Innovative Additive Portfolio for Latex Dipping Application

Roland Suecker

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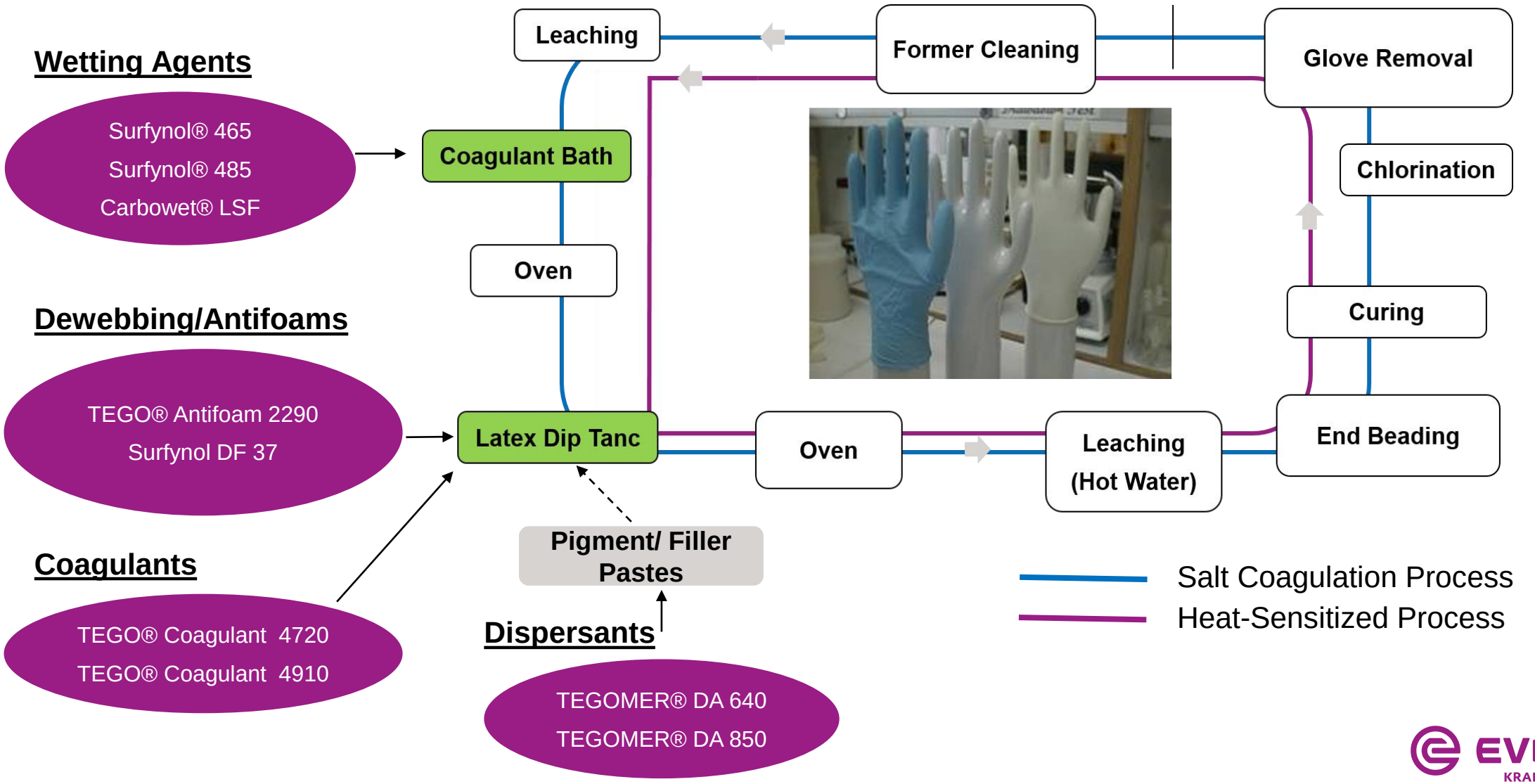
Evonik Additives for Latex Dipping Process



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Additives Summary for Latex Dipping Process

	Issue	Why	Solution
Dewebbing/ Antifoams	Foam in Latex tank leads to failures in the film	Foam coming from stabilizers in latex	**TEGO® Antifoam 2290** **Surfynol® DF 37**
	Web on Glove	"Foam lamella" forms between fingers of glove on mold	
Wetting	Pinholes and/ or thin spots in the finished glove	Foam on former from coagulant tank due to foaming surfactants Poor wetting or coagulant on former especially at higher line speeds	**Surfynol® 465** **Surfynol® 485** **Carbowet® LSF**
Heat – sensitive Coagulation	Higher endapplication: medical gloves; textile supported gloves	Managerable coagulation in SBR/ NBR latices	**TEGO® Coagulant 4910** **TEGO® Coagulant 4720**
Dispersing	Coarse filler or pigment particles lead to weak spots in the film and thus increase rejects	Bad dispersion of fillers and/or pigments. Build up of agglomerates after addition to the latex.	**TEGOMER® DA 640** **TEGOMER® DA 850**

Antifoams/ Dewebbing

Additives for the Latex Dipping Process

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Wetting			
Heat – sensitive Coagulation			
Dispersing			

