Calcium stearate and Paraffin wax dispersions

Key drivers for better glove making

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ENGINEERED CHEMICALS

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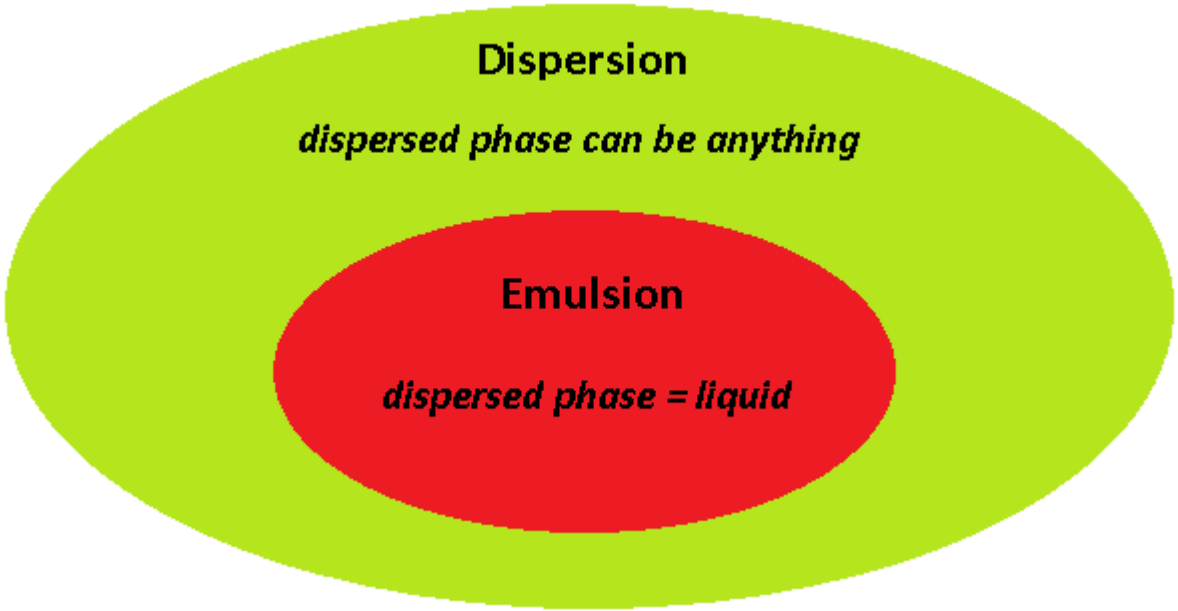
Colloidal dispersions and emulsions : definition

A *colloidal dispersion* is a system in which particles of colloidal size (nanometer to micrometer-range) of any nature (e.g. solid, liquid or gas) are dispersed in a *continuous phase* of a different composition (or state).

In an *emulsion* liquid droplets are dispersed in a liquid.



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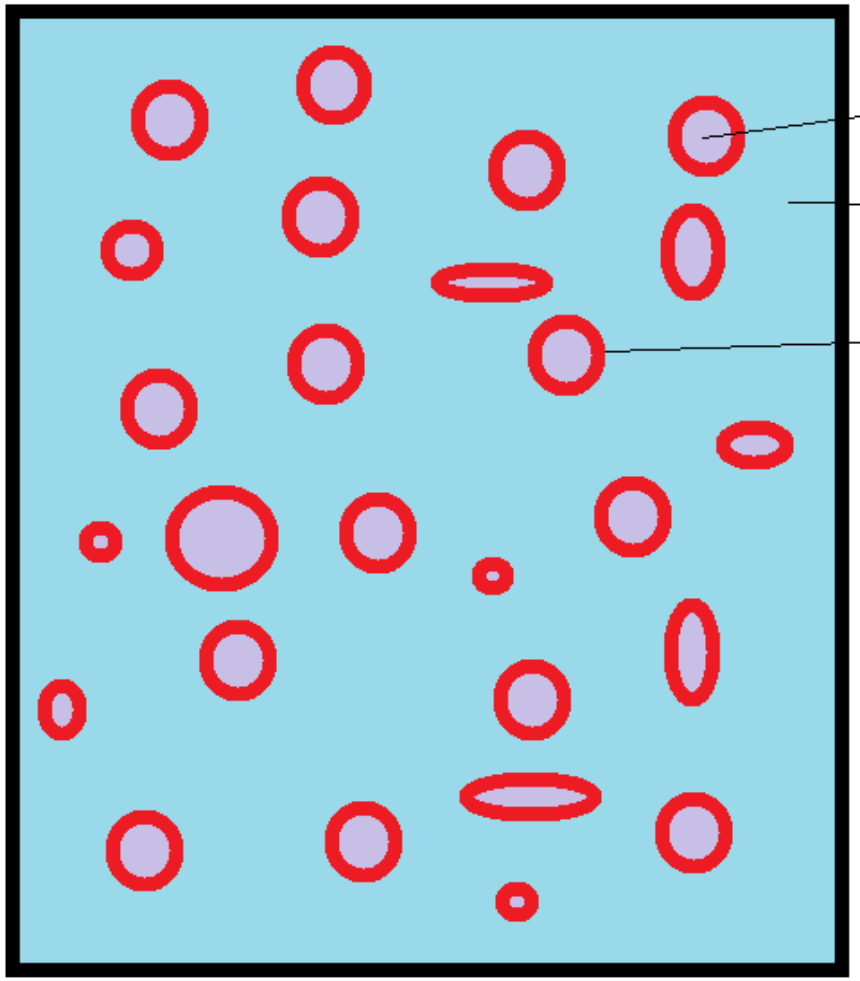
Dispersion properties

