



A journey through problems & solutions

The diagram illustrates the ceramic tile production process, categorized into five main stages: **STORAGE**, **BODY PREPARATION**, **GLAZING LINE APPLICATIONS**, **FIRING**, and **POST FIRING / PACKAGING**.

SEMI-FINISHED PREPARATION (dashed line):

- Glaze & Engobe Grinding
- Grit Suspension
- Pigment's Grinding / Dispersion for Glaze Coloring
- Kiln Engobe Preparation
- Stock

STORAGE:

- Raw Material
- Process Water
- Spray Drying
- Dry Powder Storage
- "Continua" Press
- Isostatic Press
- Cutting

BODY PREPARATION:

- Slurry Storage / To the Spray Dryer
- Slurry Discharge
- Wet Grinding Continuous Mill
- Wet Grinding Discontinuous Mill
- Mill Loading
- GRINDING PROCESS
- SPRAY DRY TECHNOLOGY
- GRINDING PROCESS
- WETTING & GRANULATION
- Dry Grinding
- Mill Loading
- GRINDING PROCESS
- EXTRUSION TECHNOLOGY
- FORMING
- DRYING
- GRANULATE COLORING
- FORMING
- DRYING
- Cutting
- Extrusion

GLAZING LINE APPLICATIONS (indicated by a large blue circle and arrow pointing to the 'Cutting' step in Body Preparation):

- Tile Storage Before Firing
- Undertile Engobe Application
- Top Glaze Application (Digital)
- Top Glaze Application (Analogical)
- Grit Suspension Application
- Digital Glue Application
- Glue Application
- Digital Decoration
- Traditional Decoration
- Primer Application
- Relief Effects (Digital)
- Relief Effects (Analogical)
- Engobe / Glaze Application (Digital)
- Engobe / Glaze Application (Analogical)
- Surface Body Wetting

FIRING:

- Third Firing Applications
- Scratch Protective Application
- After Firing Quality Check
- Cutting & Squaring
- Tile Storage
- After Treatment Quality Check
- Firing
- Surface Treatment
- Pre-firing
- Polishing

POST FIRING / PACKAGING:

- Third Firing Applications
- Scratch Protective Application
- After Firing Quality Check
- Cutting & Squaring
- Tile Storage
- After Treatment Quality Check
- Firing
- Surface Treatment
- Pre-firing
- Polishing

MACRO PHASES:

