Waterborne silicate coatings.

• Please connect to the Internet when viewing this presentation in order to view the full content.
• There are a number of hyperlinks that are essential to this subject and failure to view the content will create gaps in the data or technology.
• This is an introduction and review of “Silicate Coatings” and note a study course so you will need to build on the information that is supplied.
• You will need to have a full understanding of paint technology to be able to advance to “Silicate Coatings”.
• The chemistry is kept to the barest minimum but as it is “Reactive Inorganic chemistry” you may find that you need to learn a few new things.
• Please let me know if you feel I should correct or include any information but do remember that this is a limited and condensed review.

I hope you will find this presentation informative but contact me if you want help or need some clarification.

Kind regards, Ken Marx.
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From Sand to Paint

Waterborne Silicate Coatings

A review of the chemistry and technology of Silicate Coatings

Book One. Rev 03. 11th July 2016.
Compiled by Ken Marx.
Letter from the author

My three year course in “Chemical technology” was followed by a Marketing Diploma which was to aid in my understanding of sales as a technical sales person in chemical processing aids. The opportunity to grow my knowledge of the many chemical industries made life very interesting and quite exciting at times. Several other subjects i.e. ISO standards; Skills Development Facilitator (SDF) company compliance with the training records and claims for the Skills Levy; electronics (a three year course); ultrasonic processing (very intense 4 years); occupational health & safety Act etc filled a lot of my time.

Working in the R&D labs the practical experience was very important. My final years prior to semi retirement were as technical manger at several paint factories. I am a associate member of the SA Oil and Colour Chemist Association (ATSC) and have presented lectures at regional meetings. I was chairman of the first technical session at the 2015 OCCA symposium (Coatings for Africa 2015) in Johannesburg.

Working with ISO and related standards and legislation such as REACH, OSH Act, environmental and other programmes saw reams of regulations come our way. Following many years of lecturing in paint technology culminated in my registration as a “Subject matter expert in coatings” with the S A Qualifying Authority (SAQA).
My work was in or related to the coatings industry and has lead to this short review of “Inorganic binders”. The industry has gravitated to “Organic binders” over the past years and forgotten about inorganic coatings. The coatings industry however came to realise that we had to control the VOC and petrochemical problem. “Inorganic Silicate” coatings have made great strides but everyone appeared to ignore the opportunity to really disseminate this VOC free technology and truly embrace it.

The review that follows is an attempt to spread the word and focus on the coatings applications of silicate chemistry.

Ken Marx.
Preface

Before we get started let me say out loud that this information is not some earth shattering invention or discovery but simply a review of what the current state of the “Silicate Coatings” market is. The information is taken from various published sources and is focused on the paint industry and hopefully clarifies the technology and applications.

NB. This is not the be all and end all, you will have to build on this basic information to fully understand this technology.

It has always been a question of sharing knowledge for me. Knowing something that you can’t or won’t pass on is a sad state. The more knowledge we share the more we learn as knowing something does not mean that you understand it. The moment you start to share you will start to truly understand.

My first encounter with the use of silicate in coatings was about thirty years ago but not as a binder and rather as a water proofing additive which still stands unchallenged today. This only goes to show how effective silicates can be if used correctly.

So when I became aware of “Silicate Coating” technology I realised that this is something that needs to be clarified and shared. In addition silicate coatings are now said to be 10 or 15% of the decorative or architectural coatings used in Europe and is slowly gaining ground in the global market.
Of all the new coating technologies that are becoming available the recent developments of silicate coating technology is possibly the most important as it is based on non petrochemical raw materials. We all know that there is a need to pursue technology that will reduce our dependence on the petrochemical industry if at all possible. I hope that this condensed review on the current state of the art will make it easy for the paint chemist to understand silicate technology in the paint industry. There is a wealth of information from silicate raw material suppliers and coating additive manufacturers that can be found but it has not been compiled into a manual that can be followed by a paint chemist. Possibly the most important advantage of silicates is the fact that they are inorganic and form a chemical bond with inorganic mineral surfaces unlike the physical adhesion of organic binder systems. They are UV resistant; VOC free; do not contain any plasticizers, emulsifiers and other surfactants, are hard wearing and last for decades.

PCI journal offer a Webinar on the regulatory and VOC problem on the 14th Oct 2015 and say. Architectural paint regulations and labeling programs for volatile organic content (VOC) and emissions are constantly evolving. Globally, both mandatory and voluntary changes occur at different paces by region – and even by country or province within each region – which makes it increasingly difficult for formulators to remain up-to-date.
It goes on to say.
This webinar is designed to explain current and upcoming regulation changes in North America, Europe, Asia Pacific, and Latin America. It will also help attendees determine exactly what upcoming changes mean to their specific formulations, how to adapt to each new regulation change, and how formulators can minimize reformulation work as a result.

Most importantly this information focuses on coatings that are suitable for use on multiple substrates not only mineral types plus the possible elimination of twin pack or 2-K systems that have limited the acceptance of this technology. To think along the line of a two pack system would be retrogressive. Sort of like installing an edge runner or ball mill in a modern paint factory.

Historically silicate can be traced back to the early Egyptians but this is not important to this work and it is deliberately left out. You will only find information that clarifies the coating applications here. Furthermore you will not find any reference to such things as silicate plaster or renders as that would lead us down the path of the building or construction industry and may even require that you to start a new line of study.
The information is structured in a modular format with just enough chemistry to help you understand how things work. Once you grasp the basics you will be able to apply your paint technology knowledge to the formulating and manufacturing of silicate coatings.

I am not suggesting that you now start studying silicate chemistry as that is a vast subject and not part of paint chemistry. You should find a great deal of synergy between silicate coatings and organic coating technology. Remember that this is not an organic coating system so there are differences but also advantages in using reactive inorganic binders.

Every effort has been made to put the information in a logical easy to understand format however it will require that you work according to new rules in a number of situations. While compiling the information I have learnt far more than expected and realised that silicates have many benefits to offer the industry. It has also made me think more carefully about the clarity of the information that is available. Raw material suppliers do try to assist in supplying product applications and formulating recommendations but a quick internet search soon complicates matters and the all too often reference to the 2-K or masonry applications only serves to confuse the chemist.

When I started this project I found that there are an enormous number of silicate applications in other industrial chemical fields. Silicate coatings have to carry their own implementation costs yet the importance of disseminating the information can not be over looked.
Global distribution of coatings grade silicates has been limited as other applications and grades of silicates are much greater in volume and value. There are many grades of silicates that are available but not all are suited to the coatings industry. While some suppliers offer to make special grades on request it is not necessarily practical and will no doubt depend on volume and the possibility to get a profitable price for the new or special silicate product.

Getting the information into a step by step sequence was possibly the most difficult part of this work as you need to go from the basics to the final formulating and manufacturing and then the application of silicate coatings. There are differences between organic emulsions or solvent based coatings and inorganic silicate emulsion paints which may cause you some concern yet it is really just a question of learning a few new rules.

The information is taken from a global research of the available technology that is scattered in data supplied by many sources from related technologies and raw material suppliers. Just to complicate matters some information is imbedded in the intellectual property rights of either raw material suppliers or silicate coating manufacturers who have perfected the art. I have made reference to some raw materials and the related suppliers but would recommend that you do some of your own Internet searches. Contact me at any time for clarification or assistance. This is a totally non-commercial presentation of the available data relating to this technology.
Every effort has been taken to keep the information in an orderly easy to understand format but you are advised to treat each step of the formulation and manufacturing as separate and new. Refer back to the contents as often as possible to check the results of your work and how to improve your product’s suitability for the intended application.

The primary difference between organic coatings and silicates is that the “Binder system” is reactive and will often show up as ‘In can” or storage stability problems. You need to keep this in mind at all times and take the necessary steps as provided to eliminate in can thickening or even gelling of the silicate. There is enough information regarding the steps to be taken to allow you to be master of this problem.

**Patent rights:** due to the many unique properties of silicate technology it offers many opportunities for patent rights, it is just a question of which way your thinking and interests lie.

**By definition:** A SILICATE: Is a salt in which the anion contains both Silicon and Oxygen. **However** we are working with “WATERBOURNE ALKALI METAL SILICATES” but put more simply “Silicate Coatings”
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Potassium silicate

Inorganic coatings
Waterborne Silicate Coatings

A review of the chemistry and formulation of Silicate Coatings

The information is aligned to the German standard DIN 18 363 for single pack silicate coatings.

Ken Marx.
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Introduction.

Silicate Coatings are based on the combination of Quartz ($\text{Si}_2\text{O}_2$) and a carbonate to produce a Silicate ($\text{SiO}_2/\text{Na}_2\text{O}$), Lithium, Sodium or Potassium carbonate can be used or for certain grades by hydrothermally dissolving a reactive silica source (mainly silica sand) in the respective hydroxide which is then combined with light fast inorganic pigments. Original silicate coatings are UV resistant, VOC free and “also biocide free, plasticizer free, emulsifier free etc”.

As long as they are chemically combined with mineral substrates (so called “silicification” or “Petrification”), they last for decades. The recent evolution of silicate emulsion coatings combining silicates with organic emulsion binders plus a third type that has emerged as the "Sol-silicate paint" has extended the application range to non-mineral substrates.

This type of coating provides an excellent decorative and protective finish for buildings, due to its interesting properties of:

- Long term durability that is often quoted as being able to last for decades.
- UV resistance.
- Silicification/Petrification bond on mineral substrates.
- Excellent permeability to water vapour and gasses.
- Ability to formulate heat resistant coatings.
- Non flammability.
- Exceptionally hard wearing coatings.
- Adhesion on many substrates.
- Low tendency to fouling.
As there is very little local knowledge, plus what is available is very imbedded in supplier’s product data and related patents this short report should make it easier for would-be-formulators to understand and work with silicate technology in the coatings market.

Silicates have a long history in coatings applications and as such are estimated to be 10 to 15% of the architectural coatings volume used in Europe. This is based on “Waterborne” Silicates and therefore excludes organo silicates such as Ethyl Silicates.

What is very disturbing is the fact that this technology does not appear to have penetrated the global market. This is a non-commercial presentation to make the technical requirements; formulating information; raw materials; applications and advantages plus the availability of supplier’s products known to potential users. Waterborne Silicate Coatings are not new to the industry but they have evolved to a point of successful application and use plus recent developments in single pack multi substrate coatings make it a very worth while avenue of development.