A dispersion is more than just wax or calcium stearate in water !



dispersed phase

pH and buffer capacity

interface

particle size (distribution)

particle shape

Calcium stearate and paraffin wax dispersions are…

low viscous and water based

↓

easily mixable with other water-based systems

↓

easily applicable

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Dispersion properties

Particle size and shape

Influence of crystallinity

High crystallinity of dispersed phase leads often to a less spherical particle shape

Effect on colloidal stability

Smaller particle size give normally better stability : creaming velocity ~ (particle size)^2

Larger particle size difference between wax emulsion and latex can lead to particle flocculation.

Dispersions with broader particle size distributions show usually lower stability.

Effect on glove properties

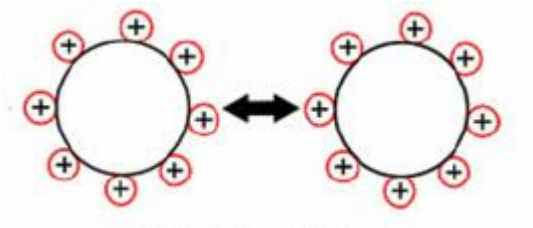
Critical for ball bearing mechanism => high impact of size and shape (see later)

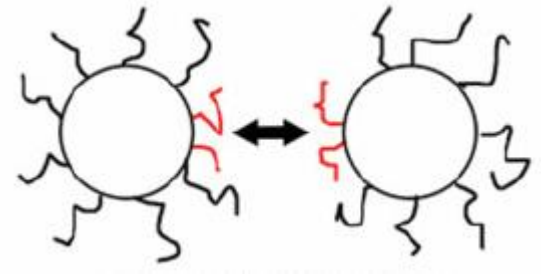
Dispersion properties

The dispersion interface

Emulsifiers at the interface are molecules composed of

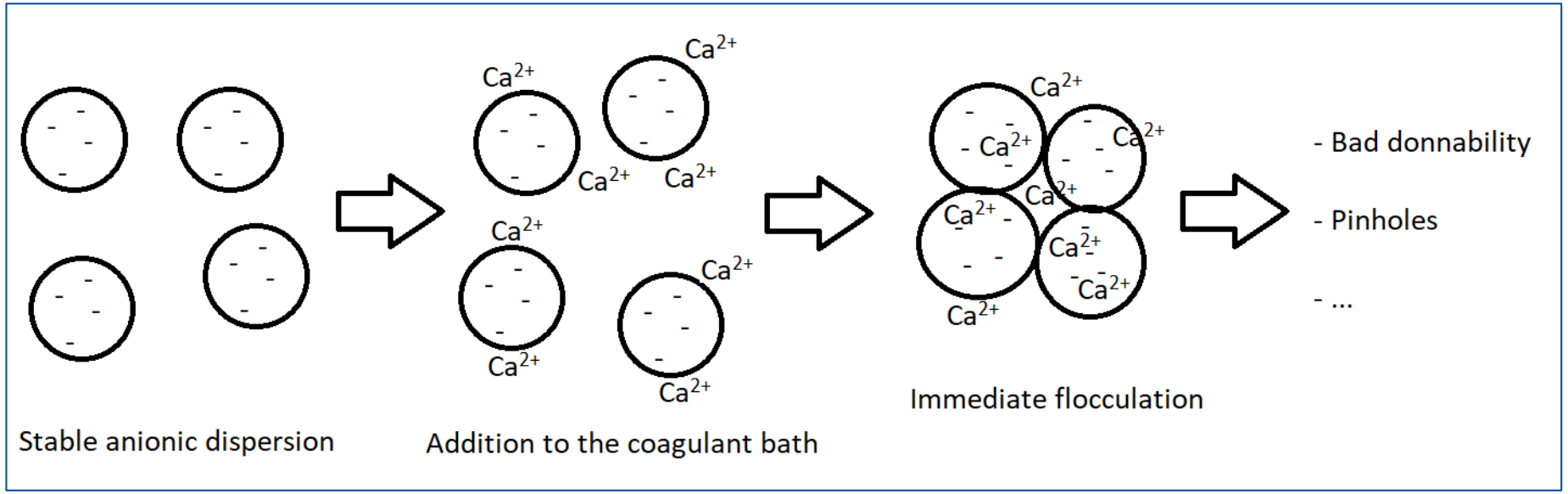
- a hydrophobic group with high affinity for the dispersed phase
- a hydrophilic group that contains
  - electrical charges => electrostatic repulsion
  - and / or
  - bulky group => 'steric' repulsion

