Silicate Emulsion Systems

Historical Background, Formulation and Application






Wöllner GmbH
07/2020

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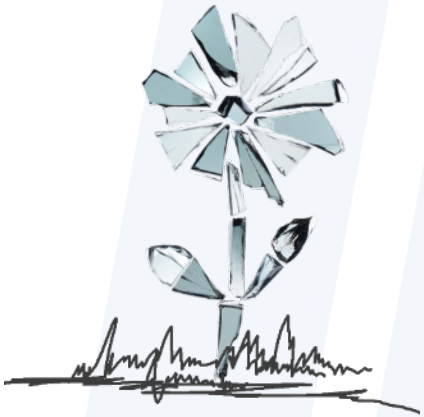


Wöllner – A Brief Introduction

Who We Are

Dr. Eduard Wöllner family foundation – owner-managed

Founded in 1896 – more than 120 years of experience

Headquarters in Ludwigshafen / Germany

Main product groups:

- Soluble silicates for large chemical manufacturers
- Raw materials and additives for the construction industry & special applications
- Process chemicals for the paper industry and industrial water circuits

Approx. 150 employees

Approx. € 50 million annual turnover

Company sites in Germany & Austria

Production Sites

Bad Köstritz

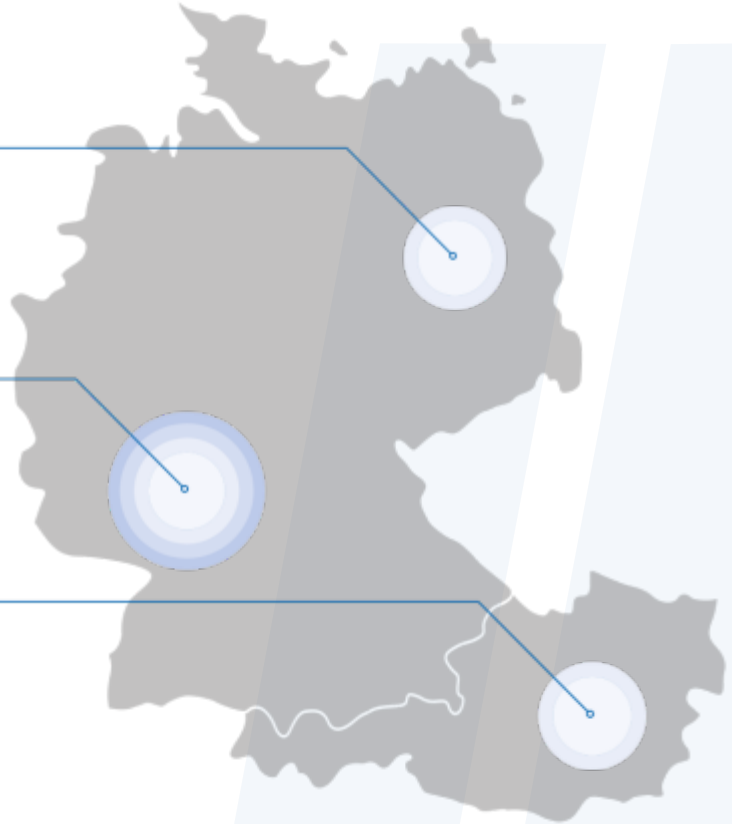
Production Site

Ludwigshafen

Headquarters and Production Site

Gratwein-Straßengel

Distribution and Production Site



Technical Expertise

Future-oriented development and application of expertise for sustainable economic growth

- Own R & D laboratories
- Own analytical laboratories
- Own microbiology
- Highly skilled team of application engineers and service technicians

combined with appropriate, modern equipment; competent and motivated employees; and ISO-certified processes

TARGET INDUSTRIES

Historical Background of Silicate based Coating Systems

- **Approx. 4.000 BC:**
  In Egypt, strong hints exist that a kind of sodium silicate has already been used for preparation of paints (as binders of pyramid paintings)

- **Approx. 200 BC:**
  In Pompei sodium silicate has been used for preparation of frescos (wall paintings) / as binder in frescos.

- **Middle Ages and Following Epoches:**
  - Pater Basilius Valentinus: „Liquor Silicium“
  - Jan Baptist van Helmot, Glauber: „Kieselfeuchtigkeit“
  - Goethe

- **19th Century: Industrial Application**
  - Buchner, Liebig, Kuhlmann, Fuchs: „Wasserglas“
  - Several developers gather experience with alkali silicates & various experiments lead to the revival of the silicate paints technique
  - 1879 Patent granted to Adolf Keim for production of mineral paints


KAISERLICHES PATENTAMT.

PATENTSCHRIFT

№ 4315.

ADOLF KEIM

BEFESTIGUNG VON MINERALFARBEN AUF WANDPUTZ ZUR HERSTELLUNG VON WANDGEMÄLDEN.

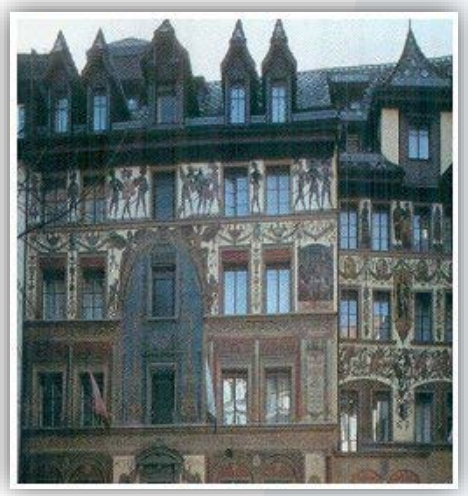
Klasse 22.
FARBSTOFFE, FIRNISSE, LACKE.