- PHASES
- MICRO PHASES

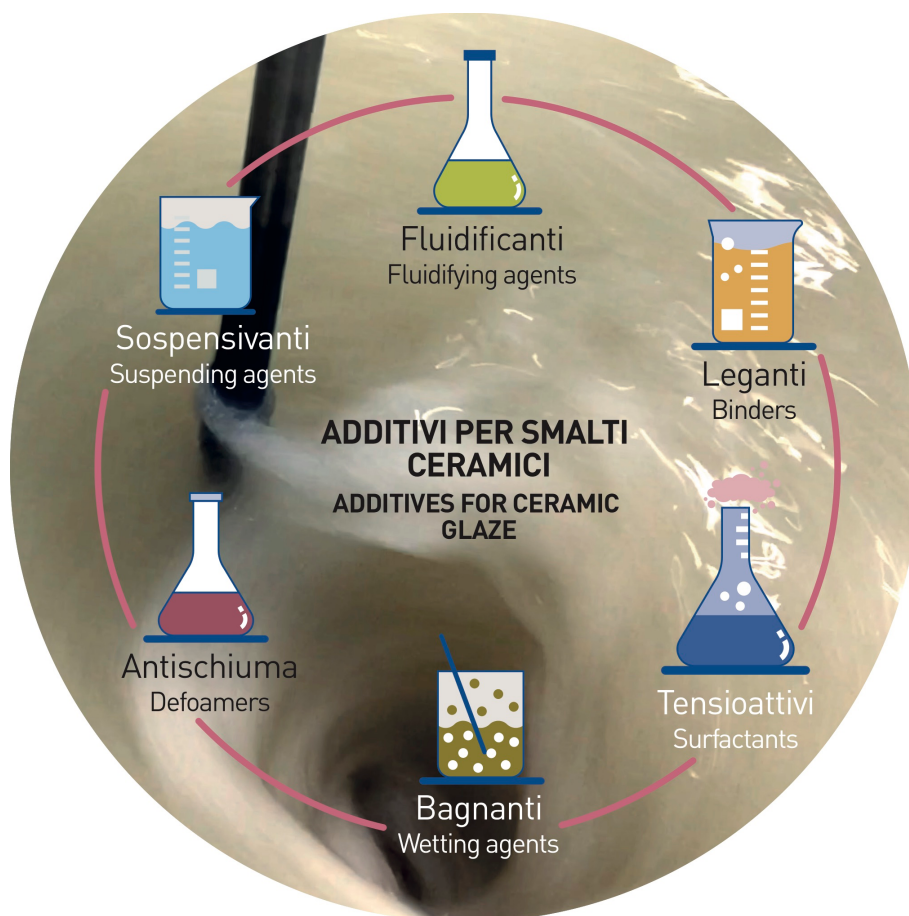


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1. INTRODUCTION

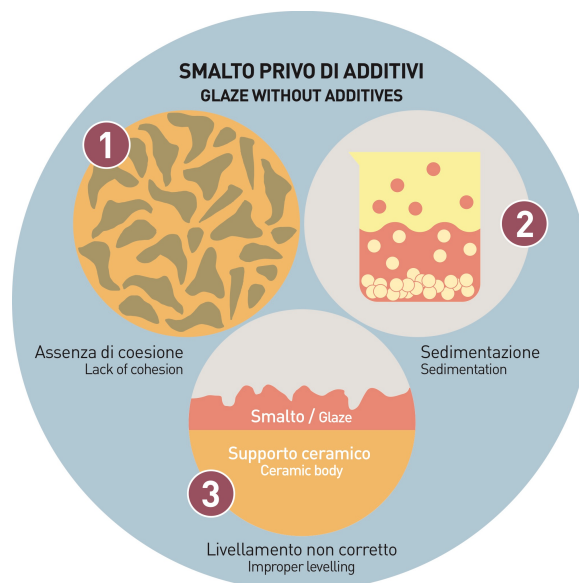
The ceramic glaze application is one of the most delicate steps of the ceramic production process. To get high performance, the glaze must be marked by specific and always different rheological features, according to the application conditions of each production line. The proper formulation of the glaze suspension is basically the precondition for a correct application and a result without technical or aesthetic defects.

That said, let's make an absurd assumption:

What would happen to a glaze if we did not add any chemicals during the grinding stage?

What would happen if we used only water?

The consequences would be very interesting but at the top of list of the problems we would find a lack of cohesion and serious problems of stability with consequently possible sedimentation phenomena. In addition, the glaze could improperly level on the raw ceramic tile.



Without making a list of all the other possible consequences, we can surely declare that, without the help of proper chemicals, the glaze does not work, and it cannot produce any performing tile.

Why?

Glazes are mainly made up of **inorganic raw materials** and **ceramic frits ground in water**.

Frits is nothing but ground glass. They usually consist of a mix of silica and minerals, able to provide oxides. They are prepared - in general - by melting the different components and then cooling them quickly. This dual process causes the glass parts to break into very small flakes, that are the frits. The formulation of the frits (that is the kind of minerals that have been selected) - of course - defines the physical as well as the chemical and mechanical features of the glaze.



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The glaze consists of a mix of elements whose features are not enough to produce a **cohesive and stable** suspension.

2. APPLICATION PROCESS AND GLAZE'S PROPER BEHAVIOR

Let's now think, instead, to a good glaze application by means of airless spray system.

What happen in this case?

1. The glaze is properly discharged on the surface by the nozzles of the spray cabin
2. It correctly performs in term of leveling
3. and it finally evenly dries