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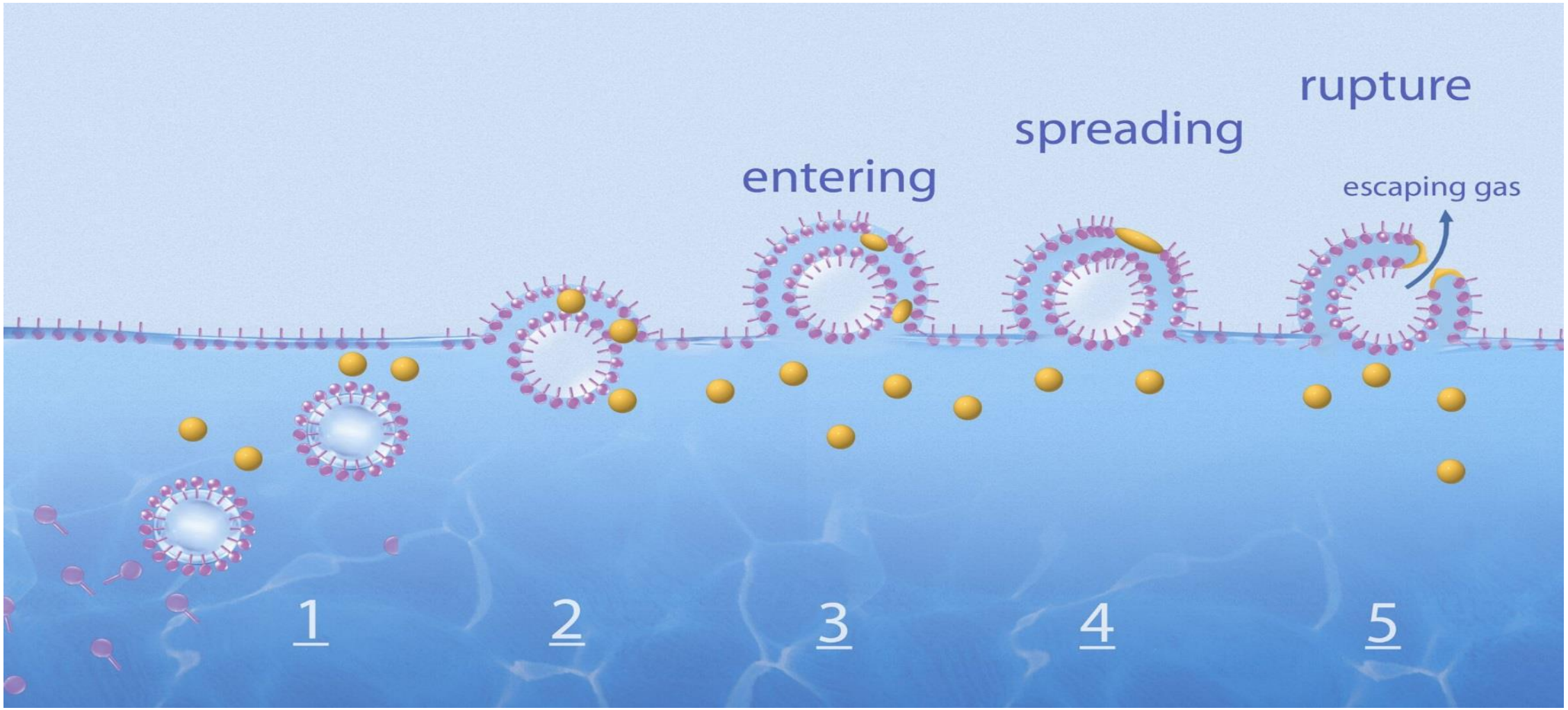
Defoaming - Mechanism



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Test Method – Shaking Test

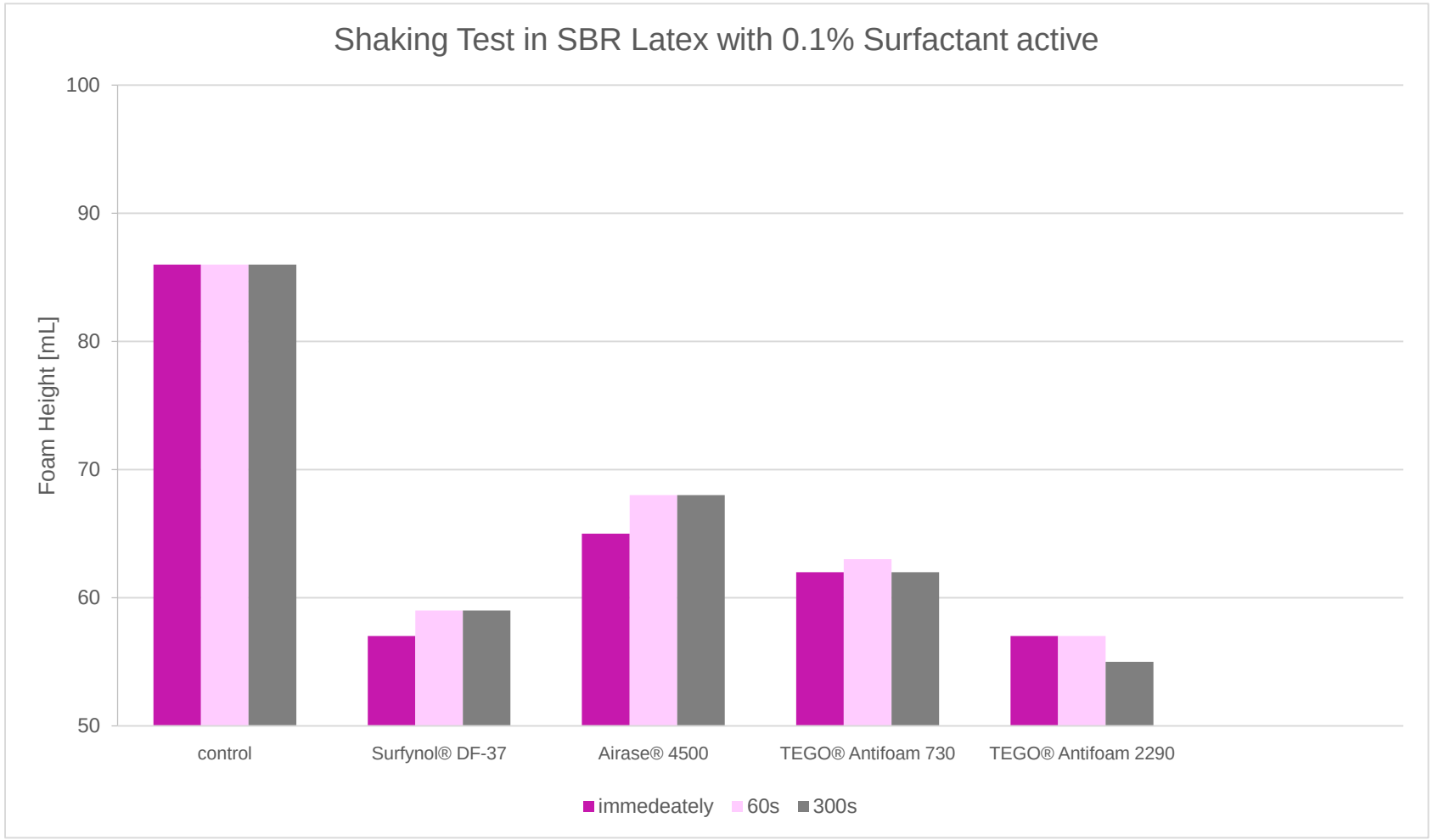
Shaking test

50 ml SBR - Latex (including additive) is given into a 100ml shaking-cylinder. The cylinder is shaken 10 seconds vigorously 30 times.

The foam height is noted down immediately and the foam collapse is measured over the time.

Tested Products	Chemistry	Active Content [%]
Surfynol® DF – 37	Gemini surfactant + Fatty acid derivatives	100
TEGO® Antifoam 2290	Paraffinic Oil	100
Airase® 4500	Fatty acid derivatives	100
TEGO® Antifoam 730	Silicone Oil	30

Results – Shaking Test in SBR with 0.1% Defoamer



All additives showed good defoaming properties.