BERLIN

- **During the 1970s**
  - Development of first systems based on potassium silicate in combination with styrene acrylic
- **Since 1980: Development of a New Generation of Silicate Paints**
  - Combination with organic dispersions
  - Further optimisation of properties
  - Starting Point for market penetration of silicate emulsion paints

Historical Pure Soluble Silicate Paints

- 2-component systems
- Systems for specialists
- Difficult to handle (pot life, maturing time)
- Not suitable for common use
- Usually no organic ingredients
- Focus on historical buildings

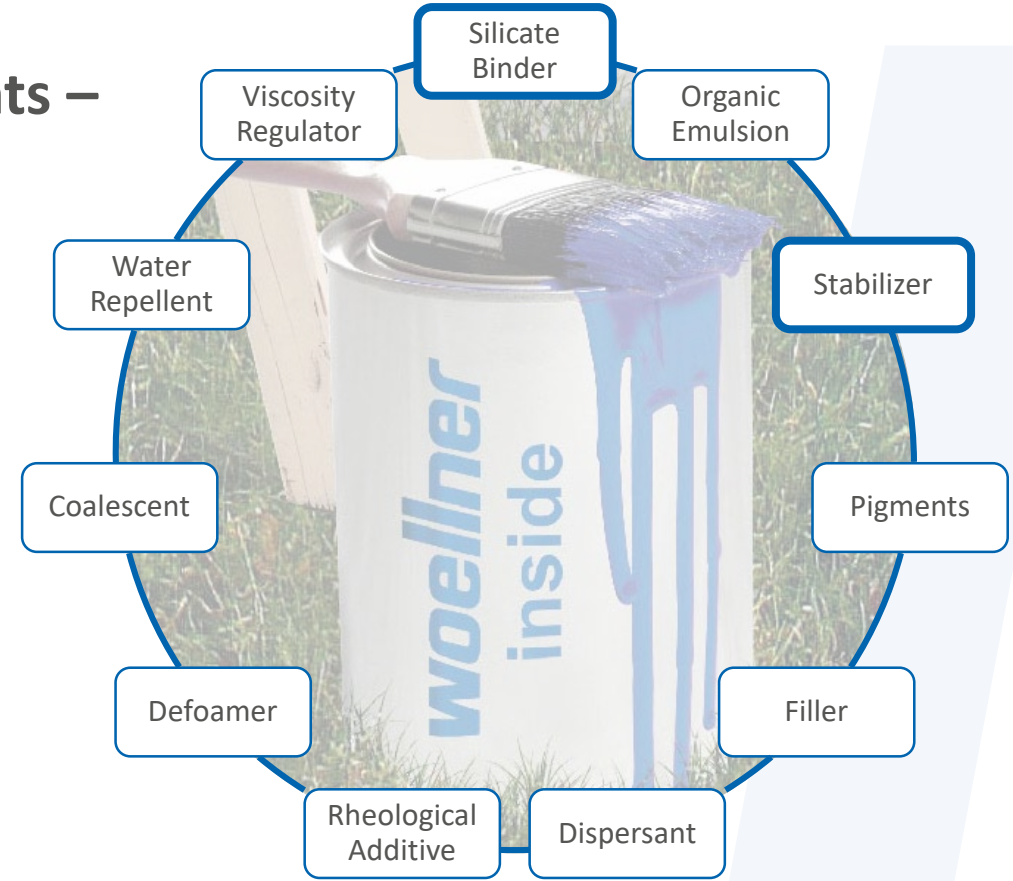


Silicate Emulsion Paints

- Up-to-date hybrid systems: combination of
  - organic binders (based on acrylic emulsions)
  - inorganic binders (based on soluble silicates)
- Suitable for common use
- Wide range of applications
- 1-component, storage stable systems
- Ready-to-use
- Early water resistance against driving rain
- Formulation according to DIN 18 363 (max. 5% organic contents)

Silicate Emulsion Systems Composition

Silicate Emulsion Paints – Ingredients



Silicate Emulsion Systems

Composition

Inorganic raw materials

- Soluble silicate solution
- Inorganic pigments (TiO_2, Ironoxide, etc.)
- Fillers ($CaCO_3$, Talcum, Quartz, Kaoline)

Organic raw materials

- Water based synthetic emulsions (styrene acrylates)
- Additives

What are Soluble Silicates

- Soluble Silicates = waterglass
  - the only type of glass which can be redissolved in water again
- Collective name for glassy frozen melts of alkali silicates with varying composition and corresponding solutions
- Represent the alkali salts of silicic acid

$$M_2O \bullet x\ SiO_2$$

M = Na, K, Li

Definition of Module

$M_2O \bullet x\ SiO_2$ M = Na, K, Li, (Cs, Rb)

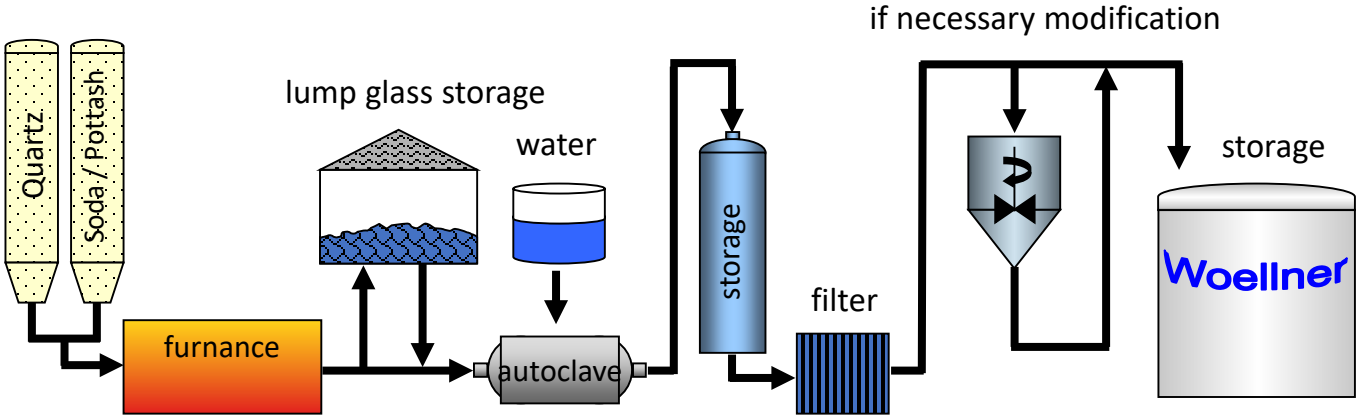
Molar Ratio:

$$MR = \frac{\text{Mol } SiO_2}{\text{Mol } M_2O}$$

Weight Ratio:

$$WR = \frac{\text{W. \% } SiO_2}{\text{W. \% } M_2O}$$

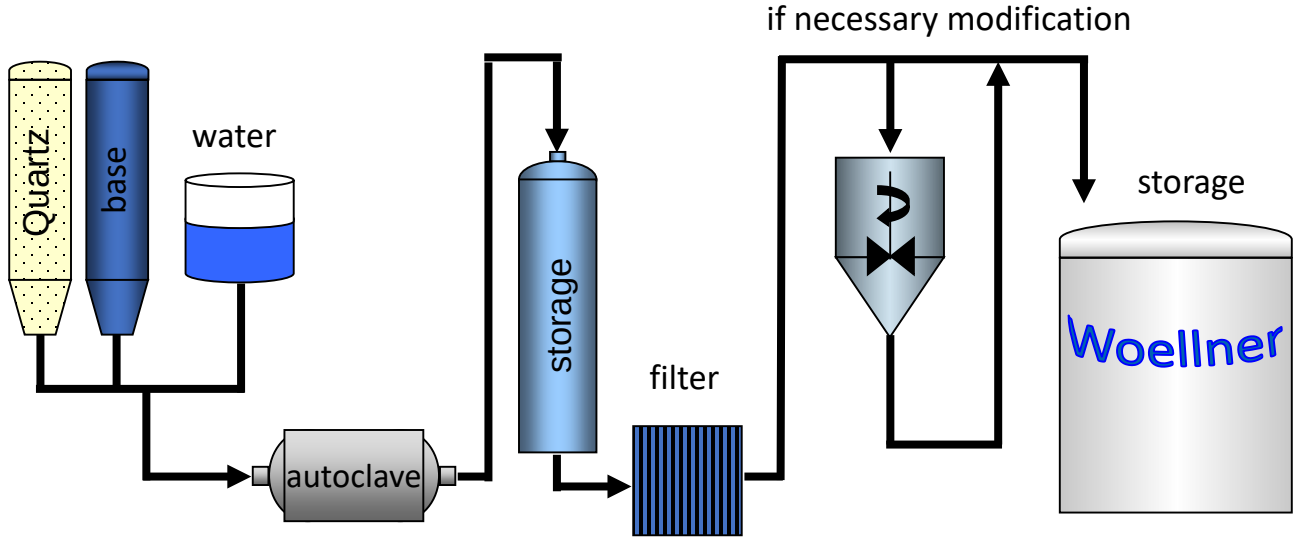
Alkali Silicate - Production: “Furnace Route”



$$M_2CO_3 + x\ SiO_2 \longrightarrow M_2O \bullet x\ SiO_2 + CO_2$$

M = Na, K

Alkali Silicate - Production: “Hydrothermal-Route”



$$2\ MOH + x\ SiO_2 \longrightarrow M_2O \bullet x\ SiO_2 + H_2O$$

M = Na, K, Li

Silicate Binder

Preferred Potassium Silicate Binders for Decorative Systems (paints, plasters: Betolin® K- resp. P-types)

- Significantly lower efflorescence
- Lower increase of salt volume
  - Potassium carbonate (up to 2 chemically combined water molecules)
  - Sodium carbonate (up to 10 chemically combined water molecules)
- No crystallization tendency
- Higher water resistance
- Stable bond with good adhesion
- Availability of products with high modules
- Increased compatibility with organic emulsions

Wöllner Product: Betolin® K 28
- pure inorganic mineral binder
- no stabilisation
- 28% solids

Silicate Binder

Prestabilized Potassium Silicate Solutions for manufacturing-friendly Formulation Properties (Betolin® P-types)

- Facilitate the combination with organic emulsions
- Stabilising additives prevent the SiO_2-polyanion from polymerisation
- Stabilise the interaction between polymer emulsion and soluble silicates
- Optimize the interaction between binders and fillers
- Passivate impurities like polyvalent metal-ions
- Have a positive effect on long time storage stability (especially viscosity)

Wöllner Product: Betolin® P 35

- pre-stabilized binder based on potassium silicates
- 29% solids

Reactions with Polyvalent Cations

Reactions between Silicate Binder and other Raw Materials of the Paint may occur

- Therefore compatibility tests between the different raw materials and alkali silicates have to be performed in advance to ensure long term storage stability
- For example with Calcium; Magnesium; Iron; Aluminium
- Might lead to increasing viscosity (gel) or solid silicate compounds (precipitation) through electrostatic bonding mechanisms

Compatibility Test regarding Emulsions, resp. Fillers

Procedure

- Dilute emulsion with water
- Slowly add waterglass while stirring the solution
- Wait until eventual foam has been destroyed
- Pour the mixture over a glass plate and examine the resulting film
- The film should be clear without any spots, particles or irregularities
- Repeat the test after 1 week furnace storage of the mixture at 60°C

	Weight (%)
Water	70
Betolin P 35	20
Emulsion, resp. Fillers	10

! Fillers and pigments can be tested accordingly (replacing the emulsion content).

Examine the eventual forming of gel structures or agglomerations !

Organic Emulsions

Demands on Organic Emulsions

- Compatible resp. nearly inert to potassium silicates
- Storage stable
- No odour (no solvents, softening agents, ammonia gas,...)
- Low temperature for film generating (MFT)
- Mainly highly stabilised acrylate/styreneacrylate copolymers -> against saponification (especially ethylhexyl- or butylacrylate/styrene as main monomers).
- But also pure acrylates or terpolymers.

