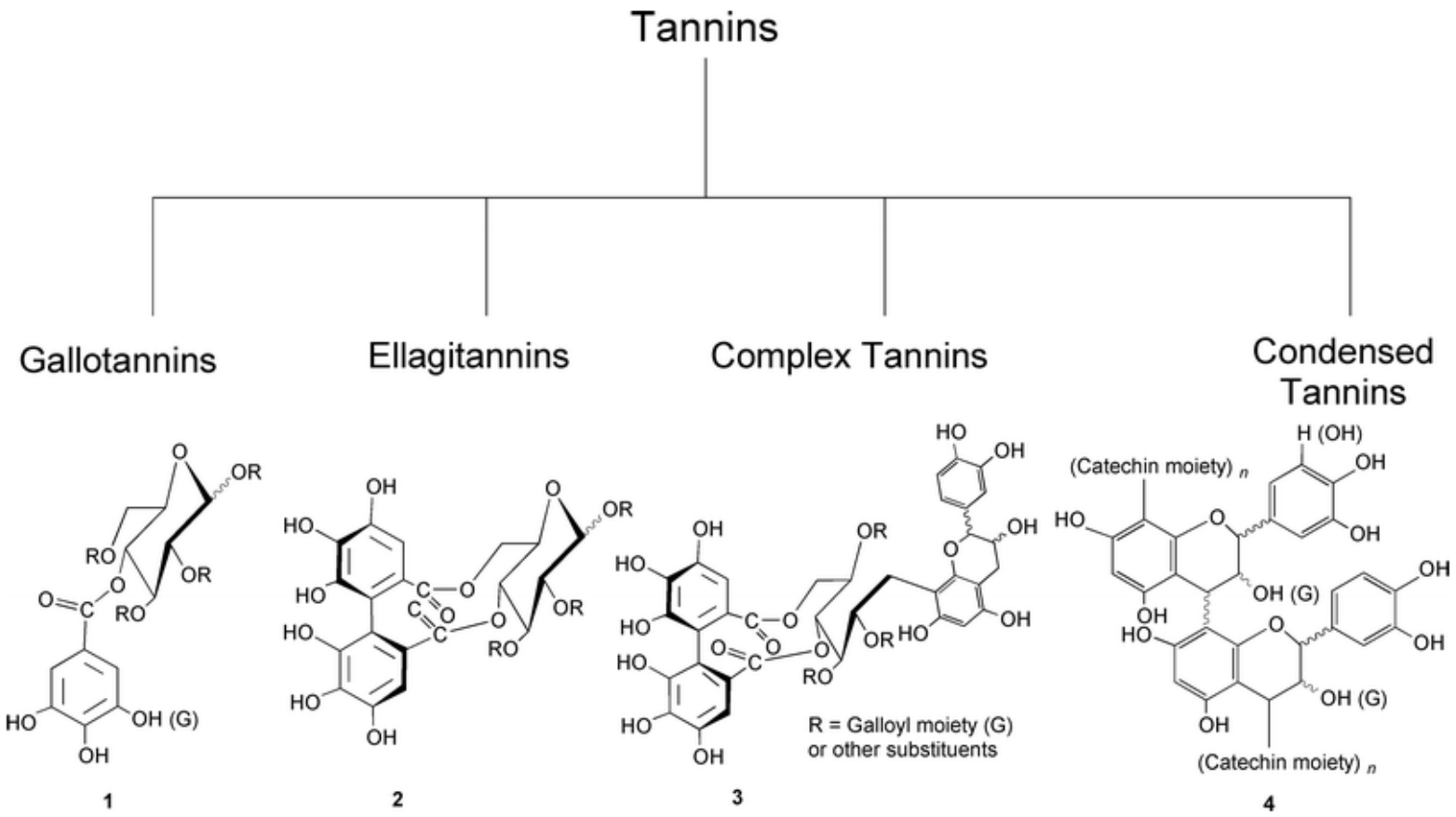
http://nzic.org.nz/ChemProcesses/animal/5C.pdf (accessed Oct 19th , 2016)