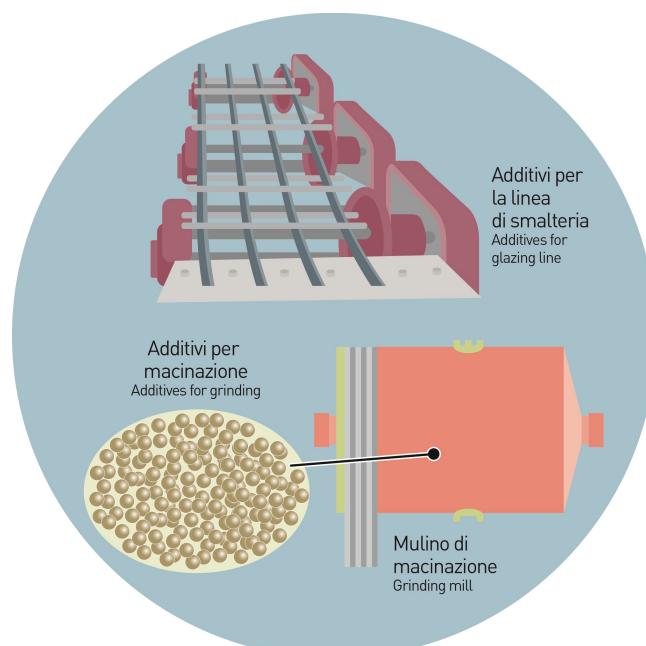
These three apparently simple steps, however, are not obvious or trivial and they are not inherently part of the glaze's nature. The proper glaze behavior is only possible thanks to the calibrated use of chemical components of organic and inorganic nature. Without chemicals the glaze would tend to sediment inside the circuit; its nebulization would be inadequate and the glaze - not cohesive and bound - would not be properly leveled and uniformly discharged on the ceramic support.

Not to mention the correct drying times or possible repellent phenomena promoted by the contact between glaze (water-based) and inks (solvent-based).

In which part of the process chemicals for glazes can be added?

They can be added in two different steps.

Chemicals can be added during the grinding phase (that is the preparatory stage) and/or directly along the glazing line, that is when the production process is already taking place.





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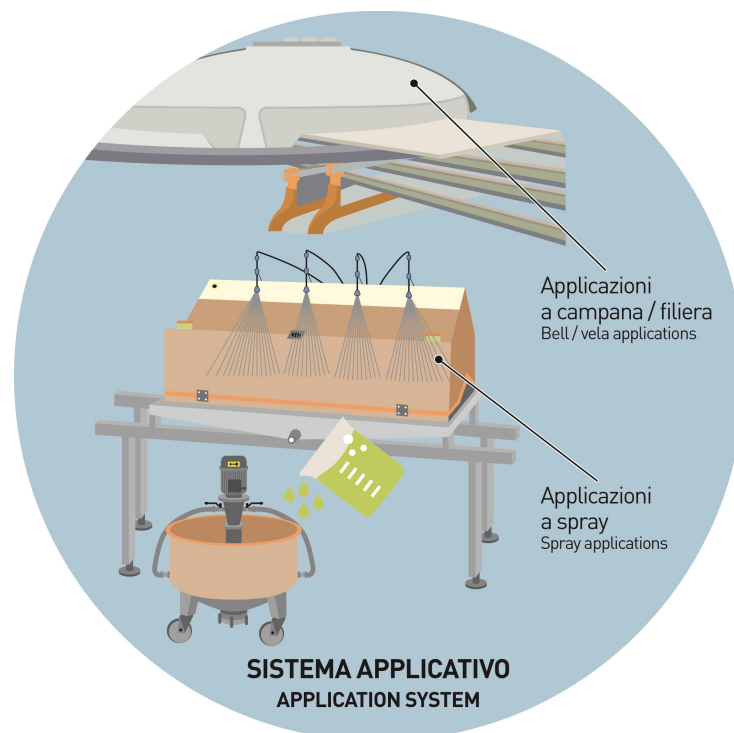
3. CHEMICALS FOR GRINDING PROCESS

DISPERSANT and **BINDERS**, in terms of formulation, can be significantly different depending on the kind of glaze to which they must be added, on the application system and on the parameters of the production line.

What do we mean with the word DISPERSANT?

This word usually refers to any substance capable of lowering the viscosity of a suspension, regardless of the mechanism of action that develops. More specifically, in ceramic, glaze dispersants are chemicals able to keep separate the watery suspended particles to avoid - or limit - possible interactions.

The actions provided by all chemicals added during the grinding process must consider the application system that will be used along the glazing line.



What does that mean?

It simply means that the grinding parameters used for glazes applied by means airless spray systems are different from those applied by bell or vela systems.

a) GRINDING FOR SUBSEQUENT AIRLESS APPLICATION

In this scenario we need to make a difference between high-density and low-density applications.

A high-density airless application (marked by low water content and high solid content) usually requires the use of DISPERSANTS able to strongly reduce the viscosity value of the suspension.