Organic Emulsions

Polymerised Supplementary Monomers

- Interaction with silicate binders
- Mainly containing carboxyl groups (acrylic- or methacylic acid)

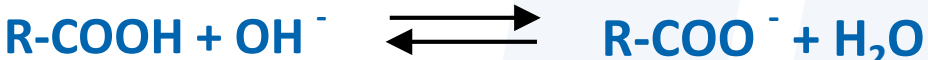
Cause

- Enhancing the stability of the emulsion (shere stability, electrolytes, storage stability)
- Easier control of viscosity
- Enhancement of the coating adhesion

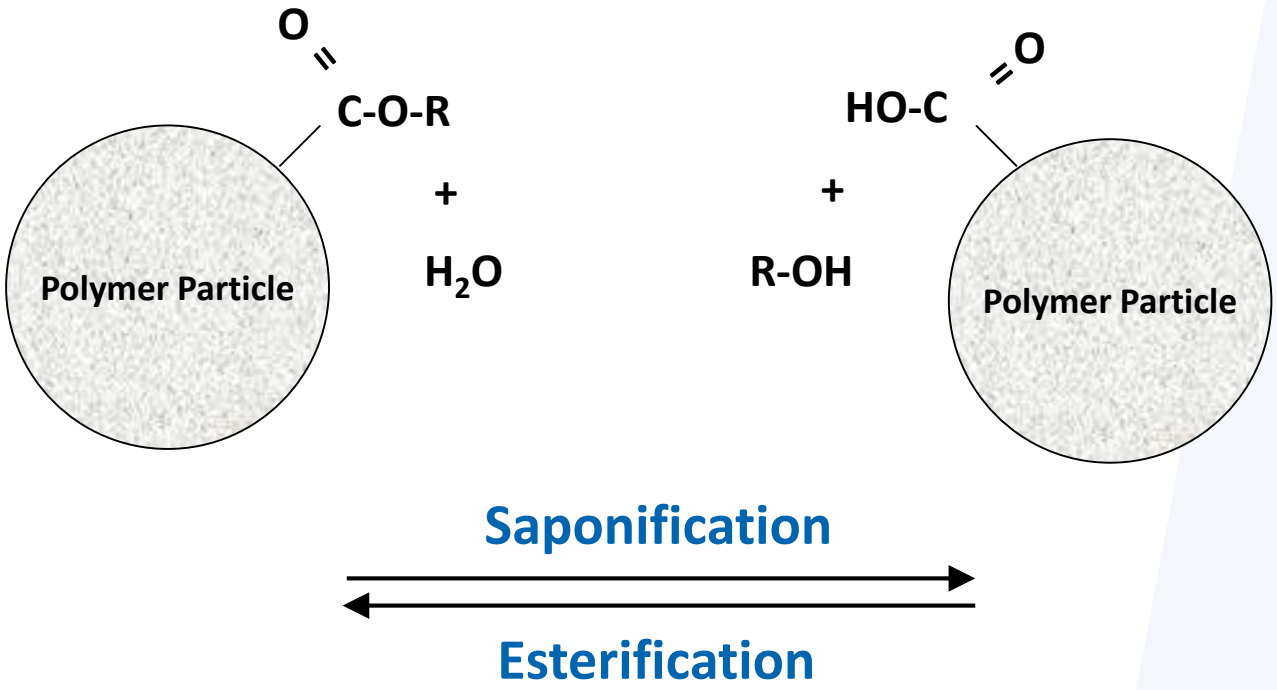
Organic Emulsions

In Alkaline Systems

- Carboxyl groups are mainly dissociated
- Growing electrostatic repulsion
- Growing hydrophilicity
- Growing solvation
- Growing moisture expansion
- Growing viscosity



Organic Emulsions



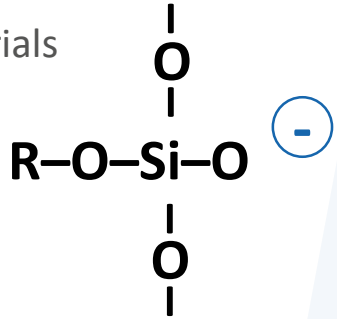
Organic Polymer Binder

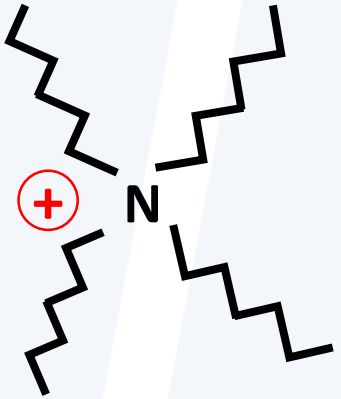
Styrene Acrylic or Pure Acrylic Emulsions

- Organic binder
- Fast curing after application, in order to protect slower curing potassium silicate in the first hours / days
- Compatible products have a high stability at high pH-value

Stabilizers

- Enhance the stability of the formulation
- Necessary amount depends on corresponding raw materials
- Partial shielding of reactive silicate groups
- Consecutive reactions are hindered
- Storage stability improved