Tanning Process



https://www.emaze.com/@AZTCCCW/sperrys- (accessed Oct 17th, 2016)

Vegetable Tanning

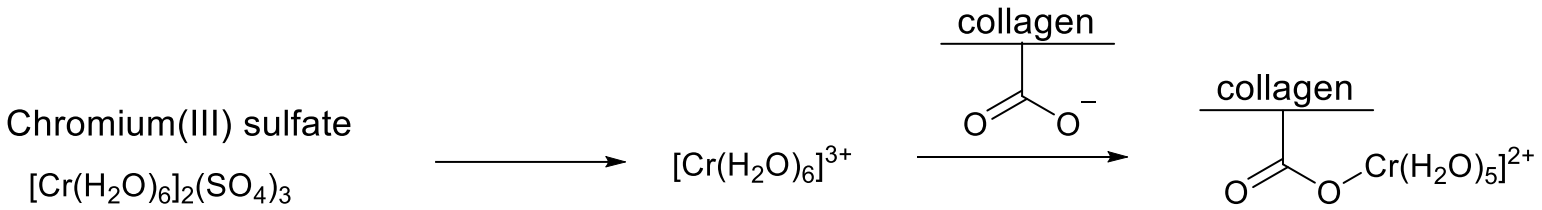


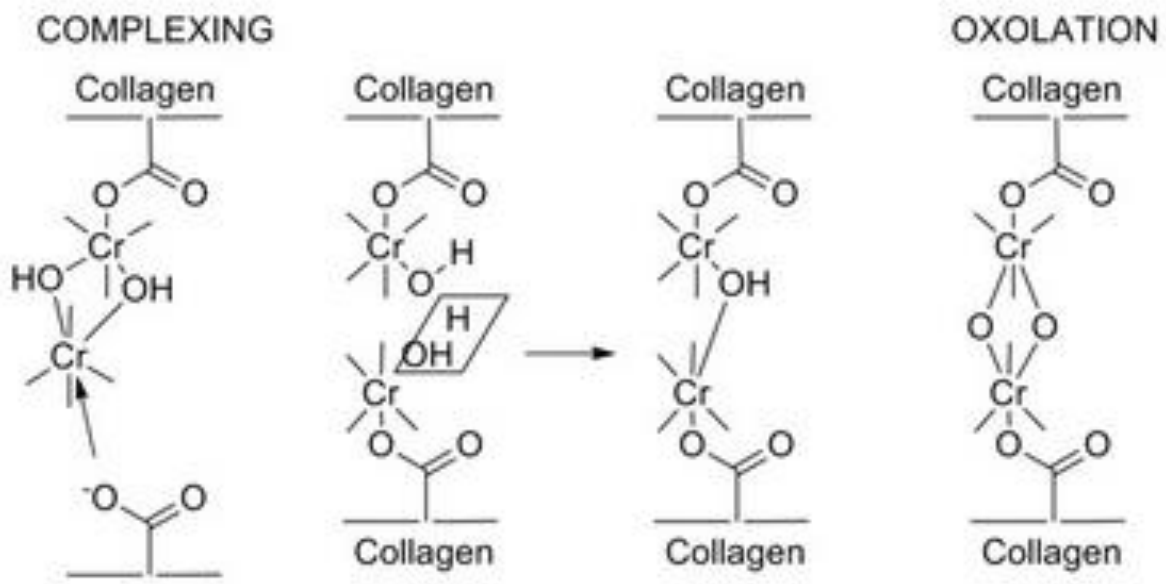
VEGETABLE TANNED LEATHER

- Historically hides tanned in a bath containing **tannins from trees and plant sources**
- Tannins bind to proteins and replace water molecules
- Often requires multiple treatments
- Uses large quantities of water