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At the same time, the use of BINDERS capable of providing cohesion in the suspension is very recommended. The lack of binders, in fact, could compromise the bonding of the glaze on the ceramic support and at same time could lead to an improper leveling process.

A **low-density airless application**, instead, (used, for example, for top glaze applications) requires dispersants marked by a less powerful action or – as an alternative – a lower dose. A very high fluidization, in fact, could deconstruct the system, leading, for example, to sedimentation phenomena.

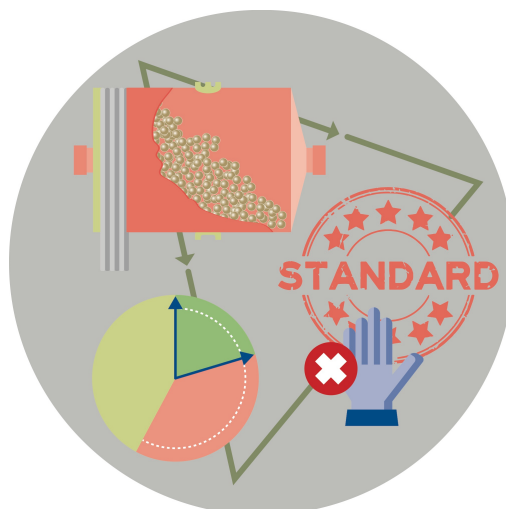
b) MILLING FOR SUBSEQUENT BELL OR VELA APPLICATION

In this case, during the grinding stage it would be important to use very noble rheological and cohesive additives, that is chemicals with a very low number of anions and cations that may be responsible for glaze defects after firing, such as pinholes.

In addition, when applied by vela or bell systems -unlike spray application systems - the glaze must be marked by good viscosity levels.

In fact, since it has not to be sprayed it must be bound and quite cohesive, to remain compact during discharge. From the machine to the ceramic support.

EPILOG



Speaking of *chemicals to be used for glaze grinding*, even with these few examples, it's clear that we can find some general rules but it's impossible to talk about standard formulations because scenarios and parameters are always different. We can also add that a proper additivation during the grinding stage results not only in a good performance in the following stage along the glazing line, but it also promotes significant benefits already during the grinding step.

Just think, for example, of the benefits that you can get by reducing the grinding time thanks to the use of specific chemicals that make the glaze cohesive, according to the needs.



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In general, the grinding process is faster and without problems when the glaze is more cohesive. And this of course is a great benefit in terms of industrial productivity.

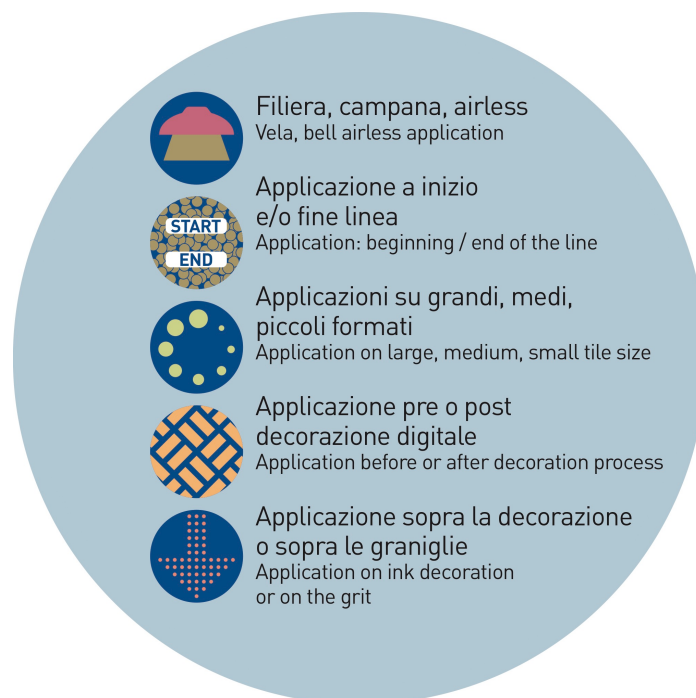
4. TOWARDS THE GLAZING LINE

POSSIBLE SCENARIOS

Once it has been grinded, the glaze can be applied by means of spray, bell, and vela applications.

The glaze application can also be developed in several and different ways such as

- Application at the beginning and/or at the end of the line
- Application on large, medium, or small tile size
- Application before or after the digital decoration
- Application on the decoration or on the grits



In all this cases, chemicals play a fundamental role. So, let's see the most important families of chemicals involved in this stage of the ceramic production process.