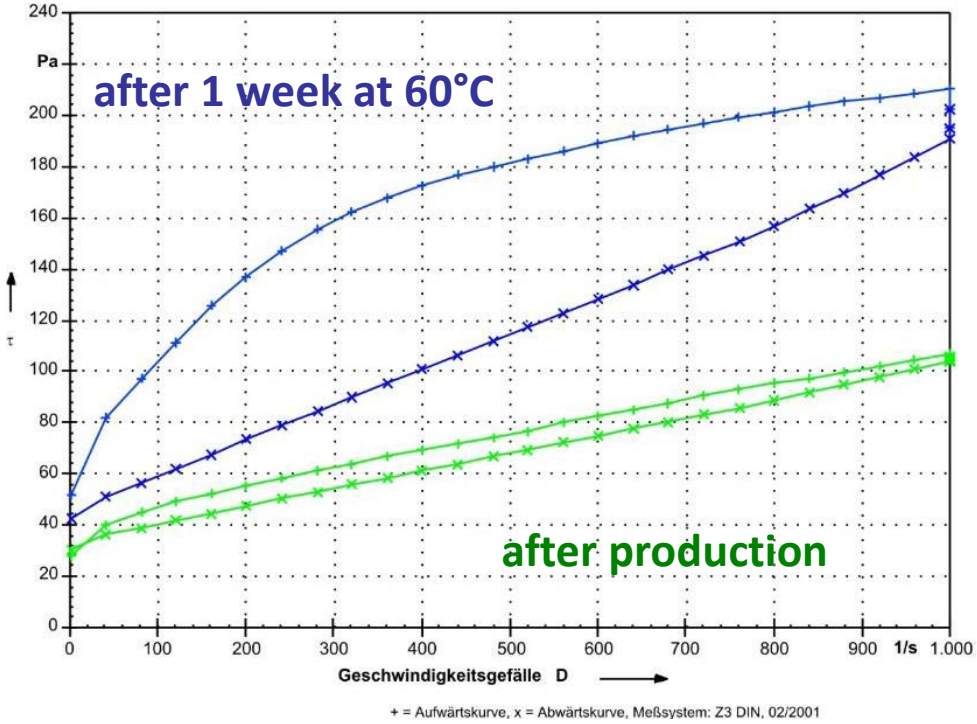


Stabilisers for silicate binders: Betolin Q 40 / Betolin Q 44

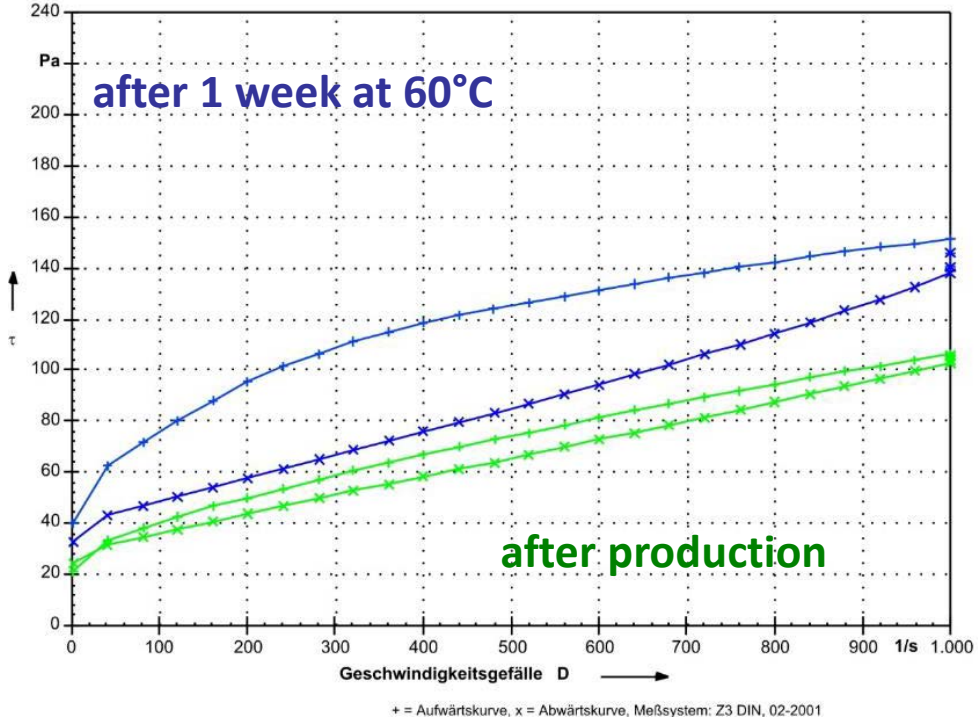
Wöllner Product: Betolin® Q 40

- waterbased stabilizer, based on alkoxylated alkylammonium compounds
- decreases the interaction between potassium silicate binder and fillers / styrene acrylics
- prevents efficiently the growing of longer silicate chains / networks
- lower risk of viscosity increasement

Silicate Emulsion Paint – not stabilized

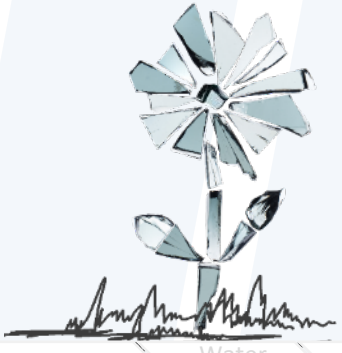


Silicate Emulsion Paint – stabilized



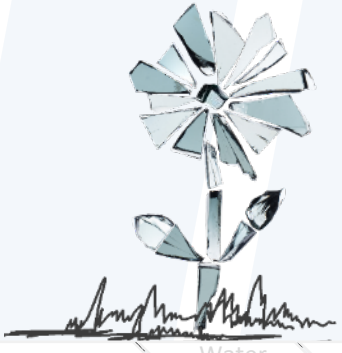
Pigments

- Titanium dioxide (TiO_2)
- Lithopone
- Inorganic pigments (e.g. Iron Oxides, Chromium Oxides, etc.)
- Inorganic ready to pigment dispersions
- Iron oxide (red, yellow, black)
- Chromium oxide (green)