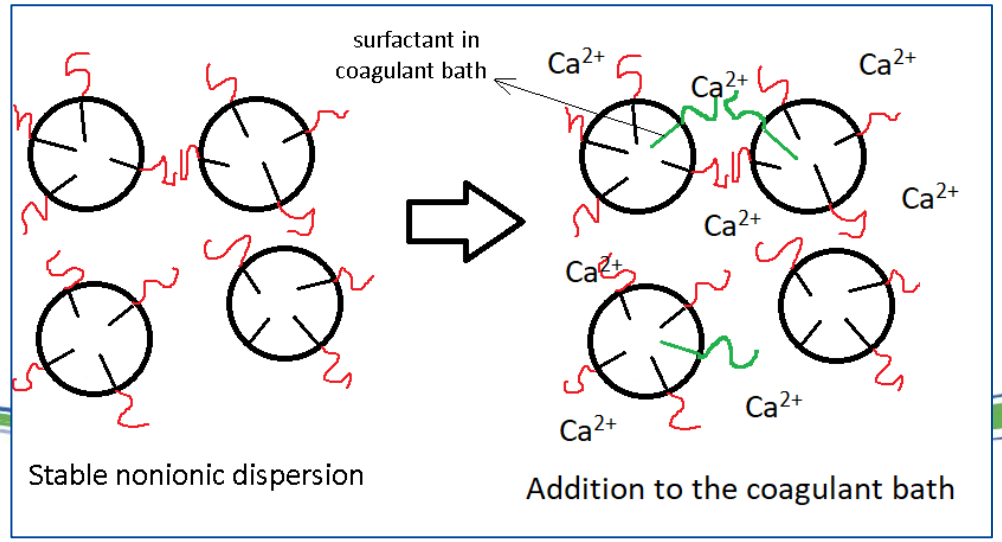




Dispersion properties

The dispersion interface : compatibility in the coagulant bath





- Electrostatic repulsion mechanism =>immediate instability due to high salt concentration
- Steric hindrance mechanism can give stability, but be aware of :
  - Salting out effect
  - Interaction with surfactants present in coagulant bath

Dispersion properties

The dispersion interface

The nature of the interface is most important for :

- dispersion stability

- compatibility in the compound

- effectiveness in the glove

Both **Aquawax** (wax dispersions) and **Chriscoat 50** (calcium stearate dispersion) show excellent dispersion stability and compound compatibility