First choice: TEGO® Antifoam 2290

Second choice: Surfynol® DF-37

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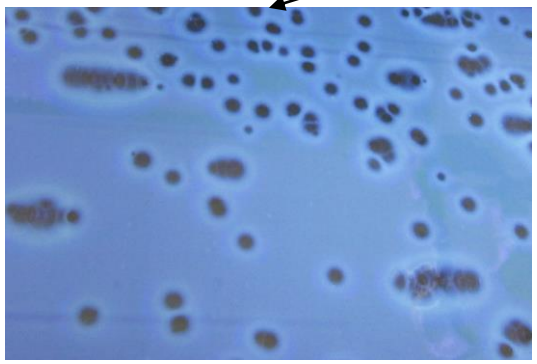
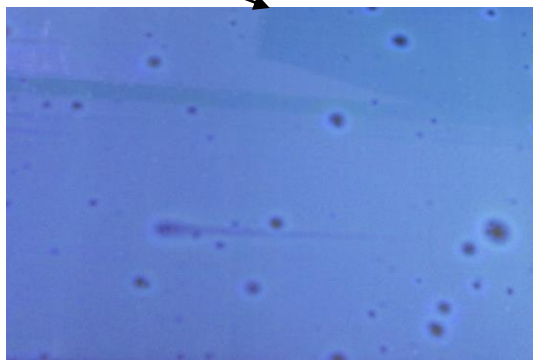
Draw Down of SBR Latex with different Antifoams

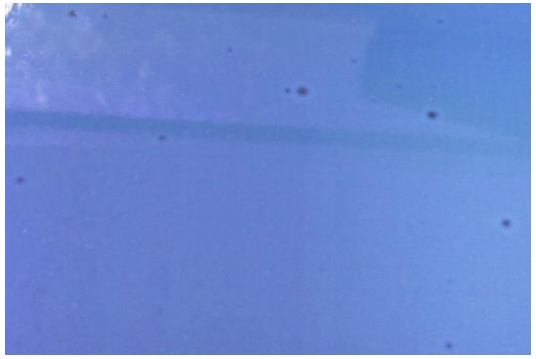
Defects caused by an incompatible antifoam



TEGO® Antifoam 730
(silicone oil)



Airase® 4500
(fatty acid derivative)



Surfynol® DF 37
(fatty acid derivative + gemini surfactant)

TEGO® Antifoam 2290
(paraffinic oil)

Test Method - Dewebbing

To SBR Latex defoamer is added and mixed by the help of a magnet stirrer for 2 minutes.

A plastic ring with 7 cm diameter is dived in the dispersion and then removed carefully. The time, until the film inside the ring bursts, is measured.

Tested Products	Chemistry	Active Content [%]
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TEGO® Antifoam 2290	Paraffinic Oil	100
Airase® 4500	Fatty acid derivatives	100
TEGO® Antifoam 730	Silicone Oil	30

Results – Dewebbing and Draw Down

Additives	Time until the bubble bursts in [s]			Film defects
Antifoam Concentration	***0.1%***	***0.01%***	***Appearance of diluted antifoam***	
Control	105	105	-	-
Surfynol® DF – 37	0	5	coarse particles	few crater
Airase® 4500	4	22	coarse particles	some crater
TEGO® Antifoam 730	0	0	coarse particles	many crater
TEGO® Antifoam 2290	0	0	o.k.	no

Wetting agents

Additives for Latex Dipping Process

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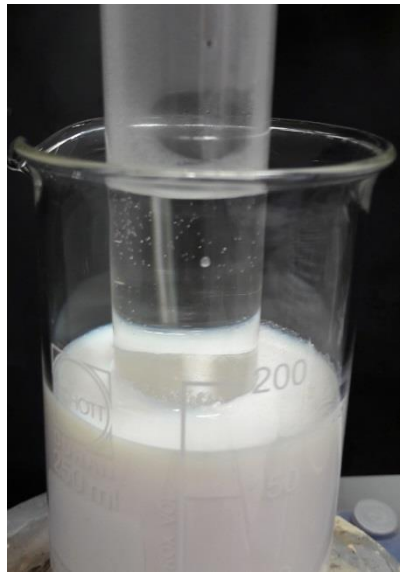
Heat – sensitive Coagulation			
Dispersing			

Coagulant Bath Formulations

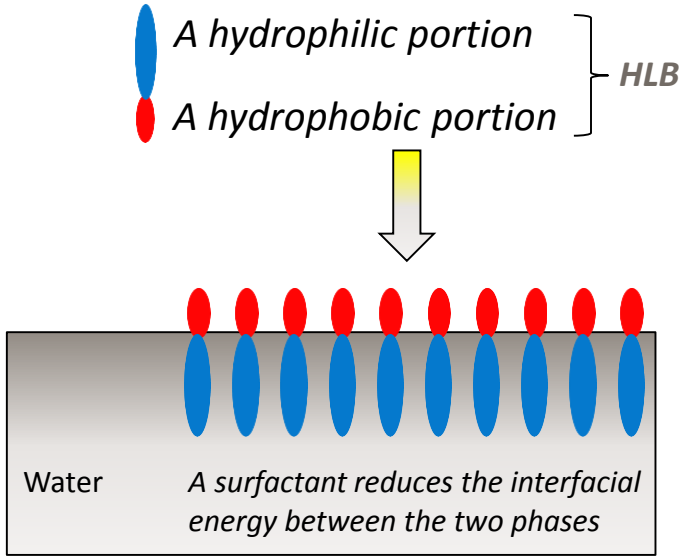
	For natural rubber gloves	For synthetic latex gloves
Water	100	100
Calcium Nitrate	5 – 15	5 - 25
Surfactant	0.05 – 0.3	0.1 – 0.5
Talc or Calcium Carbonate	3 - 5	3 - 5
Other Additives	< 0.1%	< 0.1%