The intention of this information is to consolidate technical data relating to waterborne “SILICATE COATINGS”. While some information may well be found in closely related industry applications, such information is filtered in order to maintain the focus on COATING APPLICATIONS. Let me stress that silicate renders and plasters are not included and are a separate field of application.
The recommendations are not to be taken as tried and tested but are the basis of the technology at the time of writing. It is strongly recommended that the user of this information carry out the necessary R&D work to reach a final product or formulation.

NB. There is a wealth of historical information on the subject of Silicate chemistry and its applications “which can be found on the internet” should you wish to study the many and varied applications. It is however likely to complicate the information and has therefore been omitted but feel free to search the internet for what interests you the most or contact me to discuss your applications or ideas.

A further point is the fact that the “Reactive binder” system is what makes it possible to achieve the claimed coating advantages over conventional organic binders. Just to repeat the earlier statement, you will have to take care not to introduce reactive compounds in your formulation in order to achieve the desired storage stability. This point is covered in the report and it is suggested that you follow the recommendations very carefully.

**DISCLAIMER.**
All information is in accordance with the author’s present knowledge and published data hence the writer disclaims any warranty or liability whatsoever and reserves the right to update or effect technical changes in the documentation as required. You are obliged to check the various references; website information and suggestions before starting any project in this regard.
Part 1. Some chemistry, applications & technology.

1. Understanding Silicate technology.

Silicates as you will see come in many forms and the essential fact is that we are working with an “Inorganic binder”. The adhesion to the substrates is a chemical bond with calcium or other inorganic mineral matter in the substrate referred to as silification, which in laymen’s terms means it is a single compound. This is very different to the physical bond of organic polymer binders that have an interface. With the original silicate bond there is no interface as the substrate and the silicate are a glass like chemical system.
Silicate solutions all contain silicon dioxide and an alkali metal but can vary in the amount of silicon dioxide and the amount of the selected alkaline metals used (Lithium, Sodium or Potassium). This mix is controllable at the time of making the silicate. All silicates will then react as above but the pH will vary and is always alkaline so anything that changes the pH via neutralization must be avoided. This is not strange to paint technology in that we often have fixed pH ranges to work in. Finally we have the Silica-sols and Colloidal Silica which vary by the pH and particle size or structure as well as having potentially much higher ratios of Silicon Dioxide to alkaline metal which naturally means higher percentages of Silicon. So to round this off we have a glass like chemically bonded coating that has good chemical and physical properties is non-flammable and is heat resistance. These properties lead to very long life, hard wearing coatings that can last for decades.

Silicon Metal  Silicon Dioxide/Quartz  Li/Sod/Potassium  The Carbonates

Note that we are working with compounds of metals so you can expect some tough films.
2. Current markets for silicate coatings.

**Architectural coatings.** Silicate Coatings were typically 2-component coatings which have been used in Europe for interior and exterior applications since the late 1870’s. They suffer from the disadvantages of requiring pre-mixing and an “Induction Period” before application.

**Coating Metals.** In the coating of metals and similar rigid materials, the difference in coefficient of thermal expansion between silicate and the substrate may be a limiting factor. However, where temperatures are relatively constant and there is no mechanical strain, ultrathin silicate films which have been dehydrated by baking can hold permanently.

A thin silicate film has greater flexibility and is more serviceable than a thick one for coating metals. A compatible surfactant in the amount of 0.05 - 0.1% by weight relative to the silicate will aid surface wetting and allow the reaction to progress. Good adhesion to metal can often be obtained after the surface has been thoroughly cleaned with alkali (e.g. with PQ METSO® sodium metasilicate) or is degreased or sandblasted.

**Typical metal coating applications are:**

• Thin silicate films on lithographic plates to render the surface area hydrophilic.
• Steel ingots coated with thin films of silicate to protect against corrosion.
• Silicate films on silver flatware to protect against scratches during manufacture.
• A thin coating of silicate - about .001" thickness - protects stainless steel coloured by controlled oxidation, rendering it resistant to atmospheric conditions, abrasion and fumes as well as to cleaning agents commonly used on architectural or decorative finishes. The silicate film does not change the colour of the coated steel but rather adds a depth of colour to the steel sheet. Baking at about 480°F (248°C) cures the silicate and considerably delays any moisture uptake. The silicate coating is smooth, glossy and resistant to scratching.
• A silicate coating to impregnate aluminum castings by special vacuum and pressure techniques to reduce the porosity.
• Anodized aluminum surfaces can be sealed with sodium silicate solutions.
• Sodium or potassium silicates used as a binder for zinc dust in the application of zinc-rich primers on metal surfaces exposed to moisture or weather.
• Coating of the interiors of bulk rail cars that have been cleaned or sand blasted, to act as a barrier for the metal from corrosive cargos such as salts.

3. Properties of silicate and “Silicate Coatings”

Before you go diving in it is wise to consider what advantages there are in this type of product and technology plus what limitations you may find. From a manufacturers point of view you need to consider the following.
• Do Silicate Coatings fit your present marketing mix and customer base?
• What coating applications are you most likely to be interested in? As you will see from the list that is to follow it is quite exhaustive?
• How would you structure your Silicate Coatings operation i.e. manufacturing; technical staff requirements; possible new branding; distribution channels/options; technical back up and related considerations.
• As a paint chemist you would not face these questions and will possibly find some synergy in silicate and emulsion paint technology.

NB. Silicate Coatings as detailed in this presentation are not offered as a replacement for any existing coating technology but rather as a viable option to meet the needs of the industry and some of the newer environmental legislation and technical requirements not covered by existing technologies.

To say silicates are a benign natural inorganic material is possibly an over simplification of the facts but therein lies the basis of the very reason to take a long hard look at this technology. As the industry fights the VOC and the ever increasing environmental demands “Silicate Coatings” offer a viable alternative to organic binder systems that appear to become ever more complex if one looks at the REACH legislation that is pushing the formulator’s limits.
As silicates make up around 90% of the earths crust one can accept that it is available in abundance and not part of the diminishing resources such as the petrochemical industry related organic products. For our particular application we are focused on soluble silicates such as waterborne alkali silicates that can be used in decorative and industrial coatings. Historically silicate as a binder has been used since the time of the early Egyptian era so we are about to play Catch up.

Just to identify where we start with soluble Silicates, take a look at the Periodic Table of the Elements, the Alkali Metals are the Group 1A elements on the left hand side of the Periodic Table as shown below and are: Lithium (Li) Sodium (Na) Potassium (K).

Click here if you want to view the interactive table; [http://www.ptable.com/#Compound](http://www.ptable.com/#Compound)
If you have looked at the interactive table you can see the Group 2 metals which form insoluble silicate as in window/household glass. These group 2 elements are often found in the cementitious substrates and once reacted with your soluble silicate they form our desired insoluble coating. More on this later. We are only interested in the first three Group 1 metals for our discussion on soluble silicates in coatings.


Alkali silicates are the only inorganic material which is used as a coating binder. Waterborne alkali silicates are synthetic materials of indefinite composition. Simply put, sand is mixed with an Alkali Carbonate; Lithium, Sodium or Potassium carbonate and then fired at 1300°C, with the resultant reaction. Where $M = \text{Lithium (Li), Sodium (Na) or Potassium (K)}$: 

![Silica sand](image-url)
\[
\begin{align*}
\text{M}_2\text{CO}_3 & \quad + \quad n \text{SiO}_2 & \quad \text{1300 Deg C} & \quad \text{M}_2\text{O} \cdot n \text{SiO}_2 & \quad + \quad \text{CO}_2 \\
\text{Alkali Metal Carbonate} & \quad \text{Quartz/Silicon Dioxide} & & \text{Alkali Metal Silicate. Carbon Dioxide}
\end{align*}
\]

The Molten Glass is run from the furnace onto a cooling conveyor, and the soluble glass is dissolved in hot water under pressure, any insoluble glass and unreacted sand is filtered out.

These are true glasses since they do not have any distinct stoichiometric composition, but rather the composition depends on the ratio of the raw materials used in the above process. Soluble silicates form clear or translucent colloidal solutions in water which exhibit a non-Newtonian viscosity.

The factor “n” in the equation is the basis of the Silicates. As you progress in your use of silicates it will be one means of selecting and deciding on the properties and suitability of one silicate over another. “n” is the ratio of Silica (SiO2) to Alkali-metal Oxide. This is the Molar Ratio but the Weight Ratio may be used, The Molar Ratio is more accurate when comparing Lithium, Sodium and Potassium silicates as can be seen in the table below.
Just to clarify the ratio usage, weight ratios are convenient if you are working with one silicate i.e. Sodium or one of the others but as can be seen it is misleading if more than one of the above is to be compared due to the higher molecular weights of Lithium, Sodium and Potassium.

House hold glass that contains Beryllium; Magnesium or Calcium or (Group 2 Elements) silicates are insoluble in water, but Glass that contains Lithium, Sodium or Potassium (Group 1 Elements) can be dissolved in hot water and produce an alkaline solution of various viscosities.

5. Viscosity of silicate solutions.

The viscosity of a Sodium silicate solution is a function of concentration, density, ratio and temperature, the viscosity increases with increasing ratio. High ratio solutions will increase in viscosity until they become semisolid. Comparison of viscosity at constant solids at different ratios shows that silicate solutions are at minimum viscosity at 2.00 weight ratio. Viscosity increases as the weight ratio of sodium silicate product becomes either more siliceous or more alkaline.
Silicone Dioxide.                Sodium Silicate (Lithium or Potassium)

(Increasing the Silicon Dioxide decreases the viscosity)

The above viscosity information may not be easily understood at this point but will become more valuable later. As long as it is accepted that the silicate solution viscosity is linked to the ratio of Silica to metal oxide in the product.

Now all we need to add is the percentage of the silicate solution and a final viscosity relationship can be seen. Logically the higher percent concentration of the solution the higher the viscosity but we will define this further.

The densities of the silicate solutions will vary via the ratio of silica to metal oxide and the molecular weight of the metal oxide plus the percentage concentration of the solution. Note that a gel will be formed if the concentration is too high.
6. pH. (Silicates are Alkaline)

As the silicates are based on the Alkali Metal Oxides and silica it can be expected that the solutions of the various silicates will be Alkaline. There is a correlation between the pH of the silicate solution against concentration of alkali metal for different weight (or molar) ratios. The correlation between the molar ratio and alkalinity, expressed by pH values are shown here:

Note the increasing silicate content is what causes the lowering of the pH values.