Khanbabaee, K., van Ree. T.; ***Nat. Prod. Rep.***, 2001,**18**, 641-649
http://www.carryology.com/insights/chrome-vs-vegetable-tanned-leather/ (accessed 17th Oct, 2016)

Chrome Tanning





- In 1858 chrome process developed to make tanning possible on larger scale
- Higher pH undergoes processes give polychromium(III) compounds that are active in tanning
- Leather contains 4-5% chromium
- Boiling and sun-drying can oxidize to Cr(VI) which is carcinogenic and can leach from waste water
- Process generates 20-80 m^3 of waste water contaminated with high levels of Cr and S in waste waters

https://en.wikipedia.org/wiki/Tanning (accessed 17th Oct, 2016)
Imer, S.; Varnali, T - Applied Organometallic Chemistry 2000, 14, 660-669.

Reducing Negative Environmental Effects

Kanpur, India example of how tannery chemicals and wastewater can negatively affect health and ecosystems.

- About **80% of the wastewater is untreated** and dumped straight into Kanpur's main water source, the River Ganges.
- **Farmland is swamped with blue-tinted water**, poisoned with chromium III, lead, and arsenic.
- Health problems include asthma, eyesight problems, and skin problems include: contact dermatitis, urticaria, hand eczema, fungal infection and atopic eczema.

Global aqueous-based tanning uses 27.5 billion litres of water containing 24 kilotons of Cr(III) each year

Exploration of GSK'S solvent selection guide in leather industry: a CSIR-CLRI tool for sustainable leather manufacturing

Sathish,M., Silambarasan, S., Madhanb, B., Rao, J. R.; **Green Chem**., *2016*, Advance Article

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Solvent selection guides

- Aimed at identifying sustainable solvents for greener processing
- GlaxoSmithKlien (GSK) has web-based tool which provides information on:
  - Environmental
  - Health
  - Safety
- **Authors use this guide to select a non-aqueous medium for sustainable tanning**