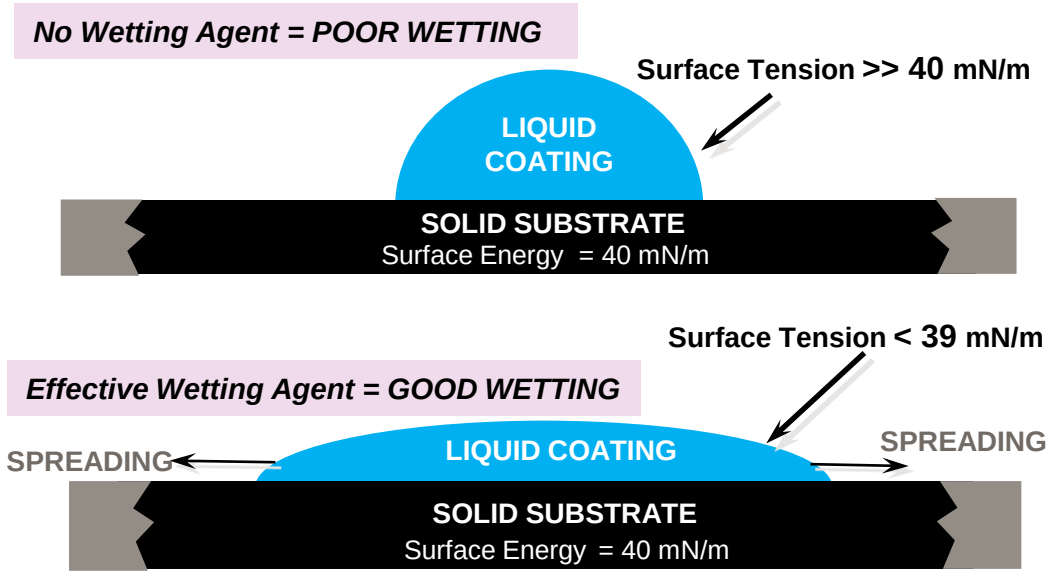


Surfactant Basics - *Surface-Active Agents*

Surfactants migrate to interfaces

- They impact interfacial energy
- They are critical in water-based systems to reduce surface tension and provide wetting
- Surfactants have a dual nature





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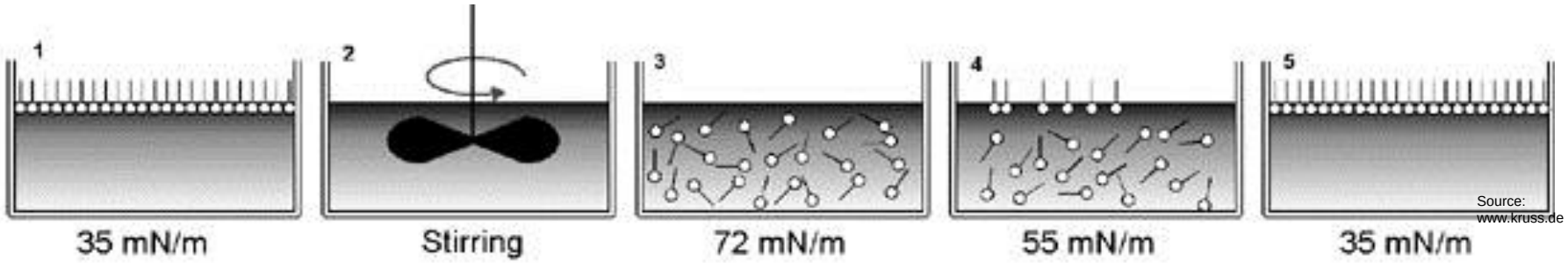
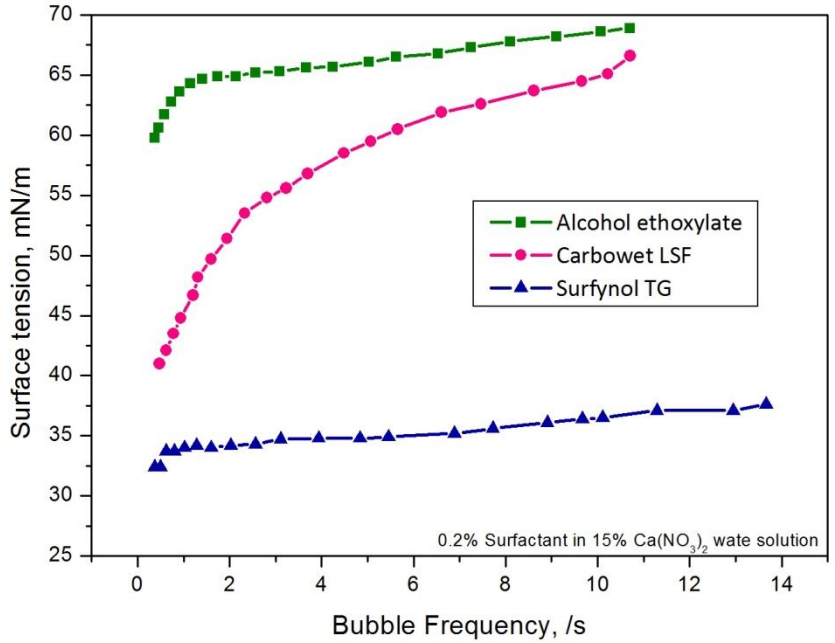
Surfactant Basics - *Dynamic Surface Tension (DST)*



- Surface tension is lowered when surfactant molecules assemble at the air/liquid interface
- Many industrial processes apply coatings at high speeds, creating large surface areas very quickly
- For uniform substrate wetting, surfactants have to migrate rapidly to those new interfaces



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Factors affecting Surfactant Performance in Coagulant

- Ease of Incorporation
  - Some surfactants require pre-dilution to avoid crystallisation or phase separation when added directly to coagulant solution.
- Surfactant Concentration
  - Higher surfactant concentration improves wetting (reduces defects) but can also increase foam (increases defects). Some surfactants can oil out (more defects) at high concentrations.
- Temperature
  - Surfactant can oil out if operating temperature is close or above cloud point. Non-ionic surfactants become more surface active (better wetting, more foamy) with increasing temperature until cloud point is reached.
- Coagulant Concentration
  - Increasing ionic concentration lowers surfactant solubility and cloud point
- Line Speed
  - Process is not very fast but don’t forget Dynamic Surface Tension