<table>
<thead>
<tr>
<th>Molar ratios:</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH of the solution:</td>
<td>14.0</td>
<td>13.0</td>
<td>12.0</td>
<td>11.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Molar Ratio (with increasing Silicon content)

So the higher silicon content gives lower pH values. The above pH relationship and Molar Ratio will be an important factor in most coating formulation considerations.

NB. Remember that most organic polymers that could be used in the Silicate emulsion coatings are likely to be more stable in the 8 to 12 pH range.
7. Molecular structures of waterborne alkali silicates.

Waterborne alkali silicates are glasses which can assume a wide variety of molecular structures that have been identified as anions which are monomers, dimers, trimers, tetramers, as well as branched chains, ring structures and even 3-dimensional networks.

Note; the repeating tetrahedral monomer around which the molecules are structured as below.

Silicon dioxide, SiO₂, a giant covalent molecular lattice. The alkali metals (Li; Na; K.) can attach to the spare Oxygen bonds and crate a complex Alkali silicate.
Remembering that this Alkali Silicate is formed at 1300 Deg C. At varying alkali content levels, the oxygen atoms are present either as undissociated silanol (Si-OH) groups or as negatively charged anions (Si-O-), with the counterion being the positively charged alkali cation (M+).

Dependent on concentration, alkalinity etc the distribution of monomeric, oligomeric and polymeric silicate groups in a solution is not fixed but is in dynamic equilibrium.

There are two principal equilibria in the solution, these are:

1. The acid-base equilibrium:

\[
-\text{Si-OH} + K^+ \text{OH}^- \rightleftharpoons -\text{Si-O}^- \text{K}^+ + \text{H}_2\text{O}
\]

2. The condensation polymerization or dissociation depolymerisation equilibrium:

\[
-\text{Si-OH} + \text{HO-Si} \rightleftharpoons -\text{Si-O-Si} + \text{H}_2\text{O}
\]
Then there is the normally irreversible reaction with polyvalent cations such as Ca++. You may also have some Mg++ or Fe and Mn ions available for reaction.

3. Irreversible reaction of a Potassium Silicate on application, with Calcium in the substrate.

These reactions influence the physicochemical behaviour of silicate aqueous systems in addition to the curing mechanisms on application.

8. Ratio of Silica to Alkali Oxide.

To repeat our earlier comment on pH. The higher weight ratio (molar ratio) alkali silicates (which contain relatively lower concentrations of alkali metal oxide and in turn proportionately higher concentrations of silica) have lower alkalinity these tend to be the main products used in coating applications.

Note that the group 1 alkali metals are the pH determining factor i.e. higher alkali metal content gives higher alkalinity.
The ratio of alkali metal oxide to silica i.e. 1.5 – 3.2 to 1 has a significant effect on the coating characteristics, as is shown in the table below:

<table>
<thead>
<tr>
<th>The higher ratio gives;</th>
<th>The lower ratio gives;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(High SiO\textsubscript{2} low NaCO\textsubscript{3})</td>
<td>(Low SiO\textsubscript{2} High NaCO\textsubscript{3})</td>
</tr>
<tr>
<td>i.e.3.75 to 1</td>
<td>i.e.2 to 1</td>
</tr>
<tr>
<td>Lower; Viscosity</td>
<td>Higher; Specific weight</td>
</tr>
<tr>
<td>Faster; Drying speed</td>
<td>Greater; Solubility</td>
</tr>
<tr>
<td>Faster; Curing speed</td>
<td>Higher; pH value</td>
</tr>
<tr>
<td>Increased; Susceptibility to low temperatures</td>
<td>Greater; Susceptibility to water influence</td>
</tr>
<tr>
<td>Higher; Chemical resistance of coatings</td>
<td>Higher; Tack and binding power</td>
</tr>
</tbody>
</table>

Silicates are commercially produced in the ratio range of 1.5 to 3.2. or higher. The ratio represents an average of various molecular weight silicate species but the low ratio (1.5) is not often used for coating formulations as will be seen.

Note that the carbonate is the part that affects the properties i.e. pH goes up as does the viscosity. YOUR CHOICE OF SILICATE IS ALWAYS DEPENDANT ON THE RATIO YOU CHOOSE.
9. Sodium silicates.

In general the most important commercial silicates are the alkali silicates of Sodium. They represent the majority of alkali silicates manufactured and are the most economic in production cost and selling price. They tend to be used wherever possible. It has been suggested that some sodium silicates with particular molar ratios are suitable for coating purposes.

Sodium silicate paints are mainly post-cured and either require stoving at 175°C (347°F) or a suitable catalyst is used to assist room temperature curing.

However, the concern with efflorescence generally precludes the use of sodium silicate in coatings.

Potassium carbonate exists in at least two forms with degrees of hydration (water of crystallization) as shown in the following table:

<table>
<thead>
<tr>
<th>Degree of hydration</th>
<th>Other names</th>
<th>Molecular Formula</th>
<th>Solubility/ Water (g/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous</td>
<td>Potash</td>
<td>K₂CO₃</td>
<td>111 @ 25°C</td>
</tr>
<tr>
<td>Sesquihydrate</td>
<td></td>
<td>2K₂CO₃.3H₂O</td>
<td>111 @ 25°C</td>
</tr>
</tbody>
</table>

However, as can be seen from the above table, potassium carbonates are not as water rich as the sodium carbonates. The anhydrous product is hygroscopic and will absorb water to form the sesquihydrate, which is not hygroscopic, with a much lower tendency to crystallize, does not generally produce a white efflorescence because small amounts of potassium carbonate formed at the surface are relatively easily removed by rain when used in exterior coatings.

Coatings based on potassium silicates are self curing and do not require the use of any added curing agent. However, when used as the sole binder without any modification they tend to be relatively slow curing and can be susceptible to leaching out from the coating during the first 24 hours.
11. Lithium silicates.

In contrast to Sodium and Potassium, Lithium carbonate only exists as the anhydrous form with relatively low water solubility (which decreases with rising temperature)

Because Lithium silicates have high molar ratios (i.e. they have a low alkali content) as well as Lithium carbonate having such a low water solubility, Lithium silicate finds use in applications where the production of water-soluble by-products or any form of efflorescence is undesirable, including 2-K inorganic zinc silicate coatings as well as the strengthening or consolidation of masonry such as natural stone or concrete.

It must be pointed out that Lithium silicates are stable at room temperature, but precipitate on heating to ± 60°C. This effect is reversible upon cooling. Hence they should not be used in heat accelerated systems.

12. Sodium-potassium silicate blends.

The combination of Sodium and Potassium Silicates creates special properties not found in each product separately. In liquid mixes, for example, it is possible to vary viscosity without varying total solids content or overall silica to alkali mole ratio.

The synergistic effect depends on the viscosity peak, relative to the individual components, shown by some aqueous Sodium - Potassium Silicate mixtures.
Because of the lack of efflorescence discussed above, you will see a significant use of Potassium silicates in coating applications as 1-K silicate emulsion coatings or as 2-K inorganic silicate coatings. At the same silica to alkali mole ratio, Potassium Silicates soften and flow at a higher temperature than corresponding Sodium Silicates. Potassium Silicate can therefore be used in high-temperature binders.

13. The chemical curing of alkali silicates.

NB. Remember that Silicates are reactive compounds and as such must be used with due consideration of the reaction possibilities. We refer to the reactions as CHEMICAL CURING which is what makes them unique as a paint binder.

The curing process of alkali silicates can involve a number of basic reactions either with the constituents of the substrate or with the components of the ingredients/formulation or with CO₂ in the air. These can be summarised as below:

**Reaction with calcium hydroxide**
Where M = Sodium (Na), Potassium (K) or Lithium (Li), as follows:

\[
\text{M}_2\text{O} \cdot n \text{SiO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaO} \cdot \text{SiO}_2 + (n-1) \text{SiO}_2 + 2 \text{MOH}
\]

Alkali Silicate  Calcium  Calcium  Silicon  Alkali Hydroxide
Hydroxide      Silicate   Dioxide
The alkali hydroxide can then react further with atmospheric carbon dioxide to produce alkali carbonate:

\[
2 \text{MOH} + \text{CO}_2 \rightleftharpoons \text{M}_2\text{CO}_3 + \text{H}_2\text{O}
\]

Alkali Hydroxide  Carbon Dioxide  Alkali Carbonate

The curing reaction with quartz sand, particularly on the surfaces of the particles, can be represented as follows:

\[
\text{M}_2\text{O}. \, n \, \text{SiO}_2 + \, m \, \text{SiO}_2 \rightleftharpoons \text{M}_2\text{O}. \,(m+n) \, \text{SiO}_2
\]

Alkali Silicate  Quartz  Higher Ratio Alkali Silicate

Curing caused by reaction with carbon dioxide from the air:

\[
2\text{M}_2\text{O}. \, n \, \text{SiO}_2 + \text{CO}_2 \rightleftharpoons \text{M}_2\text{O}. \,(2n-1) \, \text{SiO}_2 + \text{M}_2\text{CO}_3 + \text{SiO}_2
\]

Alkali Silicate  Carbon Dioxide  Higher Ratio Alkali Silicate  Alkali Carbonate  Silicon Dioxide

Incomplete silicification can occur when atmospheric carbon dioxide reacts completely with the silicate leading to the reformation of the original carbonate as follows.
Finally complete silicification results in insoluble silica gel formation, with physical water elimination as follows:

\[
M_2O \cdot n SiO_2 + CO_2 \rightarrow n SiO_2 + M_2CO_3
\]

Alkali Silicate  Carbon Dioxide  Increased ratio  Alkali Carbonate

The limiting factor. As a consequence of this, the higher concentration leads to higher viscosity which leads to gelling so silicate solutions must be made or supplied at a concentration that forms a liquid at a usable viscosity.

NB. Through the use of suitable additives, this gelling process can be produced on demand so that we can effectively accelerate the gelling process, if required.
As we can see from the above equations the inorganic alkali silicate binder systems can be cured in a variety of ways. In essence, the desired curing may be brought about by atmospheric carbon dioxide or by reactive constituents contained in the substrate. (Ca++, Mg++, Zn++, Cu++, Fe+3)

At the same time hardening of the coating may occur by physical water elimination, which may occur by the removal of water through heating. However in such situations this may only be apparent hardening, such that when further contact with water occurs the coating may soften with the possibility of binder migration.

NB. Conventional emulsion paints are known to be affected by binder migration (Absorption) into porous substrates such as poorly bound plaster which leads to under bound paint films.