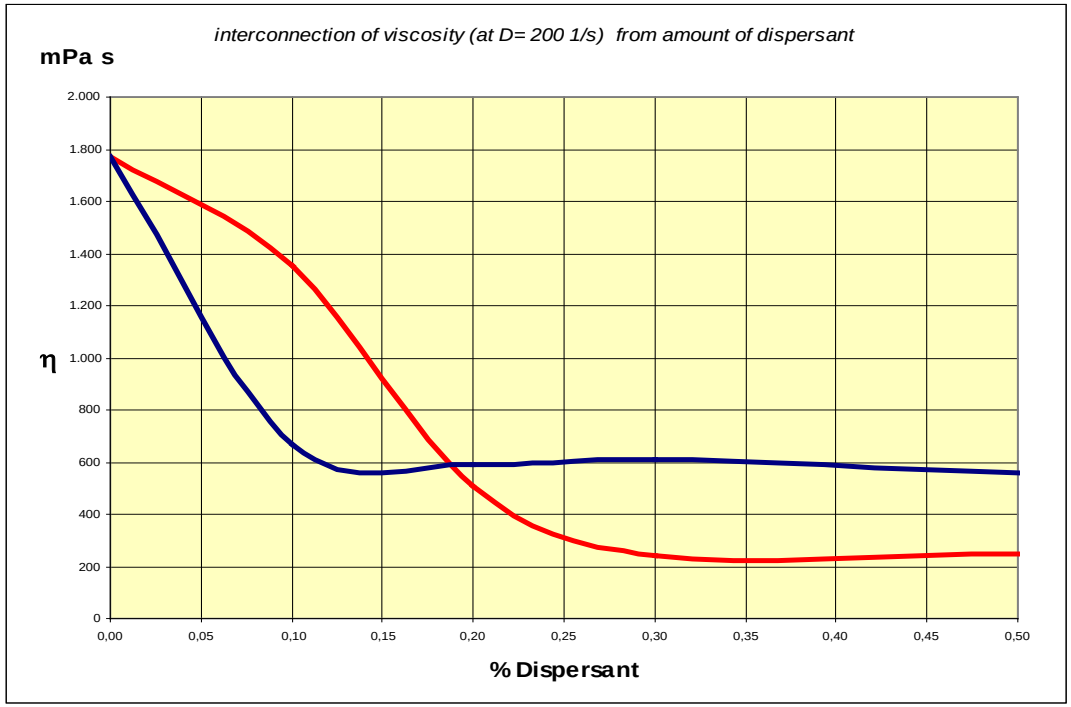


Fillers

- Calcium carbonate (Marble, Calcite, Chalkstone)
- Clay
- Talcum / Talc
- Plastorite
- Neuburg siliceous earth
- Mica
- China clay
- Quartz / Quartz sand



Dispersants



Wöllner Product: Sapetin® D 20 / Sapetin® D 27

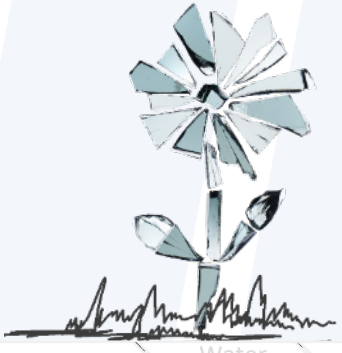
- water based formulations based on modified phosphonic acids with high pH-stability
- allows very good dispersion of fillers and pigments
- allows higher dry matter in paints
- Sapetin D 20 also compatible with lime milk

Rheological Additive

- Cellulose ether (CMC, HEC)
  - thickener to adopt water retention
  - better application properties
  - important in silicate based coatings
- Bentone
- Xantane gum
- Polyacrylates
- Polyurethane

Wöllner Product: Betolin® V 30

- Anti setting agent based on xanthan gum
- avoids sedimentation
- enhanced colour stabilisation
- good compatibility at high pH-value



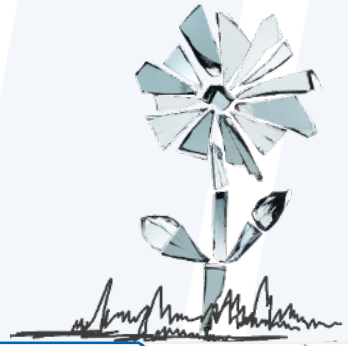
Defoamers and Coalescents

Defoamers

- Mineral oil
- Silicone emulsion
- Hydrocarbons
- Long chain based alcohols
- Anti-foaming

Coalescents

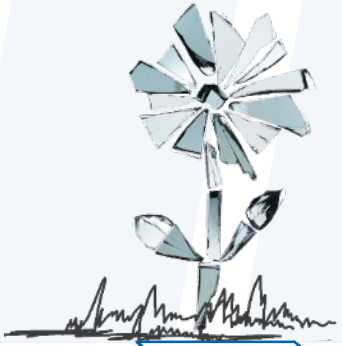
- White spirit
- Glycols
- Texanol



Water Repellents

- Siliconates
- Siloxanes (**Betolin AH 250**)
- Wax emulsions
- Fatty acids

Wöllner Product: Betolin® AH 250
- aqueous emulsion of special polysiloxane
- good compatibility at high pH-value
- efficient hydrophobizing effect



Viscosity Regulator / Hydrophobic Agent

- Supports the properties of Betolin Q 40; Sapetin D 20 / 27 and Betolin AH 250
- Increases binder stability against electrolytes
- Exerts a hydrophobic effect and thus improves the coating resistance to water

Wöllner Product: Betolin® A 11

- based on silanols and complex stabilizers
- allows the regulation of the viscosity also by post-addition
- improves resistance against water / humidity

Formulation

Starting Point Formula - Silicate Emulsion Paint (DIN 18363)

Water		Add to 100		
Anti Setting Agent (Xanthan basis)	*Betolin V 30*	0,05	-	0,1
Cellulose Ether		0,05	-	0,1
Dispersant	*Sapetin D 27*	0,1	-	0,3
Stabilizer	*Betolin Q 40*	0,3	-	0,5
Titanium Dioxide		6,0	-	10,0
Defoamer		0,1	-	0,3
Fillers (Carbonate)		10,0	-	20,0
Fillers (Silicate)		10,0	-	20,0
Polymer Emulsion		7,0	-	9,0
Specially Modified Silicate Binder	*Betolin P 35*	18,0	-	22,0
Viscosity Stabilizer	*Betolin A 11*	0,5	-	1,0
Water Repellant	*Betolin AH 250*	0,6	-	1,0

Mixing Order

Water

Thickener N°1 (HEC or CMC)

Thickener N°2 (Betolin V 30, Xanthan Gum based)

Stabilizer (Betolin Q 40)

Dispersant Agent (Sapetin D 27)

Titanium Dioxide

Anti-Foaming Agent

Fillers (Calcium Carbonate)

Fillers (Silicates, Talc, Mica)

Organic Binder (Styrene Acrylic)

Coalescent (if necessary)

Potassium Silicate (Betolin P 35)

Viscosity Regulator (Betolin A 11)

Hydrophobic Agent (Betolin AH 250)

Pigments

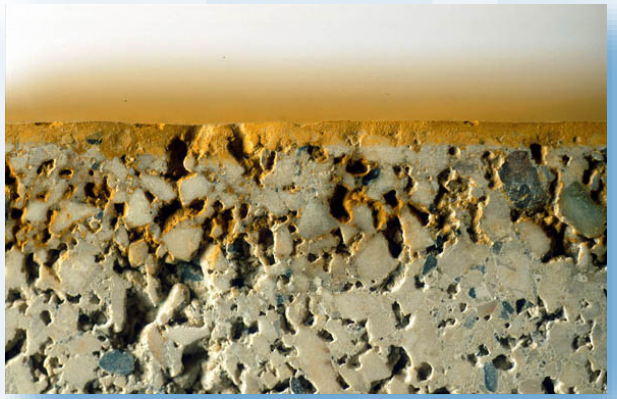
What to Take Care Of?