THE (SO CALLED) BINDERS FOR GLAZES

They provide the glaze with a proper cohesive power towards the ceramic support (or towards the layers of glaze previously applied). The adhesive power acts both with respect to the support and to each layer of glaze that are applied one at the top of the other.



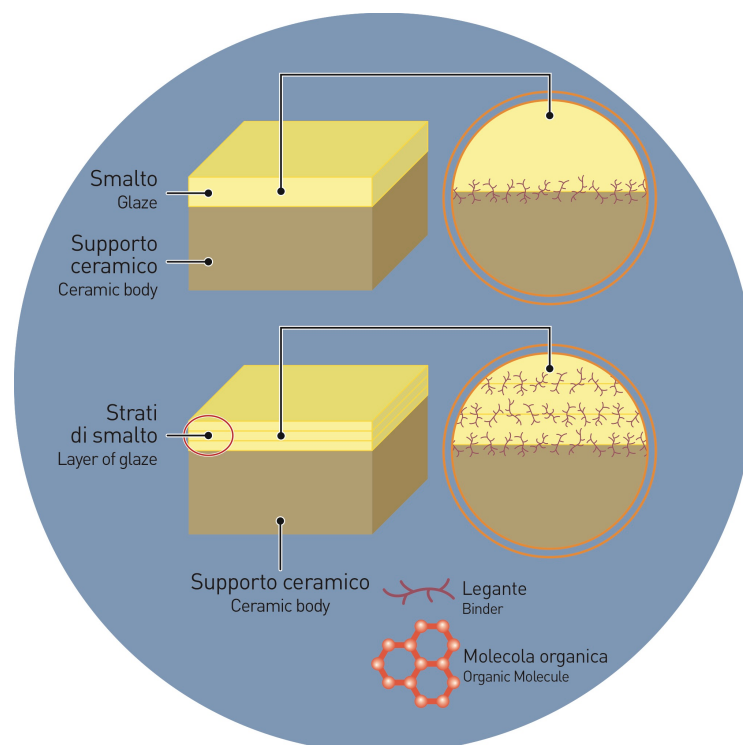
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From a chemical point of view, what is the origin of the binding power?

The binding power is provided by the presence of **organic molecules made of functional groups** capable of binding together the inorganic particles of the glaze and of binding themselves together, when they lose water thanks to the evaporation process.

Because to their ability to create a reticulation, binders can also significantly limit the dusting phenomena, that is the glaze that – when is unbound – returns to dust (or powder) after the evaporation.



Binders are also able **to provide the glaze with homogeneity and cohesion** and, at the same time to **slow down the water's evaporation and drainage process**.

Water that is in suspension to allow the application system to promote a good and homogeneous leveling, avoiding surface defects such as small air bubbles or pinholes. The binding power, in fact, also depends on the kind of **action that the chemical promotes on drying and drainage times**.

What does that mean?

It means that the proper drying/drainage times of the different layers that make up the ceramic body – engobe, glaze, ink, grit, covering glaze, etc. – are fundamental to ensure that each layer is applied only when the previous one has reached the right drainage value.

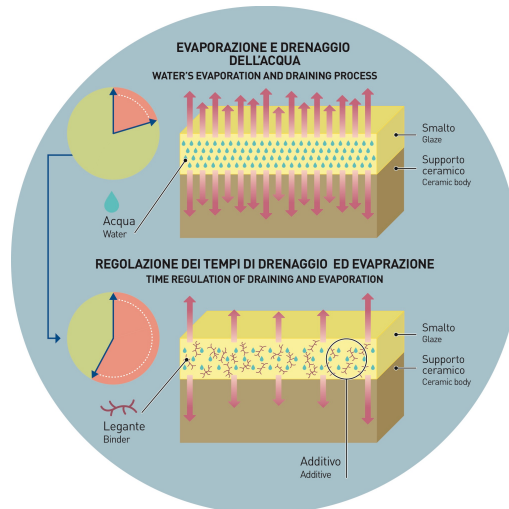
This is especially true in cases of glaze application on engobes.

If a glaze is too wet when the tile arrives under the printheads of the digital printing machine, problems may arise due to the water vapor that could affect the printing system.