In both cases it would be wise to apply a clear sealer/bonding liquid before application of a Top Coat. Alternatively ensure that there is sufficient binder in the formulation to allow for the absorption. With properly applied and cured silicate coatings the physiochemical bond between the binder system and the substrate can be very strong. These types of coatings are not regarded as film forming coatings as they become part of the substrate.
The cured binder produces a porous inorganic substrate with very high water vapour (and carbon dioxide) permeability.

These coatings can be of advantage on older or historical buildings, (which can often be damp) as well as coatings on incompletely cured concrete. In the case of damp historic buildings, the passage of water vapour permits damp buildings to effectively dry out. For coatings on incompletely cured cement or concrete, the passage of carbon dioxide is unhindered thus leading to subsequent carbonation (and subsequent hardening of the concrete).

**Shelf life.**
There has been some trouble in achieving the required shelf life of silicate coatings of one to two years, which in some cases can be traced back to the presence of metal ions such as Ca++, Mg++, Zn++, Cu++, Fe+++. Your choice of pigments and fillers must be free of soluble multivalent metal ions.

Generally one would think a shelf life of 12 months would be acceptable provided the “Sell by date” is properly used and enforced.
**Process water.**

As the alkali silicate binds all the metal ions including any that may be present in the process water and we want the reactivity and binding reaction to be available for the bond with the substrate. The purity of the process water could well be a problem and use of de-ionized water would be a way around this potential problem. Only the actual batch water would need to be de-ionized so it will not be a major cost factor. Your municipal water that is supplied at neutral pH or around 7 to 8 should be free of these potentially problematic ions. Keeping a record of the daily pH values of your tap water supply could help in locating storage stability or other quality problems by tracing back via batch numbers.

Refer to; 17. Production of silicate emulsion coatings (1-K silicates).

So Hard water is not recommended.

**In conclusion;** While multivalent cations decrease the liquid silicate solubility the level at which they are a problem depends on everything else (formulation, application, expected shelf life etc.) There are published formulations, for example in patents, prescribing deionised water and plenty of others where normal water is used. For example if in a silicate emulsion paint some Ca++ is present in the water a precipitate of a small amount of Calcium Silicate can occur, this doesn’t necessarily alter the performance of the paint significantly.
Part 2. To improve the product acceptance

14. To advance the art.

To improve the product acceptance Silicate emulsion coatings were introduced in Europe in the 1960s and 1970s. A third type has emerged as the "Sol-silicate paint". The benefits of organic emulsion paints with their attractiveness, ease of production and good storage stability has lead to this research and publication. The following listing of the requirements form the back ground of the work.

- It would preferably be a Ready-to-use single pack (1-K) product
- Must be easy and quick to make
- Rheological properties should be controllable.
- Improved stability of the binder/filler/pigment system against reagglomeration or reaction of the binder and pigments or fillers.
- Good storage stability (shelf life at least one year and preferably two years)
- Syneresis and sedimentation must be eliminated.
- Good redispersibility on stirring
- They must have good application properties
- Sufficient diffusion into the substrate to allow the silicate to react (silicification) with calcium or other inorganic components of the substrate and form a strong adhesion and surface hardening.
- Good colour retention of the inorganic pigments used.
- Perfect curing without chalking or efflorescence.
- Good weathering properties.
- Maintenance of easy water vapour permeation.
- Improved water repellency.

The above properties can be achieved using systems based on stabilised potassium silicate binders and alkali stable organic emulsion polymers plus alkali resistant light fast inorganic pigments. Appropriate additives are required to complete the formulations.

**Just to clarify the focus of this information:** It does not include; plasters; cementitious products or renders (they are more inline with the building industry). There are great similarities in the technology but this should be pursued separately if so desired.
15. Applications of alkali silicates in pure silicate architectural coatings (2-K silicates).

Waterborne zinc rich protective coatings
Solventborne ethyl silicates were and are used but are not included in this document. However, Lithium silicate finds uses in applications where the production of water-soluble by-products or any form of efflorescence is undesirable and are used in the more recent, **2-K Waterborne inorganic zinc silicate primers.**
Masonry impregnation (Bonding Liquid)
Lithium silicate can be used in applications where the production of water-soluble by-products or any form of efflorescence is undesirable, as in the strengthening or consolidation of masonry such as natural stone or concrete which is sometimes required before painting.

Waterborne consolidation primer
These would normally be clear solutions of Sodium or Potassium silicate applied to aging or damaged stone work or substrate to either preserve the surface or bind loose surface material. A pigmented top coat may be used.

Chemical damp-proofing and water proofing.
While silicate coatings are porous and will allow the free passage of air and moisture to pass through and thereby promote the drying of damp buildings, it is necessary to include a suitable water repellant in the formulation to prevent water from penetrating from the outside while allowing the internal moisture to dissipate.

In addition a water proof coating based on a suitable silicate can be formulated to seal off interior walls from water seepage. This formulation is not compliant with the German standard DIN 18 363 for single pack silicate paints but is based on the silification of Sodium Silicate.
Such coatings have the following advantages:

**2-K Silicate paints are VOC free.**
Silicate based masonry paints are suitable for interior and exterior applications.
They can be supplied at an acceptable cost level.

Their adhesion to masonry substrates is very high because of the chemical reactions between the binder and the masonry substrate.

Silicate based masonry paints have excellent resistance to industrial gaseous fall out.

**Silicate based masonry paints can provide the best exposure, durability and weathering properties of all coatings.**

A 1-K Silicate starting point formula is shown below:
Do not apply these coatings if the relative humidity is below 20%. Although this may appear to be a limitation it is unlikely that such dry conditions will prevail in most locations. 2-K coatings are still used today, but only in relatively specialized situations, and even then predominately by Master Painters who with experience can accommodate the disadvantages in mixing and application.

There is the option of using setting agents such as.

**Inorganic Salts;** \( \text{CaCl}_2, \text{Ca(OH)}_2, \text{Mg(OH)}_2, \text{NaH}_2\text{BO}_3, \text{Na}_2\text{CO}_3 \)

**Inorganic Acids;** \( \text{H}_2\text{SO}_4, \text{HCl} \)

**Organic Acids;** \( \text{H}_2\text{CO}_3 \) acetic & citric acid

**Inorganic Oxides;** \( \text{ZnO}, \text{CaO}, \text{MgO} \)
Note that we are not promoting 2-K systems as this would tend to be a retrogressive step and this information is only for a few specialized applications. We should aim to produce Single pack 1-K systems.


On the other hand it may still be required that a Zinc Rich primer is produced. Under conditions of high humidity and low ambient temperature such coatings can cure relatively slowly with water insolubility ranging from 1 to 24 hours or longer. Nevertheless from the early 1960’s to the late 1970s such inorganic zinc silicate coatings based on Potassium silicate were the most generally used silicate primers. As we are considering alkali silicates being used with a high loading of zinc dust and typically coated onto steel, we do not expect to see the same types of reactions as we discussed earlier which were primarily on masonry substrates, where the presence of calcium ions is frequently encountered.

Solubility of zinc.
As metallic Zinc has a valency of 2 and reacts with the silicate it can not be included in a 1-K system as can be seen from the solubility information.

The solubility of zinc depends on temperature and pH of the water in question.
- When the pH is fairly neutral, zinc is insoluble.
- Solubility increases with increasing acidity.
- Yet above pH 11, solubility also increases.
Zinc dissolves in water as ZnOH\(^+\) (aq) or Zn\(^{2+}\) (aq) or anionic ZnCO\(_3\) and has a solubility of 0.21 g/L as below.

\[
\text{Zn} + 2\text{H}_2\text{O} \quad \rightarrow \quad \text{Zn(OH)}_2 + \text{H}_2 \\
\text{Zn} + \text{H}_2\text{CO}_3 \quad \rightarrow \quad \text{ZnCO}_3 + \text{H}_2
\]

Initially, as the water evaporates from the alkali silicate/zinc coating, there is a concentration of silicate with initial drying and primary deposition of the coating on the substrate. After evaporation of water, a silicate prepolymer is formed as shown in the equation below:

Insolubilization of the silicate matrix by reaction with zinc ions from the surface of the zinc particles, possibly together with ferrous (Fe\(^2+\) or 3+) ions from the steel substrate to form an iron zinc silicate polymer as shown in the equation.
Subsequent to this, the silicate undergoes a hydrolysis reaction in the presence of carbonic acid (formed from carbon dioxide and water) to produce polysilicic acid which then reacts further with the zinc ions present in the zinc dust to form a zinc silicate polymer which gives a 3-dimensional inorganic matrix structure.

This final reaction, which takes many months to complete, is expected to occur at the surface of the coating with the atmosphere, and gradually moves through the depth of the coating down to the steel substrate.

Over this period the cross-link density of the coating is increased so that a very hard, durable and dense coating is achieved.
NOTE: 2-K waterborne inorganic zinc silicate primers are available. Lithium silicates with a silica ratio of up to 8.5:1 can be used to formulate waterborne inorganic zinc primers. They have the advantage of being self-curing at ambient temperatures, having long pot lives after the mixing of the liquid binder and the zinc dust, they can develop good water resistance within an hour.

Lithium silicate has the best performance in anticorrosion protection of any waterborne inorganic zinc silicate coating, because it has the lowest alkali content, producing higher binding power and less efflorescence. Cured films are regarded as being similar to those of baked sodium silicate binders and are characterized by great hardness, durability and abrasion resistance.
A typical formulation is as follows.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component A (Powder)</td>
<td></td>
</tr>
<tr>
<td>Zinc dust, ca. 7µ</td>
<td>75.0</td>
</tr>
<tr>
<td>Chromium (III) oxide green</td>
<td>5.0</td>
</tr>
<tr>
<td>Muscovite mica M2/1</td>
<td>18.0</td>
</tr>
<tr>
<td>Natural bentonite – NA (Wyoming)</td>
<td>1.0</td>
</tr>
<tr>
<td>Woellner Betolin™ V 30, thickener</td>
<td>0.2</td>
</tr>
<tr>
<td>Sub-total Component A</td>
<td>99.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component B (Liquid)</td>
<td></td>
</tr>
<tr>
<td>Lithium silicate (e.g. Woellner Betolin™ Li 24)</td>
<td>99.4</td>
</tr>
<tr>
<td>Dispersant (e.g. Woellner Sapetin™ D 20)</td>
<td>0.4</td>
</tr>
<tr>
<td>Alkali stable wetting agent</td>
<td>0.2</td>
</tr>
<tr>
<td>Sub-total Component B</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Mix Components A and B in a 1:1 ratio and mix homogeneously.