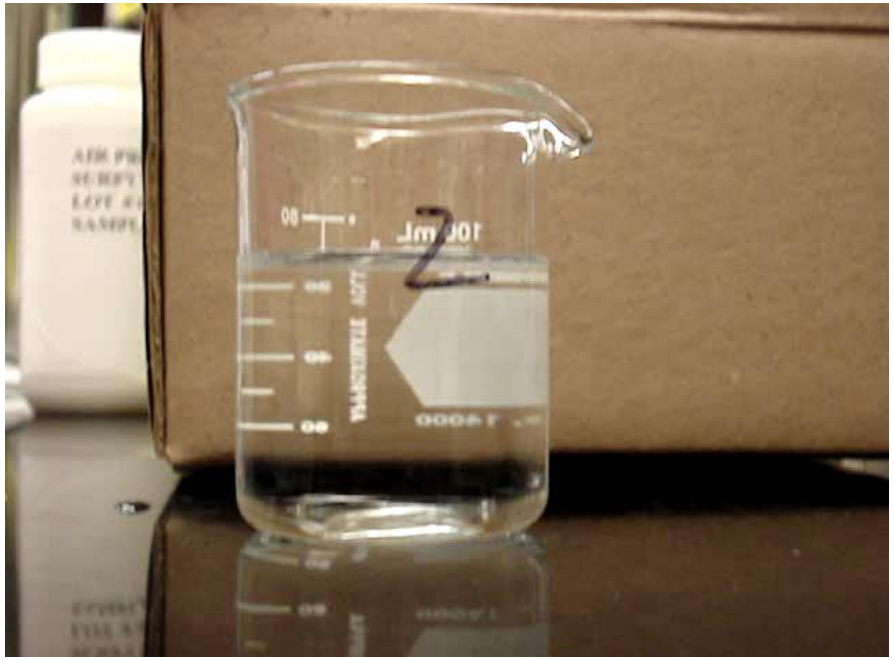
Factors affecting Surfactant Performance in Coagulant

Ease of Incorporation

- High Ethoxylated Surfactant

High viscosity surfactant has to be pre-mixed with water before use in coagulant

- Evonik Surfynol type Surfactant

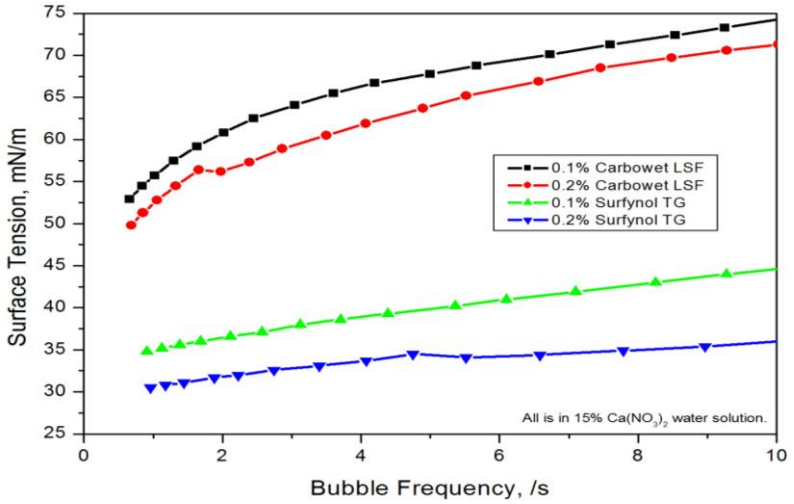


Liquid product will be easily incorporated into coagulant bath

Factors affecting Surfactant Performance in Coagulant

Surfactant Concentration

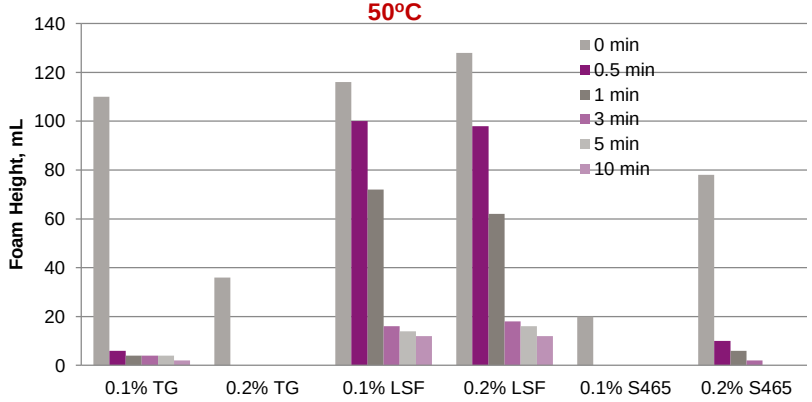
- Increasing surfactant concentration lowers surface tension and aids wetting (to a limit).
- Increasing surfactant concentration usually also increases foaminess of coagulant (exception – TG).
- Increasing surfactant concentration usually lowers cloud point and can affect stability in solution.



Cloud point of surfactant at 15% Calcium Nitrate solution

	Surfynol 465	Carbowet LSF
Cloud point, °C (0.1%)	>100	>100
Cloud point, °C (0.2%)	76	91

Foam height of surfactant in 15% $Ca(NO_3)_2$ solution at 50°C



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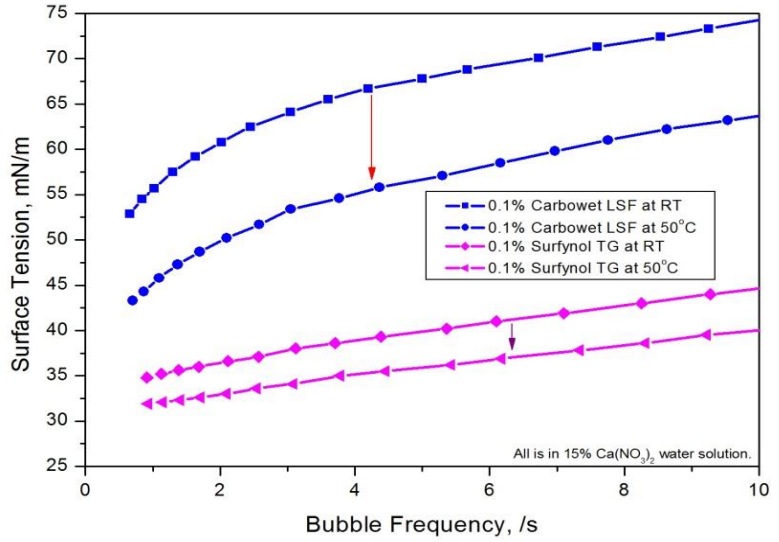
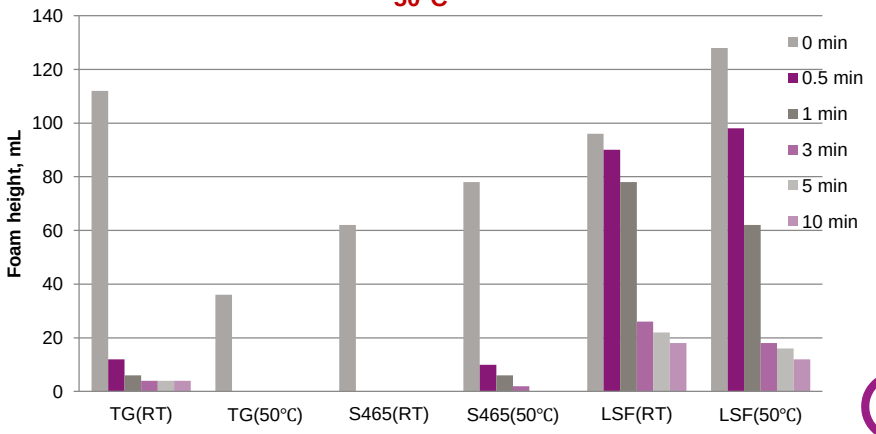
Factors affecting Surfactant Performance in Coagulant

Temperature

- The surface tension of the surfactant solution reduces (better wetting) with increasing temperature.
- The ability of a non-ionic surfactant to stabilise foam increases with increasing temperature (exception – TG).
- Increasing temperature reduces solubility of non-ionic surfactants and increases surface activity. The surfactant will start to phase separate above the cloud point and this may lead to oil out or reduced effectiveness.