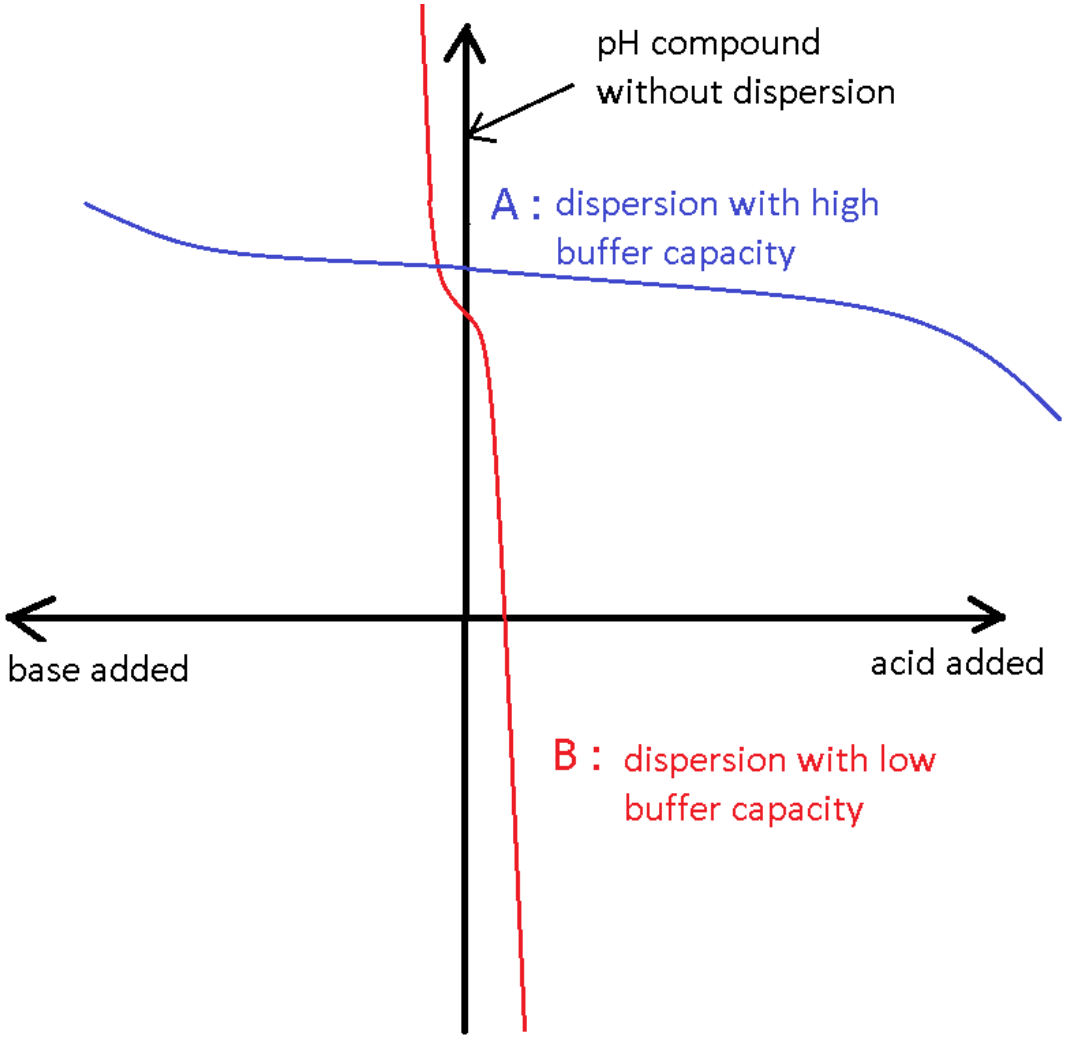
- excellent compatibility with the various surfactants, such as e.g. ethoxylated alcohols or sulfates, used in coagulation and compound bath

- Aquawax and Chriscoat 50 contain no hazardous emulsifiers (like e.g. nonylphenol based surfactants)

=> Safe + easy processing + maximum effect on the glove product

Dispersion properties

pH versus buffer capacity



Even though pH of dispersion A is closer to pH of the compound compared to dispersion B, it is expected to affect the compound pH more !

Aquawax and Chriscoat 50 have low buffer capacity and thus have little effect on compound pH.

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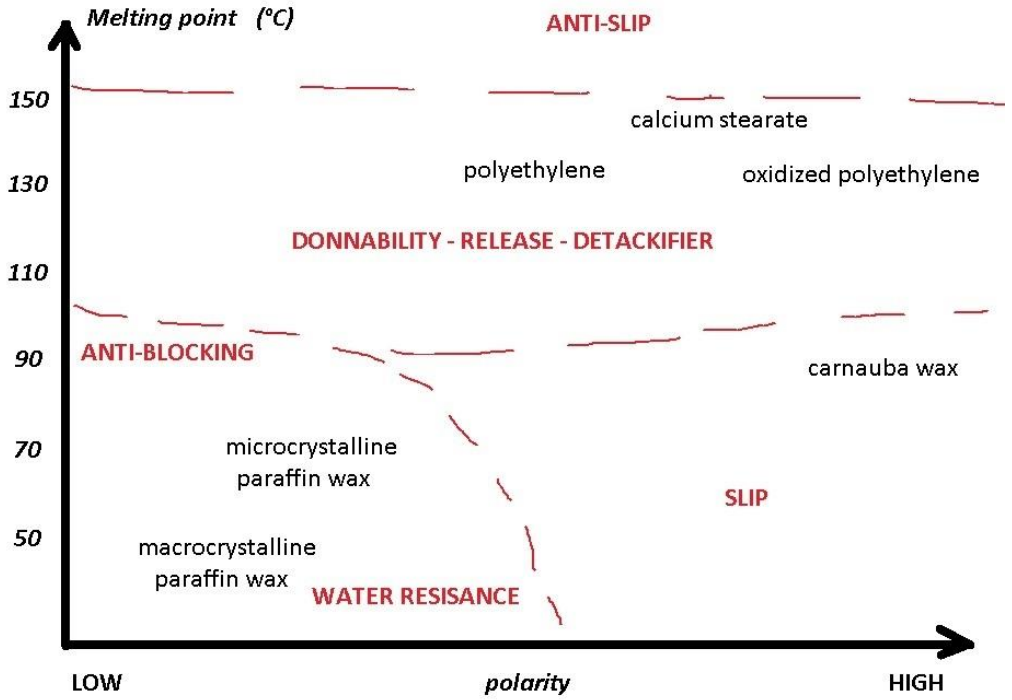
Additives for rubber gloves