17. Applications of alkali silicates in silicate emulsion coatings (1-K silicates).

Note. The German standard DIN 18 363 which refers to painting and coating defines “silicate emulsion paints” as those containing no more than 5% w/w of organic content (Binder) based on the total solids as determined by the loss on ignition at 450°C/2h (842°F) of a material pre-dried at 200°C/2h (392°F).

The previously mentioned benefits of organic emulsion paints means that the requirements of a single pack silicate coating system would have to fall inline with current waterborne/emulsion coatings and have to offer the same or better benefits.
The term “Silicate Emulsion Paints” should be self explanatory but to clarify this; the emulsion comprises a traditional polymer emulsion, a maximum of 5% may be added to bridge the gap between the two technologies.

NB: The acrylic or other polymer acts as a temporary stabilizer which prevents the silicate from being washed off while the silification reaction progresses, which can take several weeks.

They may also contain organic additives i.e. rheology modifiers/thickeners/stabilizers etc. Therefore the main constituents of silicate emulsion paints are:
- Water
- Inorganic binder (typically potassium silicate)
- Organic binder (styrene acrylic emulsions or other alkali-stable organic emulsions)
- Fillers
- Inorganic alkali resistant Pigments
- Suitable additives to produce properties that will match current emulsion paints.

In order to maintain the essentially inorganic nature of the coating on the masonry substrate and the water vapour permeability, the total level of organic content must be restricted. Strict control of the organic component level is necessary to maintain the zero VOC level benefits of silicate coatings. The formulation of a silicate emulsion paint should be an easy process for most experienced decorative paint chemists, although it must be pointed out that the individual components could cause complex interactions. Understandably, the choice of raw materials and the process of addition are important for the quality of the paints. Try this, PQ Silicate emulsion paint based on Acronal S559.
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>weight</th>
<th>Material</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lopon 890</td>
<td>1.2</td>
<td>Dispersing Agent Acrylate</td>
<td>BK Giulini</td>
</tr>
<tr>
<td>Lopon ST</td>
<td>2.0</td>
<td>Stabilizer - Quaternary ammonium</td>
<td>BK Giulini</td>
</tr>
<tr>
<td>Demin Water</td>
<td>63.2</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>Unionchem 200 Xantham Gum</td>
<td>0.4</td>
<td>Thickening Agent (Xantham Gum)</td>
<td>Union Chem</td>
</tr>
<tr>
<td>Natrosol 250 HHR</td>
<td>0.8</td>
<td>Thickening Agent (Cellulosic HEC)</td>
<td>Ashland</td>
</tr>
<tr>
<td>Mix 30' at 1000 rpm or until dissolved</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foamstar SI 2210 (Dehydran 1620)</td>
<td>1.2</td>
<td>Defoaming agent</td>
<td>BASF</td>
</tr>
<tr>
<td>10% Caustic Potash</td>
<td>0.4</td>
<td>Caustic Potash 10% solution</td>
<td></td>
</tr>
<tr>
<td>Tioxide TR-92 TiO₂</td>
<td>40.0</td>
<td>Titanium Dioxide</td>
<td>Huntsman</td>
</tr>
<tr>
<td>Mix for 30' @ 3000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Demin Water</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Omyacarb 2GU</td>
<td>72.0</td>
<td>Ground Calcium Carbonate 5 um</td>
<td>Omya</td>
</tr>
<tr>
<td>Omyacarb Extra GU</td>
<td>36.0</td>
<td>Ground Calcium Carbonate 2 um</td>
<td>Omya</td>
</tr>
<tr>
<td>Plustalc H16-AW (Microtalc WT-1)</td>
<td>40.0</td>
<td>Talcum</td>
<td>Omya</td>
</tr>
<tr>
<td>Mix for 10' @ 2000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acronal S-559</td>
<td>32.0</td>
<td>Emulsion</td>
<td>BASF</td>
</tr>
<tr>
<td>White Spirit</td>
<td>6.0</td>
<td>White Spirit</td>
<td></td>
</tr>
<tr>
<td>Tego Phobe 1401</td>
<td>4.0</td>
<td>Hydrophobic agent</td>
<td>Evonik</td>
</tr>
<tr>
<td>Mix for 10' @ 2000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lopon STA</td>
<td>4.0</td>
<td>Viscosity Stabilizing agent</td>
<td>BK Giulini</td>
</tr>
<tr>
<td>Silchem K2550</td>
<td>100.0</td>
<td>Potassium Silicate</td>
<td>PQ</td>
</tr>
<tr>
<td>Mix for 10' @ 2000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>413.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Remember: Silicate emulsion paints have very high gas and water permeability; they also have very high water absorption. To minimize/prevent absorption of water onto the cured silicate emulsion coating, the inclusion of a water repellent is recommended, or impregnation with a water repellent is recommended. The water repellent should only be included in the final coat or it could give rise to adhesion problems when subsequent coats are applied.

Very porous substrates can be stabilized with a clear impregnation coating such as:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>79</td>
</tr>
<tr>
<td>Styrene acrylate emulsion (e.g. BASF Acronal\textsuperscript{TM} S 559 or S620; Alberdingk SC 4400 or AS 6800; Celanese Mowilith\textsuperscript{TM} DM 6119 or DM 765A)</td>
<td>0.5</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>0.5</td>
</tr>
<tr>
<td>Potassium silicate (Silchem K2550)</td>
<td>20.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Record the batch QC and process control test results as listed on page No 66 and proceed with the storage and application tests.
Depending on substrate conditions, a 1:1 dilution with water, or a mixture 1 part water/1 part primer/1 part silicate emulsion paint may also be applied. Apply by brush or roller, allow at least 12 hours before over coating.

The main advantages of 1-K silicate emulsion paints are:
• Ready-to-use product
• Good storage stability with long shelf life
• Fairly easy application with good workability
• No significant health risk during application
• No allergenic potential from silicate binders
• Zero VOC systems may be formulated using zero VOC organic emulsions
• Applicable to a wide range of substrates (sometimes pretreatment may be necessary)
• Also compatible with relatively fresh plasterings containing active alkalinity
• Appropriate for interior and exterior application on new and old buildings
• Adequate technical properties of the cured coatings
• Long term stability under varying humidity of the substrate, leading to a good economic life span.
• High resistance against atmospheric influences
• No special hazard in case of fire
• Acceptable cost level
18. Production of “Silicate emulsion coatings” (1-K silicates).

It has been reported that silicate emulsion paints are permitted to stand for up to a week. During this period the viscosity may undergo thickening such that the final viscosity is achieved.

I wonder if this is to allow for the reaction or binding of the ions present in the process water which has not been addressed as far as I have seen.

The nature of the thickener is critical as well as the interaction with the emulsion binder and the choice and purity of raw materials. You are advised to test for this post thickening as opposed to storage stability over a longer period.

Note. It has therefore been recommended that stock mixtures be prepared and sufficient quantities of these ought to be kept in store. In particular this applies to textured finishes, because grain size distribution can be obtained for the individual qualities.

The compatibility test should obviate the need for this procedure.

Note: Conventional emulsion paints do set on standing and viscosity tests specify that the sample is stirred for 60 seconds before testing viscosity. This has not been reported as a fault or unacceptable with current emulsion paints.
19. The formulation, assessment and production of silicate emulsion paints. Silicate binder contents

It is recommended that the effective amount of Potassium Silicate in a finished products should be as in the following table:

<table>
<thead>
<tr>
<th>Application</th>
<th>Recommended Potassium Silicate solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exterior paints</td>
<td>4.5-7.0%</td>
</tr>
<tr>
<td>Interior paints</td>
<td>3.5-5.0%</td>
</tr>
<tr>
<td>Primers</td>
<td>5.5-8.5%</td>
</tr>
</tbody>
</table>

NB. 1. It is not clear as to the reason for the above figures and with the lack of a reference to a “pigment to binder ratio” type figure as in conventional paint formulations one has to use the above guide lines for initial R&D work.

2. As we are really looking for a chemical reaction related figure and we know that the silicate solutions are not stoichiometric solutions i.e. the Silicate to metal hydroxide can be varied at will, it becomes impossible to predetermine the available reaction characteristics of silicate solutions.
As the silicate binder content increases, generally the following will be observed:

• Higher viscosity with less tendency to thicken on storage
• Significantly larger thixotropy areas
• Slight increase in spreading resistance on application
• Film formation or leveling difficulty
• Slightly higher tendency for white efflorescence
• Higher tendency for colour variation on different substrates.
• Slightly lower water resistance at the beginning of the curing period

As the organic polymer dispersion content increases, the following will apply.

• Slight increase in viscosity
• Slightly smaller thixotropic areas
• Sometimes less tendency of colour variations on different substrates
• Earlier water resistance
NB. Don’t forget that the German spec calls for a maximum of 5% organic polymer.