Screening process

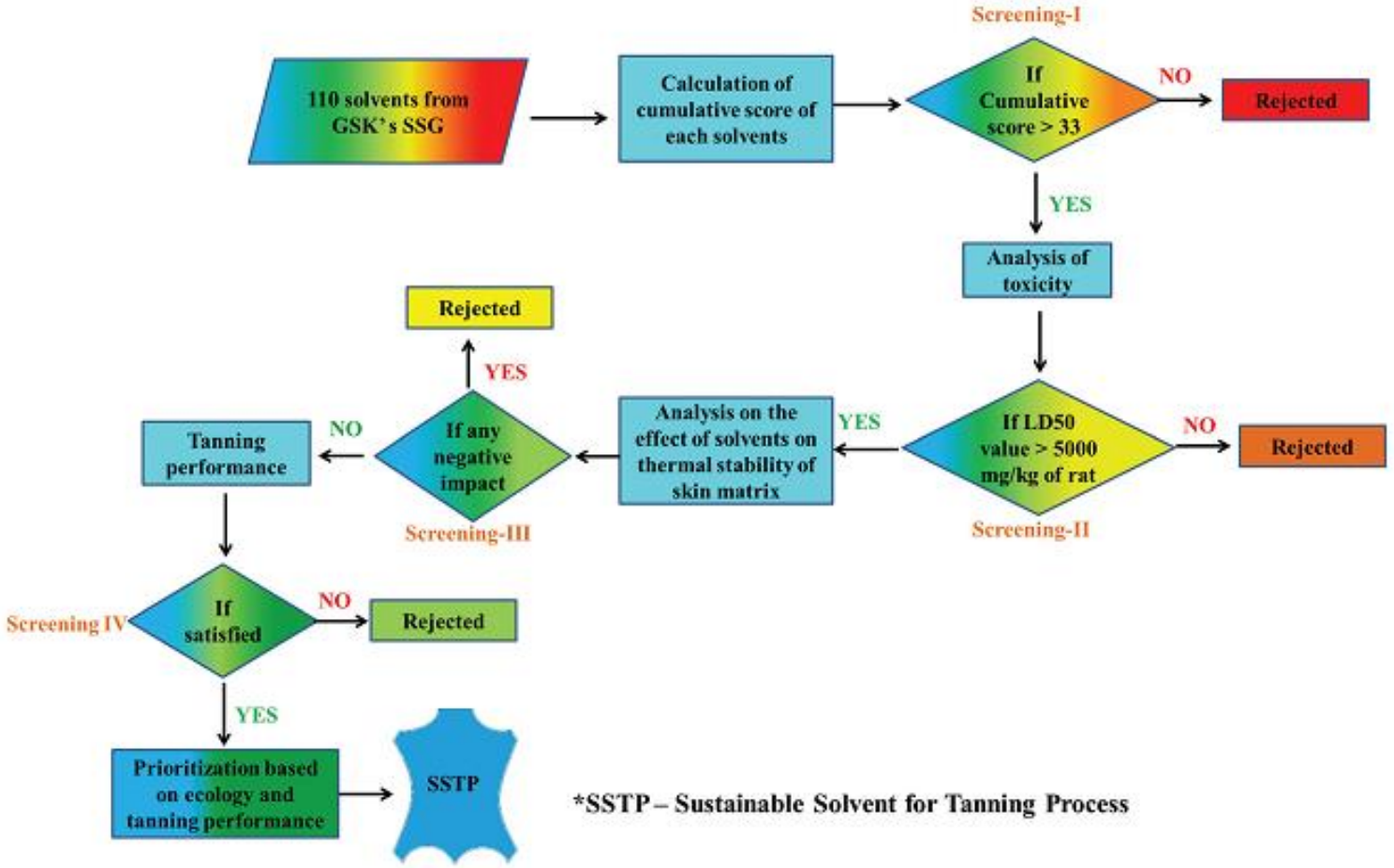


Fig. 2 Various properties employed to calculated the cumulative score of each solvent listed in GSK's SSG.

Screening process

Table 1 List of solvents shortlisted based on cumulative score >75% of the cumulative score of water (screening criteria I) as per characteristics listed in the GSK's SSG and its grouping based on family

Family name	S. no	Solvent name	Cumulative score
Alcohol	1	2-Ethyl hexanol	39
	2	Glycerol	40
	3	Cyclohexanol	37
	4	Ethylene glycol	39
	5	1,4-Butanediol	40
	6	Isoamyl alcohol	38
	7	1,2-Propanediol	42
	8	1,3-Propanediol	41
	9	Benzyl alcohol	36
	10	2-Pentanol	34
	11	1-Butanol	34
	12	2-Butanol	34
	13	Ethanol IMS	34
	14	*t*-Butanol	34
	15	2-Propanol	34
Ester	16	Ethyl acetate	34
	17	*t*-Butyl acetate	39
	18	*n*-Octyl acetate	37
	19	Butyl acetate	40
	20	Ethylene carbonate	37
	21	Propylene carbonate	35
	22	Ethyl lactate	34
	23	Propyl acetate	36
	24	Dimethyl carbonate	35
	25	Methyl lactate	35
Ketone	26	Cyclohexanone	37
	27	Cyclopentanone	37
	28	2-Pentanone	34
Acid	29	Propionic acid	34
Aromatic	30	Mesitylene	34
Ether	31	Di(ethylene glycol)	39
	32	Ethoxybenzene	39
	33	Tetra(ethylene glycol)	39
	34	Sulfolane	40
	35	DEG monobutyl ether	35
	36	Dimethylpropylene urea	34
Halogenated	37	1,2-Dichlorobenzene	36
	38	1,2,4-Trichlorobenzene	34
	39	Chlorobenzene	34
	40	Trichloroacetonitrile	34
	41	Chloroacetic acid	34