Overview

Dispersed phase	Effect				
	block resistance	slip	donnability - release - detackifier	water resistance	anti-ozone
Calcium stearate	+++		+++		
Macrocrystalline wax	+	++	++	++	++
Microcrystalline wax		+	++	+	+
Polyethylene	+	+	++		
Carnauba wax	+	++	+	+	



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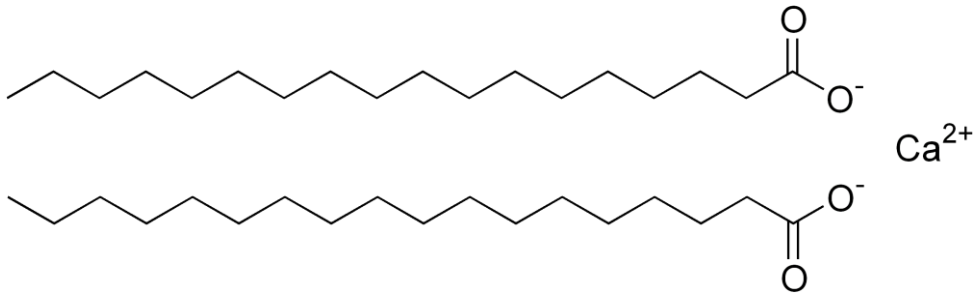
Calcium stearate

Molecular structure

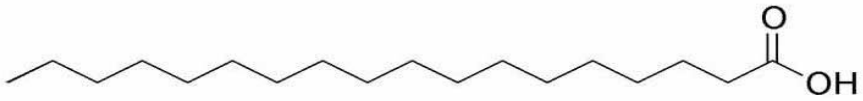
Calcium stearate



Melting point ~ 150 °C

acid

Stearic acid



Melting point ~ 55 °C

=> Easy cleaning after acid treatment

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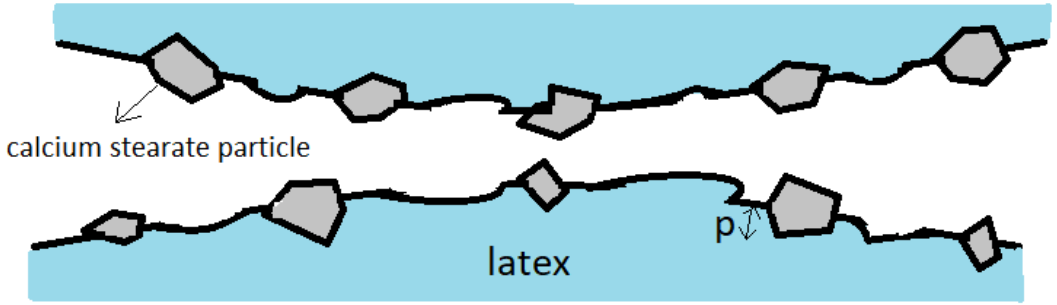
Calcium stearate

How does it work? Ball bearing mechanism.



Microscopic solid particles at the interface

Prevent close contact between rubber interfaces

Less entanglement of rubber polymer chains

Better donnability, less sticking, lower friction

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Calcium stearate

How does it work? Ball bearing mechanism.

Parameters to control

- **Interface energies** of 3 interfaces
- **Solubility parameters** of latex and calcium stearate

→ Contact angle rubber – calcium stearate (CS)

→ How deep CS particles sink in the rubber interface

- **Particle size** : important for the extent of protrusion through the interface.
- **Crystallinity** determines hardness and thus resistance towards mechanical impact.
- **Melting point** should be higher than process temperature : particles retain correct size and shape.

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Calcium stearate

How to trace calcium stearate (or paraffin wax) on a glove?

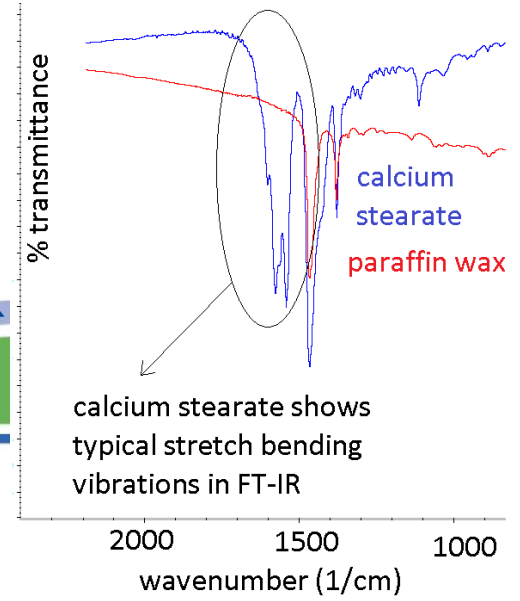
1) Extraction : inside or outside glove surface

	What solvent is used to extract …?	
	demineralised water @ room temperature	hexane @ 60°C
paraffin wax	X	V
calcium stearate at the surface	V	V
calcium nitrate	V	X