Typically the formulation components which are involved are as follows:

**Inorganic Binders**
Sodium, Potassium, Lithium Silicate solutions or combinations of these
Pre-stabilized Potassium Silicate solutions (recommended)

**Fillers and Pigments**
Alkali stable Inorganic pigments

**Organic**
Polyacrylates.
Styrene acrylates
Terpolymers

**Additives**
Refer to the list that follows later.
A starting point formulation is repeated here.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight</th>
<th>Material</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lapon 930</td>
<td>1.2</td>
<td>Dispersing Agent Acrylate</td>
<td>BK Gulini</td>
</tr>
<tr>
<td>Lapon ST</td>
<td>2.0</td>
<td>Stabilizer - Quaternary ammmonium</td>
<td>BK Gulini</td>
</tr>
<tr>
<td>Denim Water</td>
<td>83.2</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>Unionchem 200 Xanthan Gum</td>
<td>0.4</td>
<td>Thicking Agent (Xanthan Gum)</td>
<td>Union Chem</td>
</tr>
<tr>
<td>Natrosol 260 NR</td>
<td>0.8</td>
<td>Thickening Agent (Cellulose HEC)</td>
<td>Ashland</td>
</tr>
<tr>
<td>Mix 30' at 1660 rpm or until dissolved</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foamstar SI 2200 (Debytron 162)</td>
<td>1.2</td>
<td>Deleaming agent</td>
<td>BASF</td>
</tr>
<tr>
<td>10% Caustic Potash</td>
<td>0.4</td>
<td>Caustic Potash 10% solution</td>
<td></td>
</tr>
<tr>
<td>Tioxide TR-92 TiO2</td>
<td>49.0</td>
<td>Titanium Dioxide</td>
<td>Hankison</td>
</tr>
<tr>
<td>Mix for 30' @ 3000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Denim Water</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Omgacarb 2GL</td>
<td>72.0</td>
<td>Ground Calcium Carbonate 5 um</td>
<td>Omya</td>
</tr>
<tr>
<td>Omgacarb Extra GU</td>
<td>36.0</td>
<td>Ground Calcium Carbonate 2 um</td>
<td>Omya</td>
</tr>
<tr>
<td>Plustal Hig-AW (Microtole VT)</td>
<td>40.0</td>
<td>Talcum</td>
<td>Omya</td>
</tr>
<tr>
<td>Mix for 10' @ 2000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol S-569</td>
<td>32.0</td>
<td>Emulsion</td>
<td>BASF</td>
</tr>
<tr>
<td>White Spirit</td>
<td>6.0</td>
<td>Viscous Spirit</td>
<td></td>
</tr>
<tr>
<td>Tego Phos 1401</td>
<td>4.0</td>
<td>Hydophobic agent</td>
<td>Evonk</td>
</tr>
<tr>
<td>Mix for 10' @ 2000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lapon STA</td>
<td>4.0</td>
<td>Viscosity Stabilizing agent</td>
<td>BK Gulini</td>
</tr>
<tr>
<td>Kasil 1</td>
<td>100.0</td>
<td>Potassium Sulfate</td>
<td>PQ</td>
</tr>
<tr>
<td>Mix for 10' @ 2000 rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>413.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After being stored for one day and then at defined intervals of up to at least 30 days the sample is assessed for:
- Syneresis.
- Settling
- Stirrability
- Viscosity development
- Thixotropy
- Agglomeration or coagulation

This is from page No. 55.
It should be possible to formulate and produce stable products using Potassium Silicate solutions; Pre-stabilized Potassium Silicate would be most suitable in conjunction with Silica Sols or Colloidal Silica for more advanced multi substrate coatings. Un-stabilised silicates are more likely to set up and develop thixotropic properties which could be a problem although some thixotropy may be an advantage in improving the application and anti settling of your formula. Balance it out to get the better of two worlds.

You will need to do a viscosity stability test at 60°C to test for storage stability.

**20. Sol-silicate paint.**

As of 2002 a third type of silicate paint has emerged and is referred to as “Sol-silicate paint”. The binder is a combination of “Silica-sol” and “Potassium Silicate” (water glass.) an organic binder is incorporated at the 5% limit in accordance with the German specification for silicate emulsion paints. The advantages of chemical setting are however preserved.

Note that the Sol-Silicate paints have the advantage of bonding on non-mineral substrates via the chemical and physical bonding. This has revolutionised the field of application for silicate paints.
NB. These coating can be applied to all common substrates.

**How are Silica Sols produced?**
Colloidal Silica is produced by the removal of Sodium from Sodium Silicate via cation exchange which produces a polymerization and particles begin to grow. At a selected growth point the Sol is stabilized and concentrated to the desired solids content. Large particles can be created via Seeding on earlier small particle batches.

**Emulsions and water-soluble resins.**
When Colloidal Silicas have the same pH and surface charge as the emulsion or water soluble resin they are compatible with both systems. However in the case of emulsions the emulsifier must be selected for compatibility to prevent possible gelation or separation.
A **Sol-Silicate-Paint** formulation based on S 559.
The first thing you should notice is the low level of silicate (Binder) in these formulations.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>to 100% ± 58 Lt</td>
<td></td>
</tr>
<tr>
<td>Betolin V30</td>
<td>0.1</td>
<td>(Anionic thickener)</td>
</tr>
<tr>
<td>Nat HBR 250</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Sapetin D20/27</td>
<td>0.2</td>
<td>(Disper/stabilizer)</td>
</tr>
<tr>
<td>Betolin Q 40/44</td>
<td>0.5</td>
<td>(stabilizer/visco control)</td>
</tr>
<tr>
<td>TiO2</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Agitan 281</td>
<td>0.2</td>
<td>(defoamer)</td>
</tr>
<tr>
<td>Calcium carbonate 5 µ</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>Talc micro</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Acronal S 559 (styrene Ac)</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>Betol KS 402 A</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(40% solids = 0.8 Colloidal Silica)</td>
<td></td>
</tr>
<tr>
<td>Betolin K 28, P35, P50.</td>
<td>10.0</td>
<td>(29% solids = 3.0 Potassium silicate.)</td>
</tr>
<tr>
<td>Betolin A 11</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>
Silicate = 3.8  Pigments & fillers = 47.5
Silicate to Pigments & fillers = 8 %.

Note that we can not work on pigment to binder ratios and this is only for reference purposes.

We need to record the following info on all formulations and batches.
Results of the starting point formulation should be around these figures (not calculated or tested)

- Pigment to binder ratio. 12.5 to 1
- Fineness of Grind. <5 Micron
- Viscosity in Ku’s 90 to 100.
- Solids. ±42 %
- SG. ±1.5

Ultra Matt is required for some applications.
Drying/Cure time (on a standard cementitious test panel) <1 Hr. at 23°C and 50% RH.
(A fibre cement panel 150 X 75 X 4.5 mm would be most appropriate)

NB. You will only be able to test for the product stability etc if you have recorded the actual batch results.


Compatibility test.

You must test your chosen formulation components before including them in your silicate paint. A suitable compatibility test is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>70</td>
</tr>
<tr>
<td>Polymer, pigment, filler or additive.</td>
<td>10 (adjust this level for each item)</td>
</tr>
<tr>
<td>Silicate solution</td>
<td>20</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>
**Prepare as follows.**

1. Dilute the organic polymer emulsion or disperse the test material in water.
2. Slowly add the silicate while stirring.
3. Allow to stand for approx 2 hours.
4. Pour Down on a glass plate (150 X 75 X 3 mm) and examine the resulting film. Inspect the film which should be free from cloudiness, bits or signs of gelation. The film should be clear and smooth.

**NB.** 1. Repeat the Pour Down test after one week storage at 60°C.
2. Pigments can also be tested in this manner for adverse reactivity.
Part 3. Manufacturing

22. Manufacturing equipment specifications and processing methods.

One thing that is good about silicate coatings is that we do not need to mill or grind the pigments and fillers. High-shear dispersion is the correct method of processing. It is however essential that you achieve and test for full dispersion. That is to say you must disperse all particulate matter to the suppliers original or supplied primary particle size. Failure to do this will mean that you have unwetted particles or even voids in the paint film which will be physically weak and underbound. These areas of weakness will be future points of failure such as break down of the film; hair cracks and related failures.

(This is not unique to silicate emulsion paints and also applies to your every day emulsion paint)

The question of the suitability of the equipment must be answered and your High shear mixer must comply with specific parameters.

NB. Home grown paint mixers will not do and you need to download the Cowles manual here; http://morehousecowles.com/pdfs/Fundamentals%20of%20Dispersion.pdf
You will need the High-shear blade and a two speed or variable speed motor as detailed in the manual. Remember that the ratio of blade diameter to tank size and position in the tank is a critical factor as detailed. Don’t try making batches that are either too big or too small for a particular size mixing tank and motor.

The mill base or dispersion phase must be carefully formulated to ensure that you get good dispersion with minimal splashing and foaming. A smooth doughnut shaped mix is essential, the Fineness of Grind test method must be established and a pre-dilution of the pigment base before reading on the FOG gauge may be wise. By and large you will be working at <5 Microns and if you are making a course textured product the course texture filler should be added after the grind spec is reached on your pigments and standard (Fine) fillers but at lower speed.

**NB.** If you find that you are not achieving the FOG spec in 20 or 30 minutes check your mixer set up; mill base formulation; dispersant or wetting agent type; pigment particle size spec etc. Remember that batch size could affect the dispersion time but not normally.

The let down stage should not be a problem but remember to change the mixer to slow speed and limit the splashing; foam generation and air inclusion.

Here is a Hi-shear blade;
The teeth are carefully shaped and angled to create the correct Doughnut shape of the mill base at high speed. Do check your direction of rotation which is “Clock wise” when looking down on the blade and the blade must be installed right side up as in the this image.

There have been installations with the blade installed up side down which in addition to not dispersing properly will cause a lot of foam and air inclusion. Remember that the Blade wears down and the “Teeth” become too small to disperse the pigment. You must replace the blade when around 25% of the teeth area has worn away; this represents a decrease of 25% in dispersing action if not more.

High Speed is: At peripheral speeds of (4,000 - 6,000 fpm) Even if you buy a complete outfit do check the peripheral speed of the blade via the formula in the Cowles manual;

\[
\text{RPM} \times 0.262 \times \text{blade diameter (in inches)} = \text{fpm}
\]

Page 11 of the manual is copied here but please read the part about mill base volume and level as this is where most inefficiencies are found.
• The aspect ratio (working volume, height to diameter ratio = height must be 4 times diameter and working volume is 3/4)
• Blade size is 1/3 tank diameter;
• Blade position from the bottom of the tank = 1.5 times the blade diameter;
• Tank bottom should have rounded corners; as a flat bottom tanks often leave unprocessed material in the corners. **NB.** One US Gallon = 3.785 L

**Tank Configuration**

The product level should be equivalent to the tank diameter. The side of the tank is equal to the product level, plus 20% added for free-bore.

*Figure 7: Tank Configuration*

Allow 10 hp per 100 gallons of product. Single shaft dispersers are not recommended for products over 50,000 cps.

**Tank Configuration**

- Diameter = product level
- Straight side = product level + 15-20% free bore
- baffles (if needed - <1000 cps) should be
  - width = .05 - .1 of tank diameter
  - height = 2/3 of the straight wall
  - style = off the wall to not allow ebbing
  - quantity = normally 3-4 (product specific)

Typical blade tip speed: shaft rpm x .262 x blade diameter = fpm
Blade diameter = 1/3 tank diameter
Blade position = 1 to 1 1/2 blade diameter from the bottom of the tank.
Flat bottom tanks are appropriate for 500 gallons or less.
Dish bottom tanks are best choice for larger tanks.
**Application details.**

Use this as a draft for most silicate coatings and change it to suite the particular product.

When product XYZ is applied to a suitable substrate, it penetrates and reacts to form a hard, tough and insoluble silicate. It can also increase the substrate hardness, particularly with cementitious materials. When applied to these cement based materials the silicate reacts with calcium hydroxide to form harder calcium silicate hydrates.