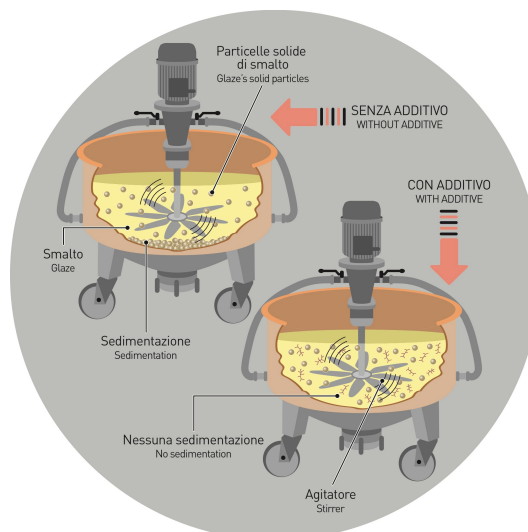


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Even if it's not one of their most important actions, binders are also capable of **slowing down or limiting possible glaze sedimentation phenomena** inside the tanks.



LEVELING AGENTS (SURFACTANTS & WETTING AGENTS) / DEFOAMERS

a) LEVELING AGENTS (SURFACTANTS)

To speak about SURFACTANTS means to speak about **high performing soluble products** that, by definition, **can lower the surface tension of the system** thanks to their molecular structure that is made of a Hydrophilic Head and a Hydrophobic Tail.

After the surfactant has been added to the glaze suspension, the following happens on the surface: the tail, due to its hydrophobic property, remains outside the water (exposed to the air) while the hydrophilic head, that is in water, separates the molecules that are on the water surface by lowering



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the surface tension. The decrease of the surface tension produces leads to a better glaze application and especially to a **better leveling**.

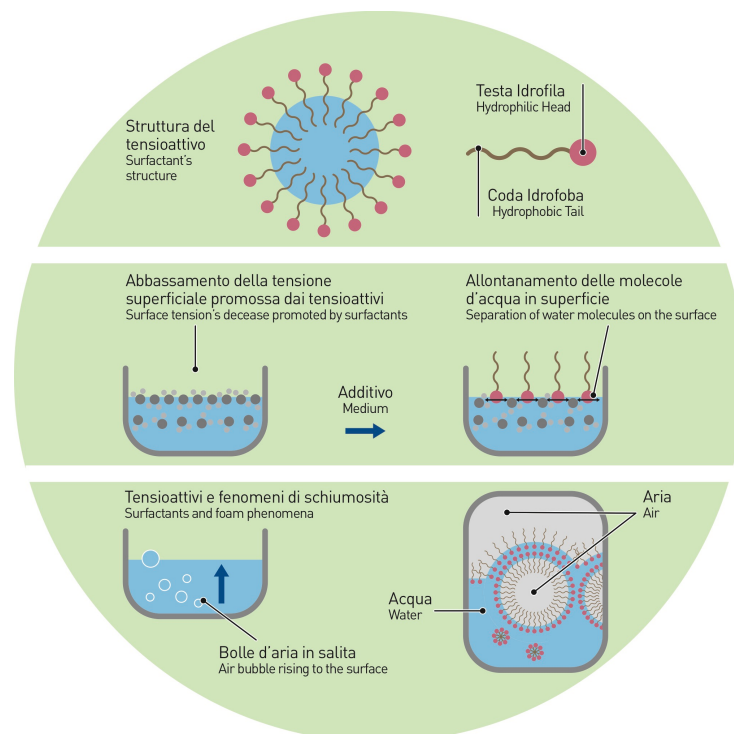
Since they are completely soluble and since they are used in very low dosages, surfactants do not normally produce any surface defects (such as, for example, holes or pinholes). However, they can be highly foaming and difficult to control.

How does a surfactant produce foam?

What is the structure of a foam bubble?

Foam bubbles generated by surfactants are nothing more than spherical films of water molecules held together by the same surfactants.

In ceramics, when the glaze suspension is under stirring inside the tank along the glazing line, the air can enter in the glaze suspension producing foam bubbles that rise to the surface (and this happens especially when the stirring process is marked by a high speed).