Table 2 List of solvents shortlisted based on screening criteria II – toxicity at LD50 value >5000 mg kg^{-1} of rat

Family	S. no	Solvent name	LD50 value (mg kg^{-1}) of rat (oral acute toxicity)
Alcohol	1	1,2-Propanediol	20 000
	2	1,4-Butanediol	18 000
	3	1,3-Propanediol	15 000
	4	2-Propanol	12 800
	5	Glycerol	12 600
	6	Ethanol	7060
	7	2-Butanol	6480
Ester	8	Propylene carbonate	20 700
	9	Dimethyl carbonate	13 000
	10	Butyl acetate	10 768
	11	Propyl acetate	8300
	12	Ethyl acetate	5620
	13	Ethyl lactate	5100
Ether	14	Tetraethylene glycol	31 700
	15	Diethylene glycol	12 565
	16	DEG monobutyl ether	9623

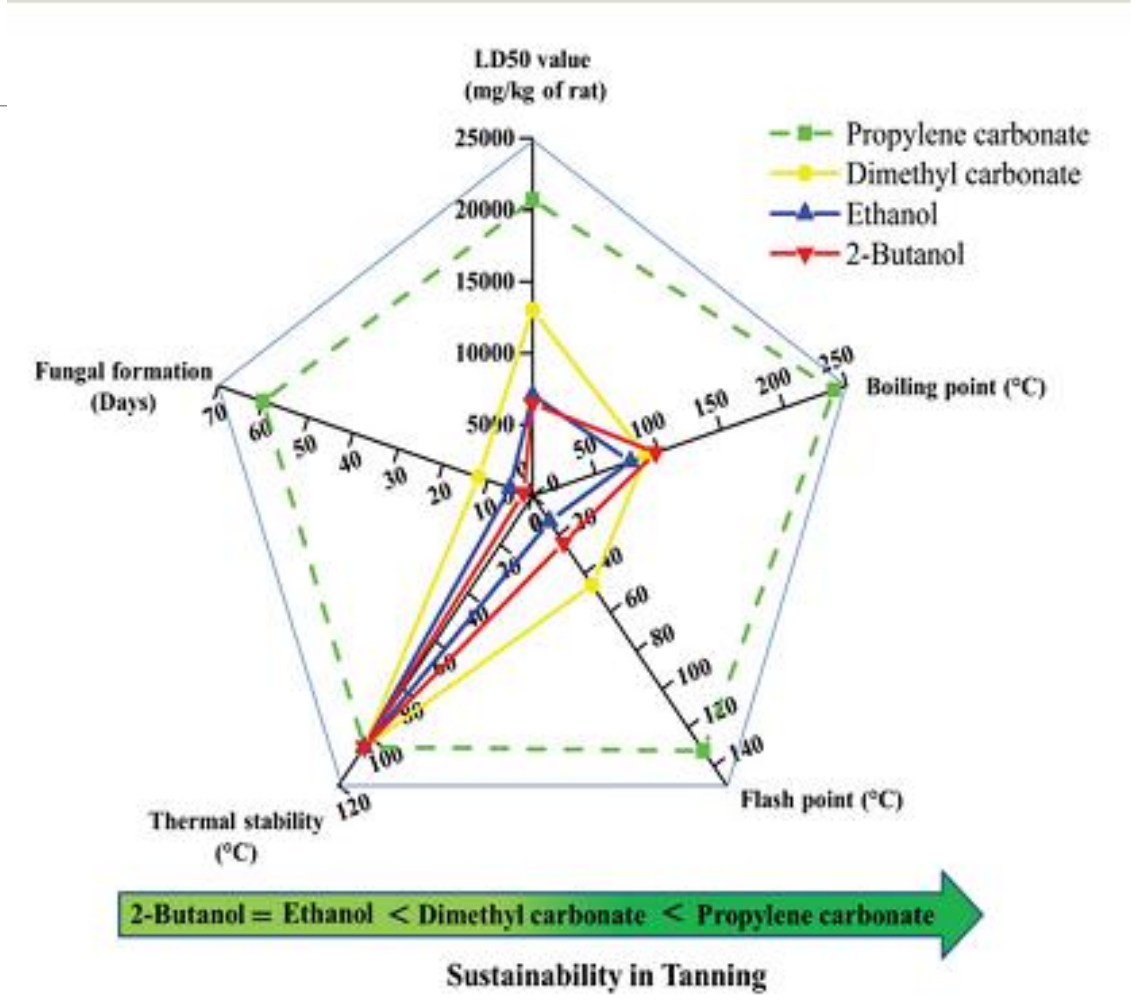
Table 3 Screening criteria III – listing of solvents based on impact of solvents on the thermal stability of the skin matrix