**Appearance.**
Product XYZ is available in a range of colours and custom colours are available. This product dries to a FLAT or MATT finish

**Properties.**
XYZ has exceptional gas and water permeability that allows a building to dry out and water to pass through unhindered. Use the water repellant grade for exterior walls as it will prevent ingress of water while allowing any dampness to pass through and dry out.
Silicate coatings do not contribute to the growth of mold, algae or mildew; have improved resistance to most common chemicals. Durable and resistant to UV radiation are non-yellowing, non-fading or peeling.

**Application.**

**Caution.**
As with all paint applications glass and other surfaces should be covered and protected from silicate paint spillage as glass could be frosted or etched by contact. This is a chemical reaction and can not be reversed.

Allow new cementitious work to cure for 7 days before coating. For maximum effectiveness surfaces must be well dried to allow the silicate to penetrate the porous substrate. Allow extra time for the substrate to dry if climatic conditions are very moist.
Always pre-test a small area before starting a large scale project.
Allow up to seven days full cure time with applications that are not repeat work before judging the final colour and finish.
Mix well before use.

**Factors affecting silicate coating penetration depth.**
Penetration depth may not be critical for all work but high wearing surfaces they should be suitably cleaned to allow for good penetration of the substrate.
Penetration is affected by poor substrate structure, moisture content and inadequate surface preparation. Apply by brush, roller or airless spray. Avoid product rundown. A thin, continuous film is required for nonporous substrates such as glazed terra cotta or hard stone. Allow first coat to dry (drying time is dependant on prevailing conditions) before second or top coat is applied.

**Protection and Curing.** As with any decorative coating it should not be exposed to rain until it is touch dry. Full cure requires up to seven days and the colour may change in hue or intensity during this period. The most suitable weather conditions
Temperatures between +5 and +25°C (during and at least 48 hours after application)
Moderately high relative humidity (but no rain)
No strong sunshine (heat) on the walls
No dry warm wind

**Coverage or spreading rate.** This will depend on the porosity and texture of the substrate but will be in the order of 10 sqm/L for normal flat smooth surfaces.
Part 4. Summing up

23. Some useful information

**Silicate:** one of the many minerals consisting primarily of SiO$_2$ combined with alkali metal ions (Li, Na or K).

**Colloidal Silica:** Is a colloidal solution of silica particles of 30 to 100 nm that are electrostatically stabilised. Pure Silica Sols are anionic and typically sodium or ammonium stabilised to a pH of 9-11.

**Sodium Silicates** have a SiO$_2$/Na$_2$O ratio of approximately 3.4, whereas colloidal silica generally has a SiO$_2$/Na$_2$O ratio greater than 50.

**The pH** and the sodium content of the solution will determine the final mixture. If the pH is reduced to below seven, making it acidic, or salt is added, the silica units will begin to fuse together, forming larger particles. These particles are called silica gels and are not stable in a solution as they can dissociate again if the solution is altered.

**Silica Sols:** When relatively dilute concentrations of dissolved silica are acidified, activated colloidal silicate solutions (**sols**) can be formed.
The pH affects a Colloidal Silica to form either a Gel or a Sol with a physical change between the gel and the sol being very significant. Gels form at pH <7 and Sols form >7.

Viscosity of sodium silicates is much higher - closer to that of a syrup, while colloidal silica’s have viscosities close to that of water.

Silica Gels; Sodium silicates react with acidic compounds. When solutions of relatively high concentrations are acidified, the soluble silicate anions polymerize to form a gel.

The cure reaction; Solutions of sodium silicate react with dissolved polyvalent cations such as Ca++, Al³⁺, and Mg++ to form insoluble forms of silicate.

Calcium chloride reacts instantaneously with silicate solutions. Remember the Ca++ reaction is also an effective mechanism for insolubilizing a silicate bond or coating.

NB. Label containers “store in warm area and prevent freezing”
**Reactivity of CaCO₃.** Mineral calcium carbonates, such as calcite, exhibit limited interaction with soluble silicate, whereas precipitated calcium carbonate shows high reactivity possibly due to reactive coatings or other reactivity.

**Organic compounds;** relatively few are compatible with concentrated soluble silicate solutions.

**The viscosity of sodium silicate solutions** at commercial concentrations can be decreased to less than 1 poise if heated sufficiently and if evaporation is prevented.

**Potassium silicate solutions** are similar to solutions of sodium silicate. One significant difference, however, is that potassium silicate solutions are somewhat more viscous than corresponding sodium silicate solutions at equal concentrations. But, like sodium silicate, the viscosity of solutions is affected by ratio, concentration, and temperature.

**The pH** of silicate solutions is dependent on concentration and ratio. pH decreases as ratio (SiO₂) increases.

**The buffering capacity** (the ability of a solution to resist changes in pH) increases with increasing proportions of soluble silica. However, even dilute silicate solutions will maintain a relatively constant pH despite the addition of acid.
All silicate solutions are alkaline, the pH of commercial silicate solutions ranges from approximately 10 to 13. The pH is a function of ratio and concentration and decreases with increasing silica content.

**The stability** of a sodium silicate solution depends to a large extent on pH. All sodium silicate solutions will polymerize to form a silica gel when the pH value is reduced to below 10.

**Gel formation.** Sodium silicates react with acidic compounds. When solutions of relatively high concentrations are acidified, the soluble silicate anions polymerize to form a gel.

**Silica sols** (also known as **colloidal silica** solutions) are solutions of colloidal silica with typical particle sizes ranging from 8-125 nm, (somewhat larger than the size of the silicate particles in waterborne alkali silicates, which are of the order of 2–3 nm). Silica sol colloidal solutions may appear nearly clear and almost colourless at the lowest particle size, and with increasing particle size and concentration may range in appearance from opaque (± 40 nm particle size) to milky at larger particle sizes. Their stability reduces with increased particle size.

**Silica Sols:** When relatively dilute concentrations of dissolved silica are acidified, activated colloidal silicate solutions (**sols**) can be formed
The degree of polymerization of the silicate anions of sodium silicate solutions depends on solution; concentration, temperature, pH and other factors.

Time-delayed gelation (unstable sols) can occur in pH ranges of 2-5 and 8-10. Gel formation is generally very rapid in the intermediate range (5-8).

**When silicates react with acid** forming products such as organic esters, the alkalinity of the silicate solution is consumed by the hydrolysis of these esters over an extended period of time. The gel forms an adhesive bond with the surrounding substrate (e.g. sand, fly ash, cement and wood).

**The extent and rate of reaction** of silicates with various metallic salts depends on the nature of the salt and its physical and molecular structure. For example, mineral calcium carbonates, such as calcite, exhibit limited interaction with soluble silicate, whereas precipitated calcium carbonate shows high reactivity.
**Adsorption.** The functional versatility of dissolved silica, as provided by sodium and potassium silicates, is demonstrated by its ability to alter the surface characteristics of various materials in different ways. When Silicates adsorb onto charged mineral and oxide surfaces the resulting effects can be:

- coagulation/ flocculation;
- dispersion/deflocculation;
- emulsification/demulsification
- and corrosion inhibition depending on the following choices:
  - silicate type SiO$_2$/Na$_2$O(or K or Li)
  - solution concentration
  - choice of sodium or potassium alkali source
  - solution conditions - principally pH

Even at the same silica to alkali molar ratio, **Potassium Silicate** softens and flows at a higher temperature than corresponding sodium silicates. For this reason, they are used in various high-temperature binders.

Electrometric titrations with acids show that a high pH silicate solutions is maintained until the alkali is almost completely neutralized.

A potassium silicate coating **pigmented with zinc oxide** proved satisfactory for use on space vehicles **requiring solar radiation absorption and infrared emittance**.
**High temperature-resistant coatings.** Mixtures of copper, nickel, chromium and stainless steel powders in the silicate vehicle provide high temperature-resistant coatings for metals.

**Resistance to higher temperatures** can be achieved by adding clay to the formulation. Depending on the aluminum or magnesium content of the clay, service temperatures up to 1760 to 1871°C (3200 to 3400°F) are possible due to the ceramic bond.

**Heat Resistance.** When silicate films are completely dehydrated, they provide excellent resistance to high temperature. Most silicates used for coatings or binders have softening points of approximately 650°C (1200°F) and flow points of 816°C (1500 to 1600°F).

**With increasing concentration**, the larger polysilicate anions prevail. When solutions are diluted there is an instant partial depolymerization and re-arrangement.

**Storage.** Prevent freezing i.e. store >25°C if possible.

**NB.** Label containers “store in warm area and prevent freezing”

**Colloidal silica.** Alone or in combination with Potassium silicate, adding colloidal silica to coatings will improve the weather resistance and durability of the underlying inorganic material. Colloidal Silica also helps reduce internal stress by reducing the shrinkage of inorganic coatings.
**Lithium silicate.** Compared to sodium and potassium silicate binders, certain surfaces can achieve better adhesion with Lithium silicate. As a binder or coating, Lithium silicate can also impart high levels of strength and water resistance.

**NB.** While Lithium silicate is considerably more expensive than Sodium silicate, improvements in adhesion can also be seen when a small amount of lithium silicate is blended with sodium or potassium silicate.