Foam height of surfactant in 15% $Ca(NO_3)_2$ solution at RT and 50°C



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Factors affecting Surfactant Performance in Coagulant

Coagulant Concentration

- Increasing coagulant concentration reduces solubility of non-ionic surfactants and increases surface activity. This will reduce cloud point of surfactant.
- The surface tension of the surfactant solution reduces (better wetting) with increasing coagulant concentration.

Cloud point of 0.1% Surfynol TG at different concentration of calcium nitrate

Concentration of calcium nitrate, %	6%	10%	15%
Cloud Point, °C 0.1% TG	79	76	67

Evonik Wetting agent for Coagulant Bath

	Carbowet LSF	Surfynol TG	Surfynol 465	Carbowet GA210
Wetting	+	+++	+++	+++
High Speed Wetting	+	+++	++	+++
Foam Control	+	+++	++	++
Oil Out/Solubility	+++	+	+++	++
Cloud Point	85°C	55°C	75°C	70°C
Predilution Required	No	No	No	No
Low Defect Rate	++	+++	+++	Not known
APEO Free	Yes	No	Yes	Yes

Thermo-coagulation

Additives for Latex Dipping Process

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Dewebbing/ Antifoams			
Wetting			
Heat – sensitive Coagulation	Higher endapplication: medical gloves; textile supported gloves	Managerable coagulation in SBR/ NBR latices	**TEGO® Coagulant 4910** **TEGO® Coagulant 4720**
Dispersing			

Thermo Coagulants for Latex Dipping

Heat sensitising (Thermo-coagulation):

By the addition of certain polyethers, many latices can be made heat sensitive.

The latex compound is then stable at room temperature for an indefinite period of time but coagulates spontaneously on reaching an elevated temperature which lied between 35 and 60°C and is dependent on the formulation.

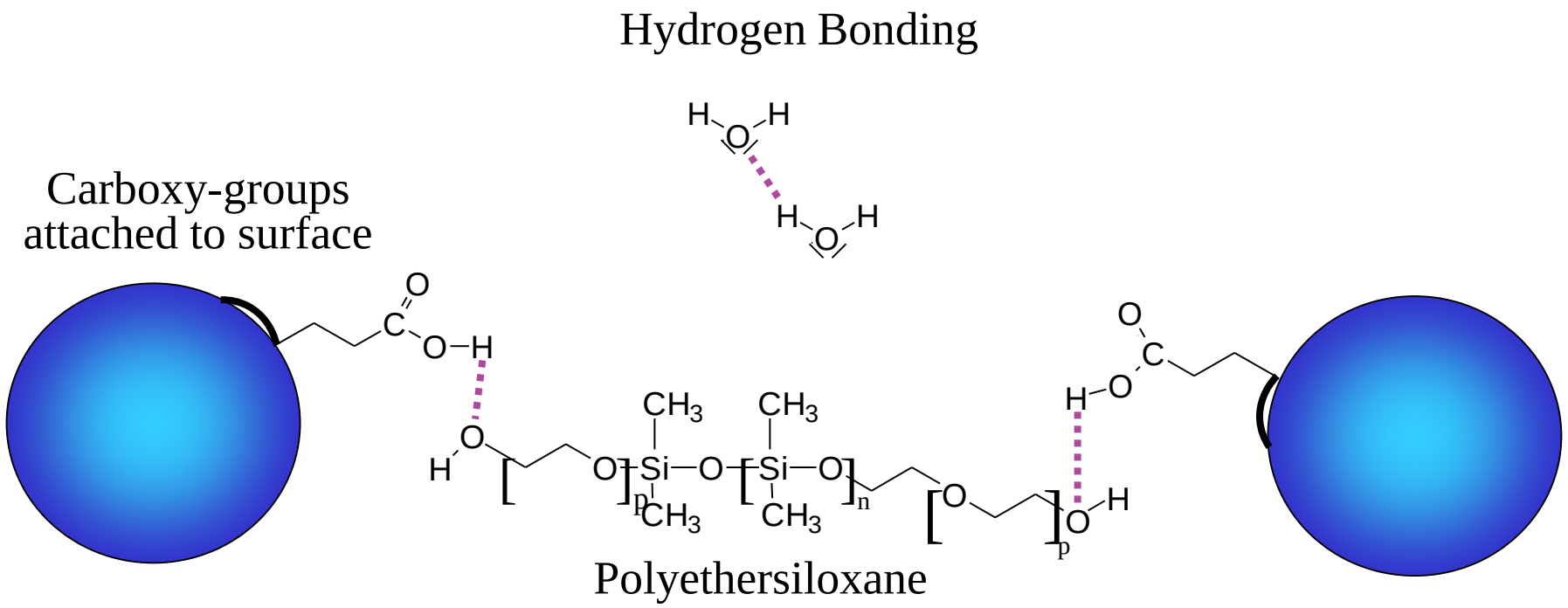
Suitable ethers are polyvinyl methyl ether, polyoxypropylene glycol, polysiloxane ether, cationic (quaternary) polyether amines and certain polyether polyurethanes. The choice depends on the type of latex and processing method.

Thermo Coagulants for Latex Dipping

- **TEGO® Coagulant 4720**
  is based on polyfunctional non-ionic ingredients. It is built up out of polybutadiene, polyethers and polysiloxane.
- **TEGO® Coagulant 4910**
  is a polyethersiloxane.

- improved film building properties
- controlled coagulation
- combination with salt coagulation possible
- high compatibility with the latex
- react completely with the polymer (4720)
- 100 % active

Possible Mechanisms of Thermo-Coagulation



Hydrogen Bonding

This denotes a form of chemical bonding between the unpaired electrons of e.g. oxygen and a hydrogen that is attached to a highly electronegative element. These bonds can be either inter- or intramolecular in nature.