Calcium stearate in water = anisotropic upon mixing

2) Analytical methods

Method	analyse what …?			Quantitative?
Visual observation	calcium stearate	~~paraffin wax~~	~~calcium nitrate~~	X
IR spectroscopy	calcium stearate	paraffin wax	~~calcium nitrate~~	X
ICP-OES	sum of calcium stearate and calcium nitrate			V
Conductivity	~~calcium stearate~~	~~paraffin wax~~	calcium nitrate	V
total organic carbon	calcium stearate	paraffin wax	~~calcium nitrate~~	V

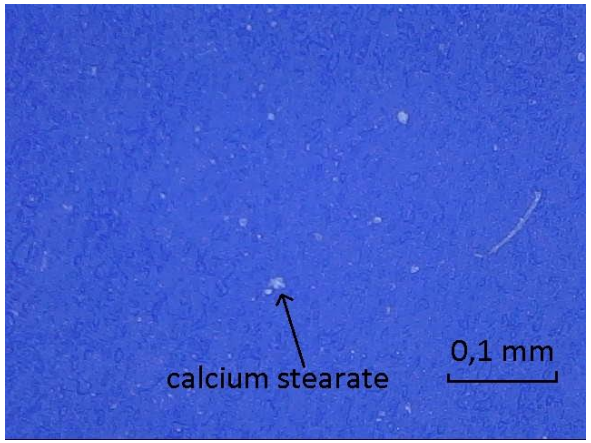


3) Visual light microscopy

Calcium stearate dispersions

Example of what should not happen…

What did we see?



Microscopic image of glove surface

- **Bad donning**
- **Bad anti-blocking**

How it was explained?

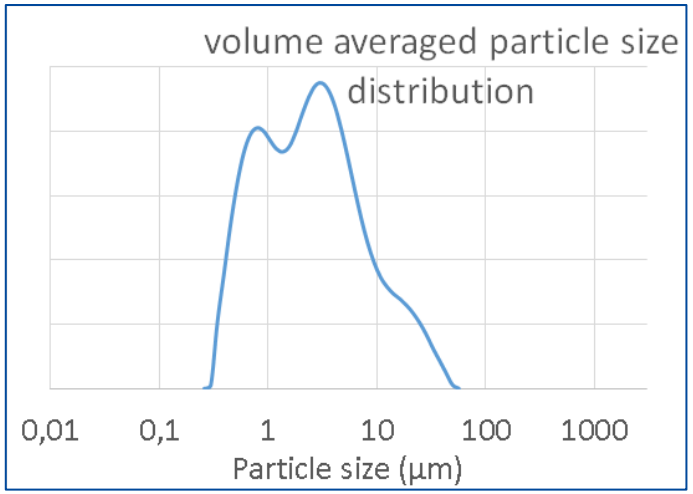
Instability in the coagulant bath → Uneven distribution and larger particles at the glove surface

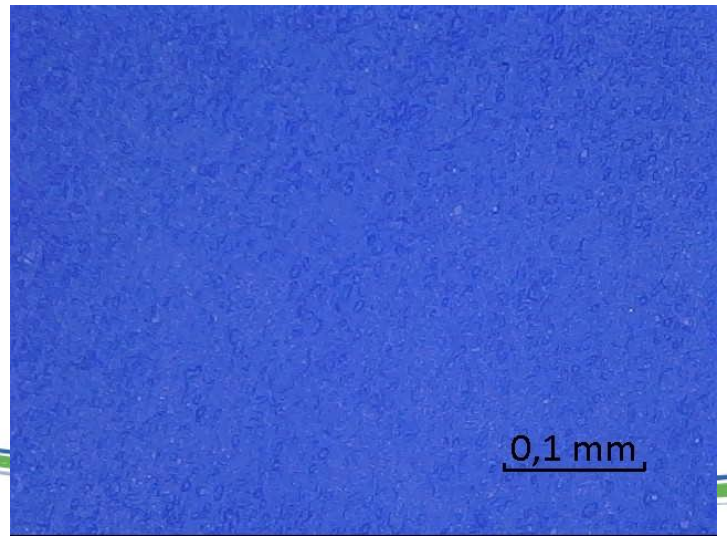
Drying/gelling temperature > melting temperature → Lower amount extractable calciumstearate

Calcium stearate dispersions

Chriscoat 50

- Small and narrow particle size distribution
- Excellent stability in the coagulant bath
- High melting point