This ability to produce foam is the reason why surfactants are not frequently used in the ceramic production process, and they are replaced - when possible - by WETTING AGENTS that are more manageable.

b) LEVELING AGENTS (WETTING AGENTS)

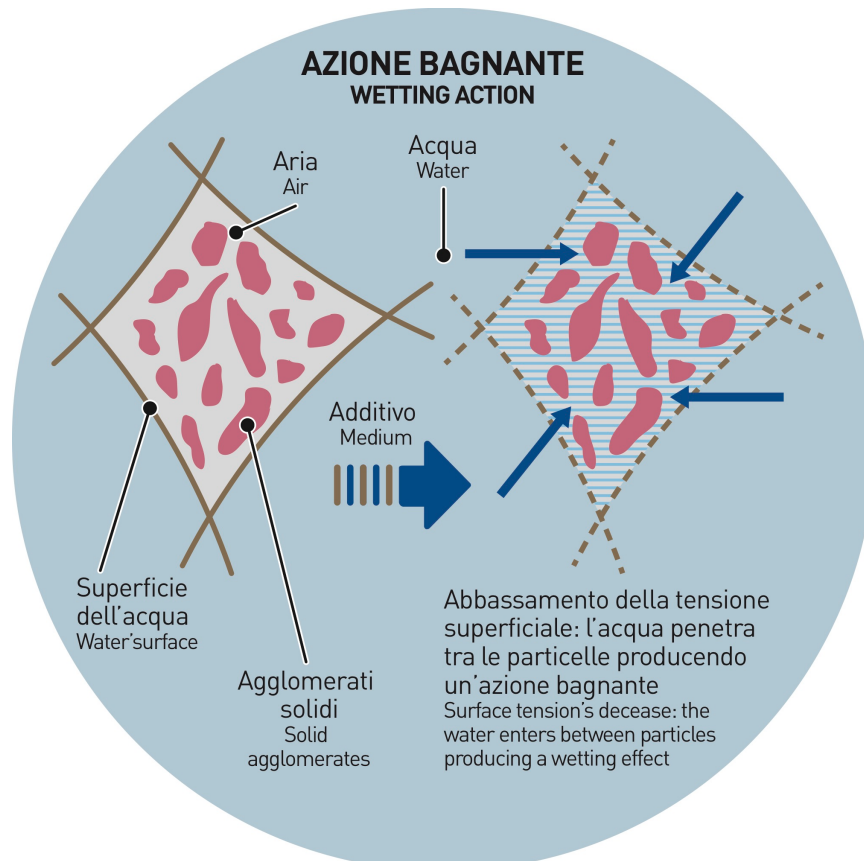
In some cases, to face or avoid the problems promoted by surfactants, it is possible to use PARTIALLY HYDROSOLUBLE LEVELING AGENTS that on the one hand do not possess any antifoaming properties, but on the other hand, can wet the inorganic glaze particles by lowering the water's surface tension, encouraging a de-agglomeration of the particles, thus facilitating their homogeneous dispersion within the system.



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The decrease of water's high surface tension lets the water move between the suspended and agglomerated solid particles, producing, and creating a distance between one and the other. The de-agglomeration, together with the lower glaze's surface tension, turns in the proper leveling effect.



In other words:

wetting agents are organic molecules that act both in the inter-phase between the ceramic/glaze substrate and in the glaze/air inter-phase: the leveling action they promote is specifically produced by decreasing the surface tension of water in the glaze/air inter-phase.

c) DEFOAMERS

DEFOAMERS are chemical agents able to prevent and/or remove air bubbles that can sometimes be trapped inside the glaze or on its surface. They can be added both inside the stirring tank and after application on the glaze surface already discharged on the ceramic support.

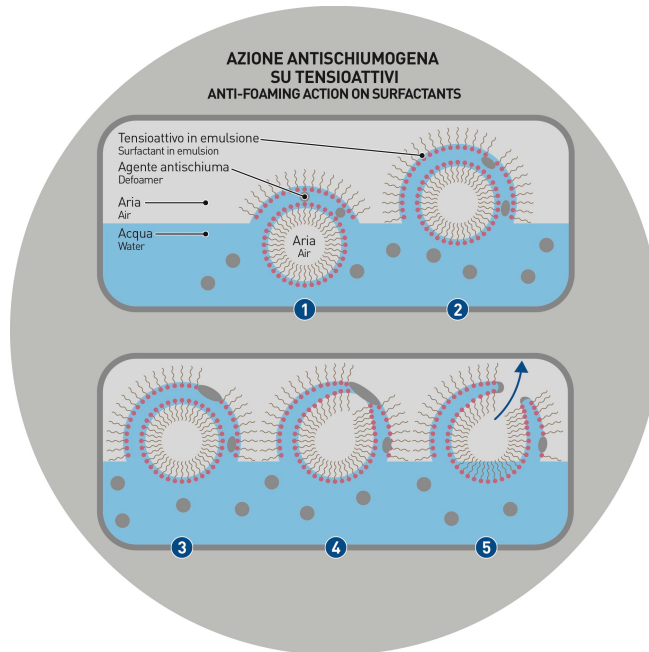
How does the defoamer work?