- Use soluble silicates compatible raw materials
- **In case of problems:**
  Main focus should be taken on carbonate fillers and emulsions
- Prefer usage of prestabilized potassium silicate solutions!
- Add soluble silicate binder at last and slowly
  → Avoidance of alkaline shock!

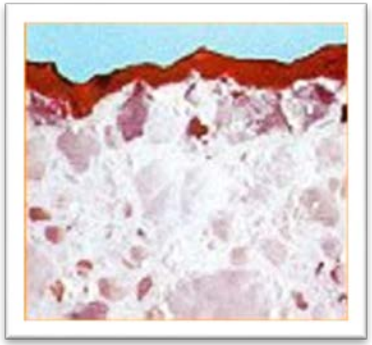
Substrate Types & Application

Potassium Silicates

- Inorganic binder
- Penetration into the porous mineral substrate followed by chemical reaction with components
- Reticulation of the silicate
- Consolidation / reinforcement of the mineral substrate
- High durability
- Low efflorescence effect



Potassium Silicates – Penetration Properties



Pure Emulsion Paints

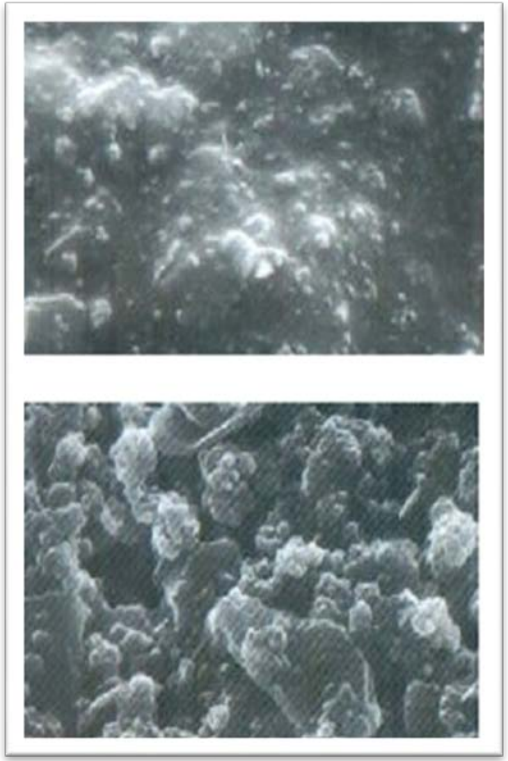
→ mainly remain on the surface

Silicate Emulsion Paints

→ penetrate into the surface up to 5 mm and consolidate the structure

Pure Soluble Silicates or Primer even penetrates deeper

Potassium Silicates – Coating Structure



Pure Emulsion Paints

- mainly show closed film structures

Silicate Emulsion Paints

- feature open coating properties (according to DIN 18363)

Substrate Types

Suitable Substrates

- Fresh or set high calcium lime and sand mortar
- Fresh or set lime cement rendering
- Concrete surfaces
- Sand lime brick masonry
- Natural stone
- Bricks
- Fibre cement board
- Aluminium surfaces

Unsuitable Substrates

- Plastic materials
- Fatty, oily or heavy soiled surfaces
- Existing oil paint coatings
- Concrete if protection against carbon dioxide is desired

Substrate Types

Conditionally suitable substrates (sometimes pre-treatment required)

- Gypsum finish
- Cellular concrete (too porous)
- Old limewash coating
- Old emulsion paint coating
- Natural stone with closed surface
- Clinker brick walls
- Inorganic foamed materials (foamglass)
- Iron

Gypsum Substrates

- Gypsum containing surfaces
- Gypsum plaster boards
- Wood fibre lightweight building boards

→ Suitable for silicate emulsion systems after corresponding pre-treatment.

Substrate Pre-Treatment

The use of primers is recommended if:

- Substrate has to be reinforced
- Unequal surface properties
- High absorption of solvent water

Starting point formula - primer:

Water	**70**
Polymer emulsion	**10**
Betolin P 35	**20**

- As reinforcement of sanding plasters: pure
- As primer: mix 1 : 1 with water

Substrate Pre-Treatment

The use of primers is recommended when …

- Surface has to be reinforced
- Surface has to be equalized if it is has not been completely cured
- Unequal surface or high volumes regarding the up taking of solvent water

Fluates may be used:

- For removing of sinther skin
- If very even mineral surfaces have to be roughened

Note: Fluates are no longer up to date

Substrate Pre-Treatment

- Mineral based surfaces need to have enough time to settle and to cure (2 - 4 weeks / according to Product Information). If the coating application starts too early the coating is not able to bridge cracks in the plaster below
- Stability and carrying capacity of the substrate has to be checked with a knife under wet and dry conditions
- Substrate has to provide even sucking properties
- Soluble silicate systems are easier to handle on pre-treated surfaces due to slower penetration of solvent water. The open time is extended and the visual appearance of the resulting surface will be more even
- Pigmented primers help to protect the valleys in structured plasters and help to cover the undercoat if it has a different colour
- Let primer dry for approx. 3 days

Application of Silicate Emulsion Systems

Due to the properties of silicate emulsion paints some points have to be followed:

- Covering of glass, ceramics, eloxal surfaces, lacquer surfaces because of the high reactivity of potassium silicate
- No application while raining and temperatures below 8°C
- Avoid application under direct sunlight and high temperatures
- Freshly repaired wall parts have to settle. The use of fluates is possible in such cases (bigger area than repaired part)
- Application only on well cured sub plasters