Even distribution of calcium stearate at the glove interface

- **Excellent donning**
- **Excellent anti-blocking**

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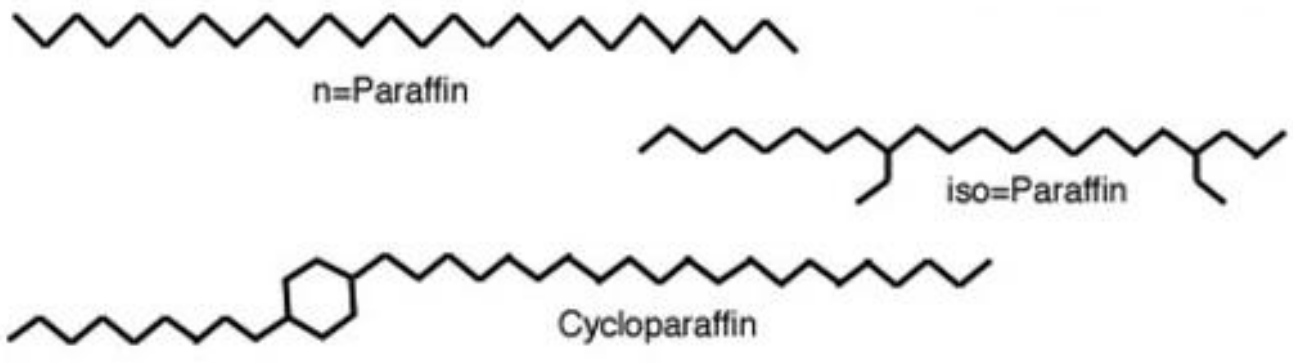
Paraffin wax

What is a paraffin wax?

- Mixture of different molecules made from C and H atoms



No double bonds = no risk of effect on curing

- Originates from the dewaxing of process oils

- Characterized by :
  - Congealing point
  - Carbon chain lenght distribution (measured by gas chromatography)
  - Residual oil content

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Paraffin wax

Migration : what happens to the wax during gelling and subsequent stages?

- Rubber polymer molecules grow
- Paraffin intermolecular forces grow as temperature decreases (especially upon congealing)

- System entropy decreases and enthalpy increases

- Wax solubility decreases = driving force for migration to the rubber surface

solubility of paraffin in rubber dependent on the type of rubber :
natural > butadieen ~ styreen-butadieen > nitrile

Paraffin wax

Migration : what happens to the wax during gelling and subsequent stages?

Driving force for migration

Large alkanes > small alkanes

Linear alkanes > branched alkanes

Migration kinetics

Small alkanes > large alkanes (based on end-to-end distance)

Due to this apparent contradiction, paraffin amount and composition at the glove surface is dependent on :

- Measurement temperature
- History of the glove before the experiment

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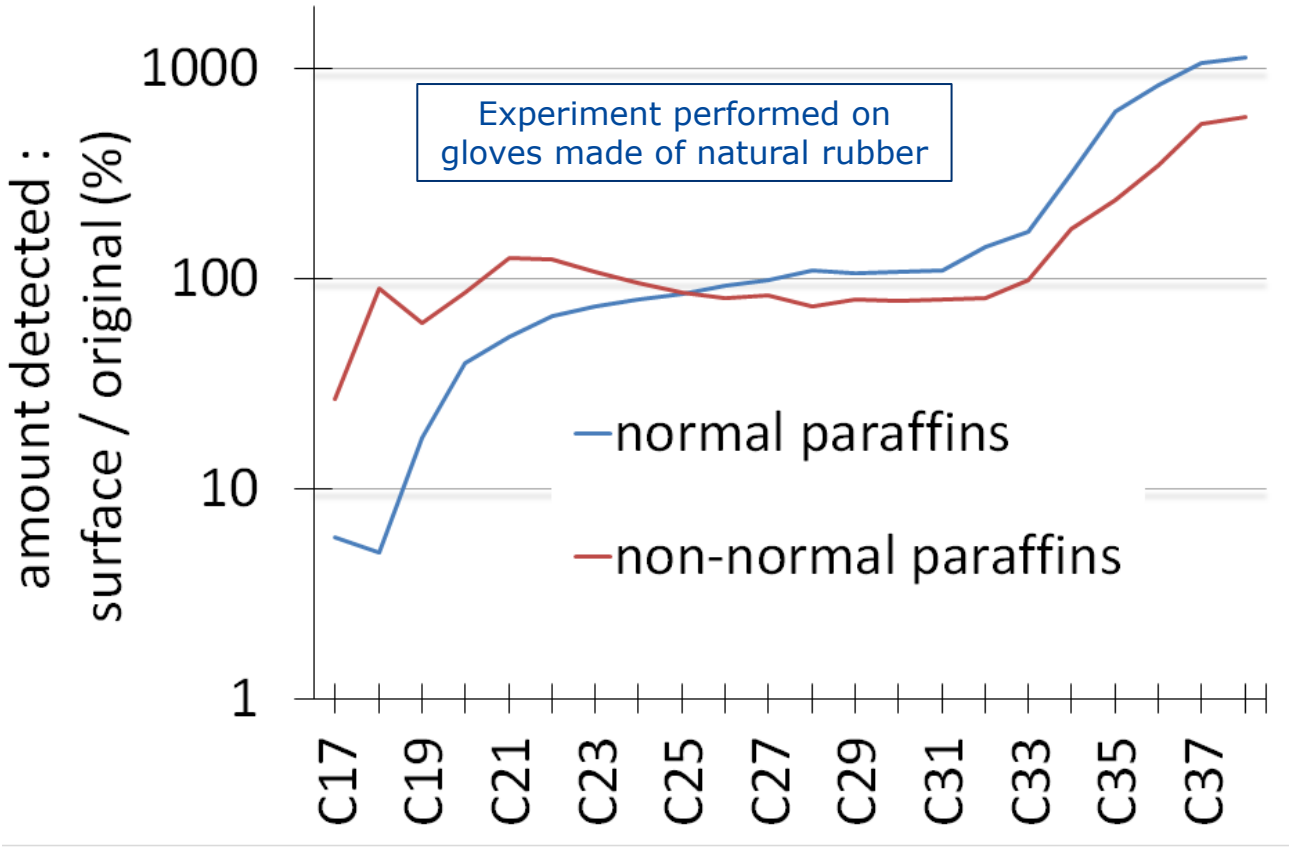
Paraffin wax