**24. Silicate emulsion coatings can be applied on various substrates.**

Such as:

- Metal surfaces, especially aluminium and galvanized iron
- Fresh or set high calcium lime-sand mortar (interior)
- Fresh or set lime-cement-sand rendering
- Fresh or set cement rendering
- Concrete surfaces (after removal of formwork and release agent residues)
- Sand-lime-brick masonry
- Brick masonry
- Fibre cement (e.g. cellulose/glass fibre cement) sheets/boards or panels
Silicate emulsion paints can be applied (after pretreatment or where necessary with specially formulated products) on:

- Natural stone (depending type)
- Kiln fired brick
- Light weight or foamed concrete (porous with high absorption)
- Inorganic foamed insulation materials
- Iron surfaces (e.g. interior fire proofing coatings)
- Fresh limewash coatings
- Old limewash coatings
- Old but strongly adherent emulsion paint (Note: water vapour permeation will not be obtained)

Silicate emulsion paints are unsuitable for application (or only after special pretreatment) on:

- Gypsum finishes (pretreatment required)
- Particle board
- Existing oil paint
- Plastic surfaces
All substrates should be of such condition that good penetration of the paint into the pores and capillaries can be achieved. For example, cement or lime sinter surfaces on concrete or plaster are pre-treated with a fluorosilicate etching liquid if necessary. Where highly absorbent substrates are encountered, it is recommended that a dilute silicate emulsion paint or a special silicate emulsion primer as shown should be used:

25. Listing of silicate based coatings types.

The list of types of coatings is quite endless and should show that there is no limitation except your imagination. Once you start developing your range of silicate paints you should be able to put them in order of application and importance. Some grades or types will be specific to an application while others will be part of a “Coating System” for specific applications

Possible silicate paint types or grades possible with inorganic pigment colours are;

1. Colour match for concrete surfaces to create a uniform concrete finish can be semi transparent.
2. A filler coat or base coat for imperfect cementitious substrates based on fine fillers and may contain fiber reinforcement.
3. A pure 1-K silicate exterior paint.
4. Silicate Filler for use on mineral substrates, interior and exterior.
5. Photocatalytic mineral paint to convert Nitrous Oxides and other harmful pollutants into harmless nitrates via Titanium Dioxide Photocatalytic reaction.
6. General purpose exterior sol silicate paint based on a silica sol and potassium silicate.
7. High build Filler Coat but not suitable as a top coat.
8. Water repellent Exterior silica sol/potassium silicate for general purpose coating for use on mineral and previously applied organic coatings.
9. High water repellent algae and fungal growth resistant coating.
10. Deep penetrating silane modified sol-silicate bonding clear for consolidation of porous mineral, stone or other work.
11. Hydrophobic impregnation water repellent silane primer for mineral substrates that will resist waterborne salts.
12. Stabilised Potassium silicate dilution liquid for use with other pigmented coatings for reduction of or control of substrate absorbency.
13. Extreme climate water repellent and vapour permeability grade coating.
14. Sol-silicate colour wash semi transparent coating to equalise stone or brick work repairs or colour differences.
15. Sol-silicate clear binder for use with the colour wash.
16. Texture coat based on sol-silicate can be fine or coarse for interior or exterior use.
17. White pigmented 2-K primer and stain sealer.
18. Exterior filler coat, not for use as a top coat but fills hairline cracks and evens out the surface.
19. Eco paints. Silicate paints are suitable for use in hospitals; nursing homes and in areas where the occupants suffer from allergies. Choose your label and brand it.
20. Silicate concrete paints retain the natural appearance of concrete and can be selectively formulated to suit this industry.
21. Silicate based primer coat for interior use according to DIN 18 363
22. Anti-carbonation coatings based on silicate can be formulated to conform to the relevant specs and protect the reinforcing from low pH development over long periods.
23. 2-K anti corrosive primers such as Zinc Rich can be made with Lithium Silicate and Sol-silicates.
24. Dynamic Light scattering coatings are possible due to the Matt and Ultra-matt finish giving unique and beneficial lighting properties.

To clarify this.
25. As silicate coatings reflect IR rays a climate control or heat shield coating is well within the range of possible coatings. Add the IR reflective pigments and some Zinc Oxide to sort out the UV radiation.

26. High temp Pigmented Gloss coatings can be based on Potassium or Lithium.

27. Clear Silicate coatings to impregnate aluminum castings by special vacuum and pressure techniques to reduce their porosity.

28. Potassium Silicate wood coatings to render the wood non-flammable in clear or pigmented matt finish. This could also be developed for thatch roofs.

The extreme/Ultra matt possible with the silicates crystalline structure can be tailored to give vibrant, delicate textures and unique beneficial lighting properties.
29. When used to create ceramic non-stick Boron Nitride coatings, colloidal silica acts as a co-binder. In both cases, colloidal silica helps increase surface hardness, abrasion and temperature resistance properties of the resulting surface.

30. Potassium silicate solutions may be used in the impregnation of masonry substrates for chemical damp-proofing against rising damp. 5 to 10% of a water repellent such as potassium methyl silicateate may be added to enhance the properties.

31. Silicate based paint reflects IR rays so you can make a truly heat reflective paint if you used IR reflective pigments in a Silicate Roof paint. Life expectancy would be many decades not just one. Power savings via this cooling effect would be excellent.

26. Additives. (Suitable for used in silicate emulsion systems)

**Dispersants:** polyphosphates, polyacrylates, phosphonates, naphthene and lignin sulfonates

- **Wetting agents:** anionic, cationic, amphoteric and nonionic surfactants

- **Defoamers:** silicon emulsions, hydrocarbons, long chain alcohols etc.

- **Stabilizers:** Quaternary ammonium compounds; special polyfunctional, mostly cationic compounds
**Coalescents:** (if needed): alkali-stable esters, glycols, hydrocarbons

**Rheology:** cellulose derivatives (CMC, HEC), xanthan gums, polyurethane, polyacrylate, modified starch, bentone, acrylic polymers and lamellar silicates (mica, Kaolin, talc)

**Water repellents:** alkyl siliconates, siloxanes, wax emulsions, fatty acid Li salts

**Biocides:** (Due to their alkalinity and lack of or low organic content silicate emulsion paints do not need special in-can preservatives, but it may be necessary to incorporate special algaeicides or fungicides for film preservation).

As with conventional emulsion paints the pH of the final silicate emulsion paint is expected to be around 8.0-10.5, so any additives should be stable at these values.

27. **Raw material suppliers.**

The primary suppliers of liquid Silicates and additives are.

**PQ Corp.** [http://www.pqcorp.com/pc/NorthAmerica/Products](http://www.pqcorp.com/pc/NorthAmerica/Products)
The initial link is above so look for the coatings products. You will see a second “products” link on the right hand side of the products page. The range of products is extensive and data sheets are available for download.
Vonbaerle.  
Search the website for these products and more info.

Some noteworthy Vonbaerle products are;  
INOCOT K-2837 Pure K-silicate  
INOCOT 320 Pre-stabilized K-silicate  
INOCOT 910 Stabilizer for silicates  
INOCOT 925 Viscosity regulator  
INOCOT 930 Dispersant  
INOCOT 935 Anti-foam

Woellner.  
http://www.woellner.de/woellner/en/Products/Product%20lines/Water%20glass/  
Their range of alkali silicates and related products include:  
Lithium Silicates, marketed as Woellner Betolin™ Li series  
Potassium Silicates, marketed as Woellner Betolin™ K and P series  
Sodium Silicates, marketed as Woellner Betol™ series  
Aqueous Silica Sols. marketed as Woellner Betol™ series.

W. R. Grace & Co.  WWW.grace.com  Look for their LUDOX® Colloidal Silica
Woellner additives are classified as:
Dispersants, marketed as Woellner Sapetin™ series
Hardeners, marketed as Woellner Betolin™ HT series
Protective Agents, marketed as Woellner Betolin™ series
Rheological Additives, marketed as Woellner Betolin™ series
Stabilizers, marketed as Woellner Betolin™ Q series
Wetting Agents, marketed as Woellner Sapetin™ series

Other suppliers of additives and related products.

Wacker Silicones; IMCD South Africa (Pty) Ltd. 011 293 2000

You will find a list of SILRES®. Silane - Siloxanes products,

Suitable for mineral paints or plasters
Significant and durable reduction of water uptake
Long lasting effect in mineral paints or plasters
Durable efficiency even after a long storage of the liquid paint / plaster
Dosage levels between 1% and 4% achieve a great effect.
Akzonobel. Modified colloidal silica for use in silicate paints
(refer to Akzonobel folder containing Bindzil CC30 solution)

Dow Silane;
http://www.dowcorning.com/content/publishedlit/26-1208-01_Evolution_of_Silicon-Based_Technology_in_Coatings.pdf

BASF:
Huntsman to Showcase ALTIRIS® Infrared Reflecting Pigment;

Lansco colors; Mixed Metal Oxide pigments.

You may want to try one of these products in place of the 2-K Zinc Chromate.

MK Chemicals
DE-Bockenem-Bornum
http://www.mkchemicals.de/silicolor.html info@mkchemicals.de
Offer their Silicolor range of pigment dispersions that are offered for use in silicate paints and renders but they have not clarified the PSD as requested.

Inorganic unreactive pigments e.g.
Red iron oxide; Cadmium Red; blue—ultramarine; green—chrome oxide; yellow—ochre; brown—umber or sienna; black—carbon black.

Don’t forget that transparent Iron oxides are very useful in creating your own unique Silicate Coatings as well as being a great wood finish application.
As silicates are IR reflective you can try the IR Reflecting inorganic pigments if you really want to make a special ECO product. These are available from “Shepherd pigments” and others.
http://www.shepherdcolor.com/products/arctic/

**Heubach** pigments, IR reflective;
http://www.heubachcolor.de/en/home.html
HEUCODUR® IR Pigments (Yellow to Black but missing a Red)

You may want to try one of these products in place of the 2-K Zinc Chromate.
Nanoguard Zinc replacement pigments.
http://www.nanoguard.info/

Inorganic non-reactive pigments e.g.
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http://www.shepherdcolor.com/products/arctic/

AICL Performance Products. BK Giuliani. Lopon range of additives.
us/Solutions/Industrial/Paints_and_Coatings/Pages/generated_application.aspx
28. Summary.

Remember that silicate coatings are used and currently make up 10 to 15 percent of the decorative paint sales volume in the EU. They outperform organic binder systems hands down and the systems are improving all the time. In the past 60 years while organic binders and decorative paints have gone from dry distempers; PVA’s; acrylic copolymers and water reducible alkyds etc to ever more complex formulations with just too many additives to speak of, Silicate coatings have risen to take their rightful place.

I would venture to suggest that you start your investigation of silicate coatings with the PQ Corporations Silicate Emulsion Coating on slide No. 55. You will be able to cut your teeth on this well balanced formulation. Once you have control of the technology you will be able to produce many exclusive products in the architectural coatings field. Let me know what takes your fancy after that and we can really get your silicate coatings started.

This overview should help you start your work on “Silicate coatings” but experience is what is needed now.

In Book Two we will look at Fine tuning and trouble shooting your formulations.
Understandably there are possibly many questions begging for answers but we already have too much information for an introduction so a follow up is possibly needed.

I hope you have found this information useful and informative. Contact me for any further clarification or assistance.

Two other presentations that you may be interested in are “Sonochemistry 2015” which details the use and applications of ultrasonic processing in the industrial chemical industry and “pigment particle size distribution” which clarifies the correct particle size required for pigments by their type and colour.

Let me know if you would like a copy of either one.

Kind regards,

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