Advantages of TEGO® Coagulants

Compared to available competitor products,
TEGO® Coagulants offer the following advantages:

- lower dosage requirements
- combination with salt coagulation possible and advantageous, respectively
- acceleration of production due to minimized dipping times
- improved feel of the final product
- additional emulsifier is not necessary for the stabilisation of the latex

Sample Receipes with TEGO Coagulant 4720 and 4910

Please find below some guide lines to use our products.
The quantities are given in units per hundred parts of dry substance (phr).

Formulation 1

Perbunan N-Latex T (50%)	200
NH_4OH (25%)	1
Water	4
TEGO® Coagulant 4720	0.5
Vulcanisation paste	19
China Clay T dispersion (60%)	24
concentration	48,7
coagulation temperature	39

Formulation 2

Butofan DS 4033X	100
Ammonia	until pH 9
K-Scriset 540	0.25
Tammol NN 4501	1
Water	(188)
ZnO Dispersion	2.5
Sulfur Dispersion	0.5
ZMBT Dispersion	0.5
ZDEC Dispersion	0.5
TEGO® Coagulant 4720	1

Formulation 3

Butofan DS 4025X	100
Potassium hydroxide	until pH 8.5
K-Scriset 540	0.25
Tammol NN 4501	1
ZnO dispersion	3.5
Sulfur dispersion	0.8
ZMBT dispersion	0.5
ZDEC dispersion	0.5
TEGO® Coagulant 4720	0.5

Formulation 4

Carboxylated nitrile butadiene rubber (dry)	100
Sodium dodecylbenzene sulfonate	0.25
Potassium hydroxide	0.7
Sulfur dispersion	1.0
Zinc dibutyl dithiocarbamate	1.0
ZnO dispersion	0.5
TiO_2	4.0
Michemlube 135	3.0
TEGO® Coagulant 4910	2.0
Stantone WD 2467 pigment	0.1
cherry flavor	0.7

Dispersants

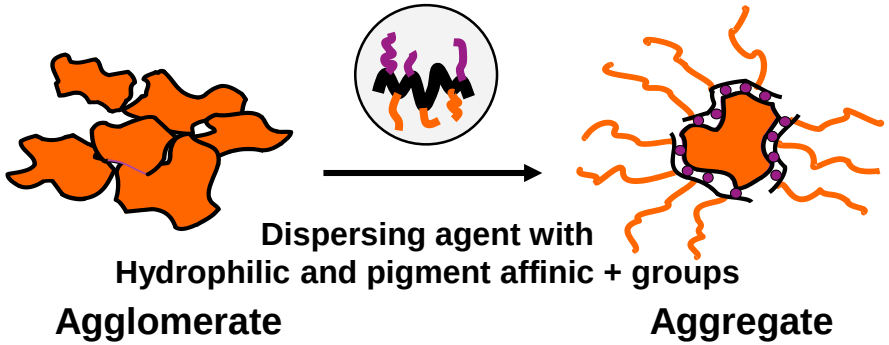
Additives for Latex Dipping Process

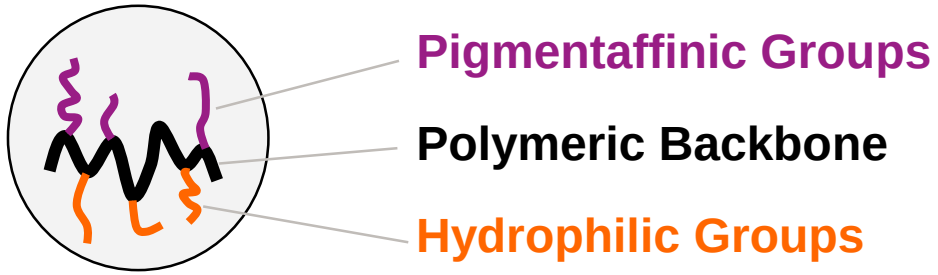
	Issue	Why	Solution
Dewebbing/ Antifoams			
Wetting			
Heat – sensitive Coagulation			
Dispersing	Coarse filler or pigment particles lead to weak spots in the film and thus increase rejects	Bad dispersion of fillers and/or pigments. Build up of agglomerates after addition to the latex.	**TEGOMER® DA 640** **TEGOMER® DA 850**

TEGOMER® – Amphiphilic Dispersing Agents – Mode of Action

Due to their special chemical nature they -

- **are temperature stable.**
- **will stabilize the pigment/filler dispersion in the water phase**
- **are compatible with dispersed systems and latices**
- **can interact with the pigment surface and will form a stable layer on it.**





TEGOMER® Dispersants allow high flexibility in application and excellent efficiency due to high temperature stability and amphiphilic character

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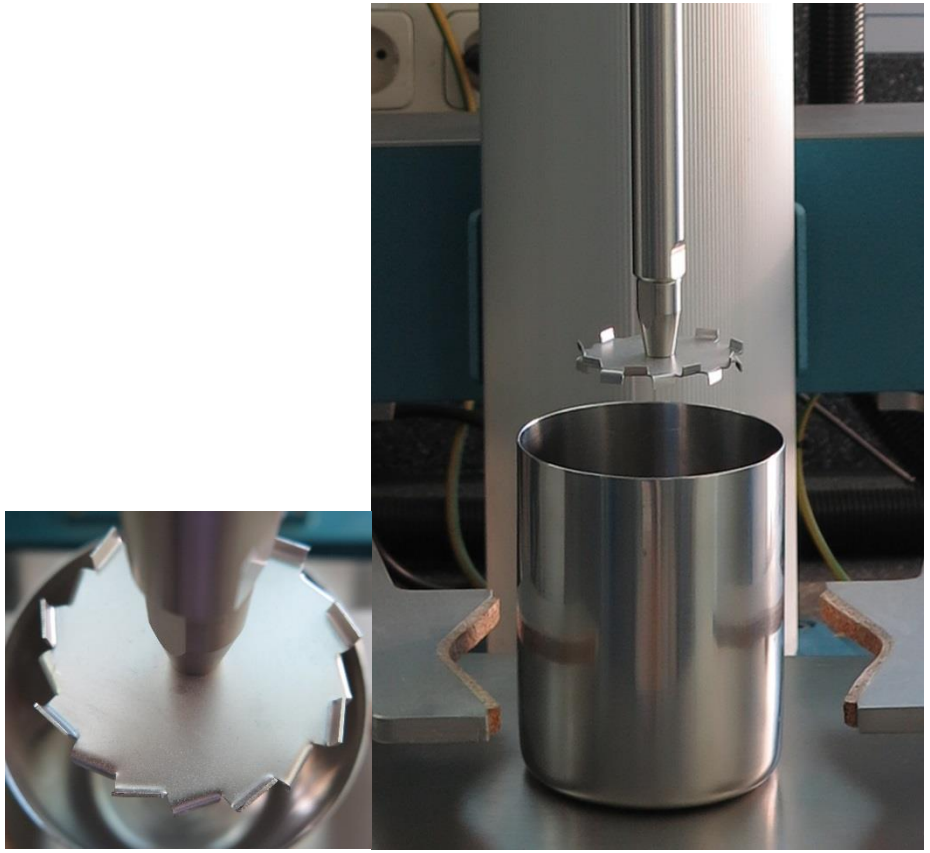
Pigment Paste - Dispersing