Migration : what paraffin fractions are migrating?



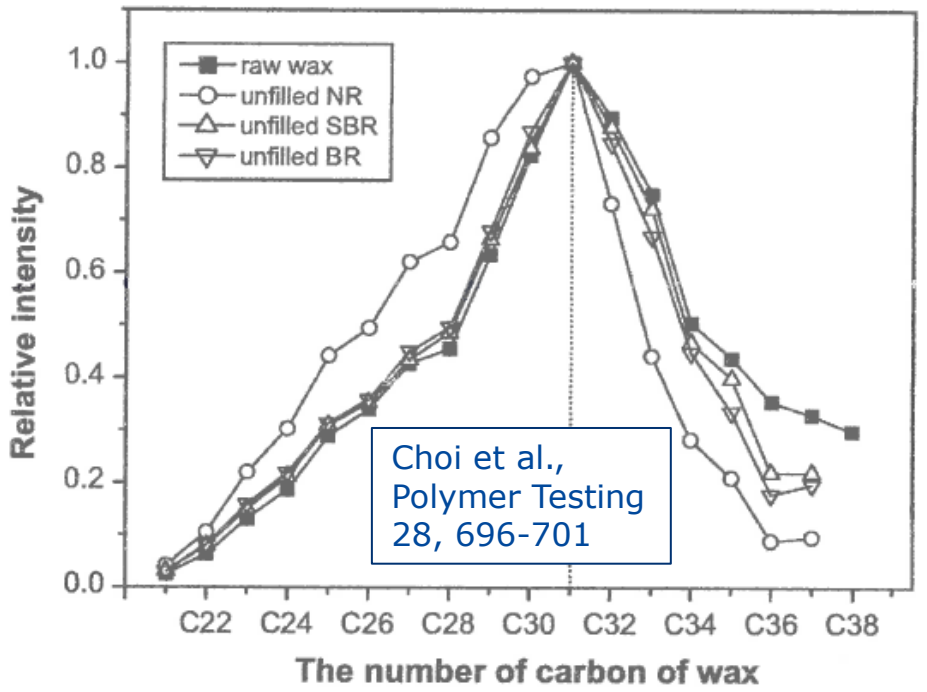


Fig. 7. Relative molecular weight distributions of wax dissolved in unfilled rubber samples using the wax solution in toluene. Squares, circles, up-triangles, and down-triangles indicate the raw wax (5000 ppm), NR, SBR, and BR samples, respectively.

Longer linear chains migrated more to the surface : this corresponds well to the difference in solubility found in literature.

Unbranched longer chains migrate even more : this also agrees with lower solubility in rubber.

Paraffin wax

How to make it work?

Macrocrystalline Paraffin wax		Microcrystalline paraffin wax
shorter	chain length	longer
less	chain branching	more
large	crystal size	small
lower	solubility in rubber	higher
higher	mobility in rubber	lower
irregular	structure at surface	smooth layer

Aquawax wax dispersions have a well balanced carbon chain distribution

=> Excellent coverage, flexible wax surface layer, lower friction and optimal protection of the glove.

Summary and conclusion

- Compatibility of both calcium stearate dispersions and wax dispersions in the baths is vital for a hassle-free process and a superior glove quality.

- Calcium stearate particle size distribution is tailored for maximum effect on the glove.

- First-rate performing calcium stearate and wax dispersions were made without the use of hazardous emulsifiers.

- Paraffin wax migration to the glove surface is driven by a (lack of) solubility in the rubber.

- Composition and amount of migrated paraffin is influenced by the history of this rubber glove.

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