S. no	Solvent name	Shrinkage temperature (T_s, °C)
1	Water (reference)	62
2	Propylene carbonate	61
3	1,2-Propanediol	61
4	2-Butanol	61
5	Ethyl lactate	60
6	Tetraethylene glycol	60
7	Ethyl acetate	60
8	Butyl acetate	60
9	Ethanol	60
10	Dimethyl carbonate	60
11	Glycerol	55
12	DMG monobutyl ether	55
13	Diethylene glycol	50
14	Propyl acetate	50
15	1,3-Propanediol	45
16	1,4-Butanediol	45
17	2-Propanol	45

Table 4 Performance of the non-aqueous medium in the tanning process (screening criteria IV)

	Tanning performance		
Name of the solvent	Mass transfer efficiency (%, w/w)	Physical appearance of tanned leather	Hydrothermal resistance
Propylene carbonate	99.4 ± 0.1	✓ Uniform color	No change in leather dimension while in contact with hot water up to 5 min
Dimethyl carbonate	99.2 ± 0.1	✓ Flat grain	
Ethanol	99.1 ± 0.1	✓ Good chromium penetration	
2-Butanol	99.1 ± 0.2	✓ No chrome patches	
Ethyl acetate	99.2 ± 0.1	✗ Chrome patches ✗ Wrinkled grain	
Butyl acetate	99.3 ± 0.1	✗ Rough surface	
Ethyl lactate	56.1 ± 2	☒ Untanned effect	Immediate shrinkage on contact with boiled water
Tetraethylene glycol	8.1 ± 3	☒ Chrome patches	
1,2-Propane diol	5.6 ± 1	☒ Poor chromium penetration	

Screening process



Advantages

- Considering toxicity towards workers
- Less chromium in waste propylene carbonate
- More efficient tanning – high Cr uptake
- No fungicides

Criticisms

- **Cost!!**
- Lifecycle analysis? How are solvents made? – by-product of another industry?
- How do they degrade – greenhouse gases
- Different metal?
- Human cost of production?
- Transfer of knowledge between workers and researchers
- How to recycle propylene carbonate – high boiling?

Conclusions

- From 110 solvents on GSK SSG, propylene carbonate found to be ideal
- Might be difficult to change tanning industry in developing nations due to cost
- Leather made from mushrooms are more easily tanned and have better flexibility and durance
- Go back to vegetable tanning even though more time-intensive

References - solvent selection guides

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- Astrazeneca (AZ) guide has not been published, but it was presented in the Green Chemistry Institute Pharmaceutical Roundtable – collaboration to deliver a solvent selection guide in 2008. The information is available in the following website https://www.acs.org/content/dam/acsorg/greenchemistry/industriainnovation/roundtable/acs-gcipr-solvent-selection-guide.pdf.
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- Central Leather Research Institute
  - http://www.clri.org/

- Council for Scientific Industrial Research
  - www.csir.co.za/ (South Africa)
  - www.csir.res.in/ (India)
  - https://www.csiro.au (Autralasia)