Application of Silicate Emulsion Systems

- Let primer dry for approx. 3 days
- Application of silicate based systems only on pre-treated or reinforced surfaces
- Do not store primer, paint and plaster under air for a long time
- Clean application tools immediately after work with (warm) water
- Carry standard protection cloths

Application Tools

- Brush
- Paint roller
- Traufel
- No spraying (spray dust)

Curing Mechanisms

Curing: Reaction with Surface

- Physical network building of organic component for early water resistance
- Chemical curing of inorganic component through:
  - Reaction with polyvalent metal ions from the mineral substrate (fillers / pigments / cementitious binders) to connect the silicate network through –Me–O–Si–bondings
  - Reaction of quartz particles in substrate
  - Reaction of carbon dioxide (CO_2) from the air
  - Evaporation of solvent water

→ mainly sol gel reactions and 3D-network building

→ Results in high bonding strength between coating and substrate

Possible Curing Reactions of Alkali Silicate based Coatings

- Fresh substrate

  $Ca(OH)_2 + K_2O \times nSiO_2 \rightarrow CaO \times SiO_2 + (n-1)SiO_2 + K_2O \times CO_2$

- Quartz in substrate

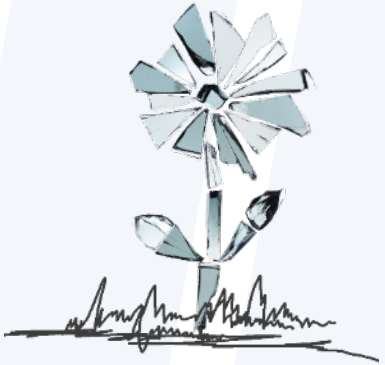
  $(x+y)\ SiO_2 + K_2O \times nSiO_2 \rightarrow K_2O \times (n+x)SiO_2 + ySiO_2$

- Carbon dioxide from air

  $K_2O \times nSiO_2 + mH_2O + CO_2 \rightarrow K_2O \times CO_2 + nSiO_2 \times mH_2O$

- Physical water elimination

  $K_2O \times nSiO_2 + H_2O \rightarrow K_2O \times nSiO_2$



Potential Pitfalls of Paint Application

Efflorescence

Reaction of carbon dioxide and waterglass leads to potassium carbonate (potash).

Water soluble salts move to surface.

Soiling Tendency

Silicate products have no thermoplastic properties.

Therefore the soiling tendency is very low.

Algae / Fungus Resistance

The high pH-value of silicate emulsion paints initially prevents the wall from fouling with algae and fungus.

Long term film preservation necessary.

Burning Behaviour

According to DIN 4102 silicate emulsion paints are categorized as **Fire Class A2** depending on the organic constituent.

Chalking

The addition of up to 5% emulsion (solids content) leads to lower chalking tendency.

The low chalking property leads to some kind of **self cleaning effect**!

Chalking may occur in case of:

- Wet substrate for a long period of time
- Salts
- High absorbency of substrate
- Fresh plaster
- Unsuitable substrate
- Temperature

Colour Variation

Colour Variation may occur in case of:

- Rain or fog
- Temperature
- Direct sunlight
- Organic pigments
- Inhomogeneous surface

Spots

(Stripes, Varnish Runs, Efflorescence)

Spots may occur in case of:

- Different suction effects
- Sinter layer
- Ground coat too concentrated
- Substance bleeding through coating
- Potash, silica
- Micro organisms

Flaking

- No supporting ground
- Frost after fresh application
- No silification possible with surface
- Sinter layer
- Wrong layer composition
- Ground or primer hydrophobic

Dangerous Substance Directive

- It is possible to obtain formulations with no need of declaration through the selection of suitable raw materials
- Not classified as dangerous according to CLP - Regulation
- No H + P – phrases

Influence on Aging

- Friction and pressure
- Heat radiation
- Sunlight
- Ultraviolet radiation
- Humidity
- Oxygen
- Carbon dioxide
- Exhaust gases

Wall Damage

Advantages

Benefit from Silicate Emulsion Systems – Exterior

- Insensitive to various air pollutants in different climatic regions
- Very low soiling tendencies
- High colour stability
- Enhanced optical appearance for a longer period
- UV-stable (even in combination with photocatalytic pigments)

- High water vapour permeability
- Strengthen weathered or sandy mineral substrates
- Harmonic in structure and material to mineral based substrates
- Environmentally friendly
- After curing resistant against water and driving rain
- Suitable for new and old buildings for inside and outside applications

Benefit from Silicate Emulsion Systems – Interior

- UV-stable (even in combination with photocatalytic pigments)
- Fire protection certification due to low fire loads possible (< 5% organics)
- No decomposition of soluble silicates
  - ➢ even at high temperatures
- No in can preservatives
- No allergenic effects
- Wash and rubbing resistant
- Not classified as dangerous according to EU dangerous substance directive

Conclusion

Famous References for Silicate Paint

- Brandenburg Gate (Berlin)
- White House
- Kremlin
- Buckingham Palace
- Sydney Opera

Silicate emulsion systems possess a high ranking in praxis.

They are most welcome problem solvers for the preservation and designing of historical and modern buildings for inside and outside applications.

Wöllner Products for customized Silicate Emulsion Systems

Silicate Binder: Betolin® K 28

Silicate Binder: Betolin® P 35

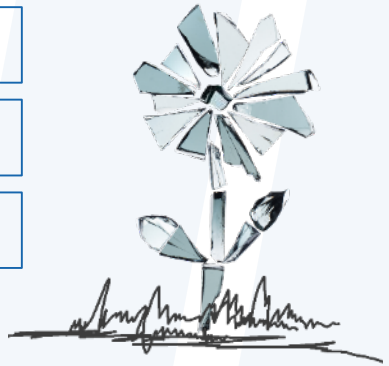
Stabilizer: Betolin® Q 40

Dispersant: Sapetin® D 20 / Sapetin® D 27

Rheological Additive (Anti Setting Agent): Betolin® V 30

Water Repellent: Betolin® AH 250

Viscosity Regulator / Hydrophobic Agent (Stabilizer): Betolin® A 11

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