Recommended Products	Chemistry	Active Content [%]
TEGOMER® DA 640	anionic modified polyether	30
TEGOMER® DA 850	Polymeric Copolymer	40



Lab Dispermat equipped with a Dissolver blade

Dosage Recommendation for TEGOMER® Dispersants

	% AOP* (100% dispersant)	% AOP TEGOMER® DA 640 (30% active)	% AOP TEGOMER® DA 850 (40% active)
Filler	0.2 – 2.0 %	0.7 – 7.0 %	0.5 – 5.0 %
Inorganic Pigment	1.0 – 5.0 %	3.5 – 16.5 %	2.5 – 12.5 %
Organic Pigment	10 – 30 %	35 – 100 %	25 – 75 %
Carbon black	10 – 50 %	35 – 165 %	25 – 125 %
Nano particles	5 – 15 %	17 - 50 %	12.5 – 37.5 %

% AoP: Additive calculated on pigment in parts by weight

Red Pigment with 5% Additive Active Ingredient to Pigment

Control

- High viscous mixture
- Course particles
- Bad handling properties

TEGOMER® DA 850

TEGOMER® DA 640

- Homogenous distribution
- **No larger particles**
- Easy to handle

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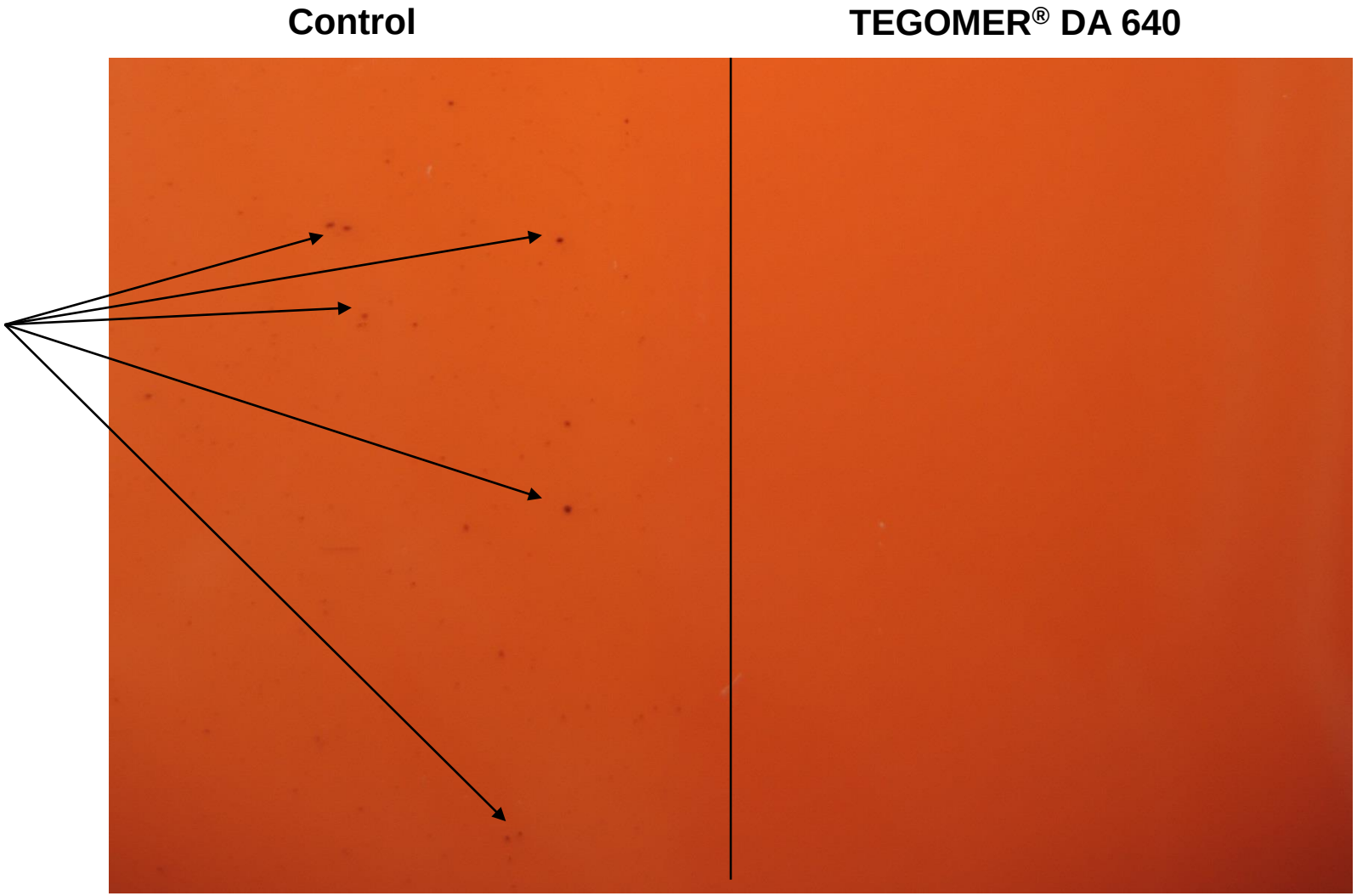
Colored Film with different Pigment Pastes

Large pigment particles that may lead to film rupture



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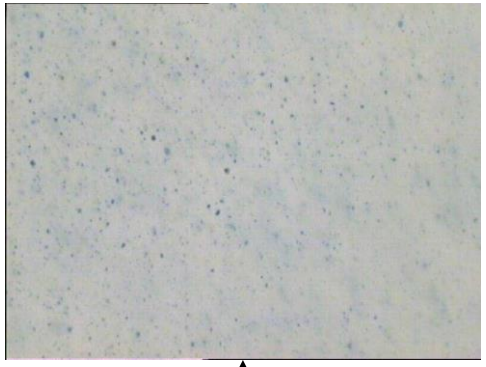
Pastes with 66% CaCO3 with 2% Dispersant (100%) on Pigment

Control

TEGOMER® DA 640

TEGOMER® DA 850



Many large particles
that may cause defects

Much better dispersion
and only few particles

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