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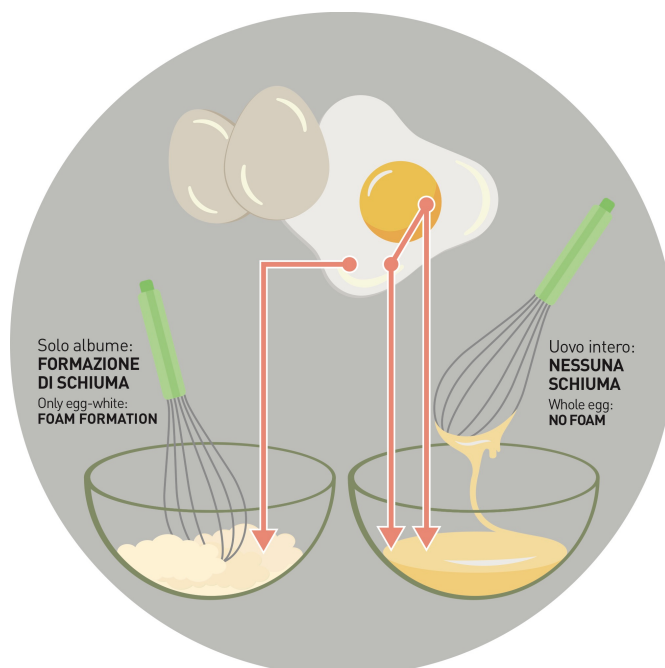
Since the defoamer is **water insoluble**, it can destabilize the foaming system by acting on the foam's surface tension by breaking the surfactants' hydrophobic tails and therefore causing the explosion of the bubbles.



To better understand let's make an example from the world of cooking.

Let's start to beat an egg. If we beat only the egg white, the foam appears. Instead, if we beat the entire egg (egg-white + yolk) no foaming phenomena will be produced. Why?

Egg yolk contains very high percentages of fats (particularly triglycerides) that act as a defoamer, by containing or avoiding the formation of foam.





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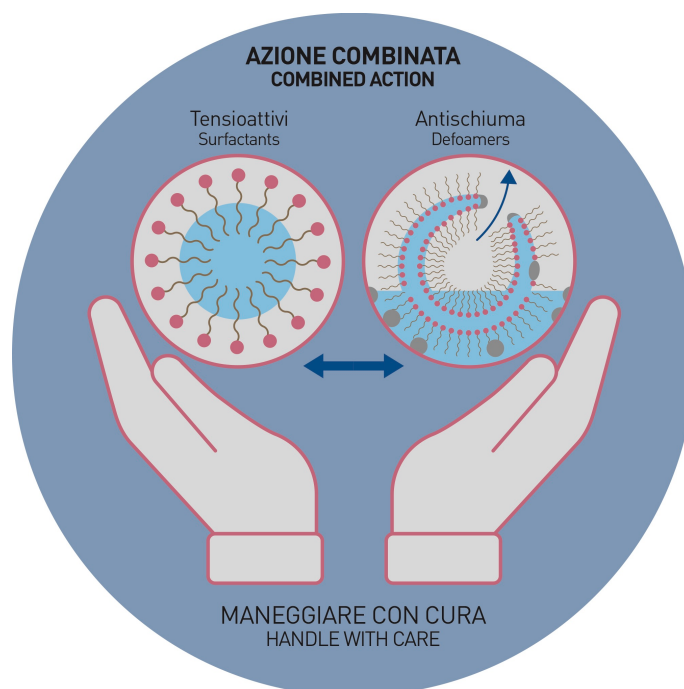
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When applied to not very plastic glazes (marked by a low clay content) or hard glazes (such as glazes containing only frits), defoamers tend to remain micro-dispersed in water, sometimes causing defects such as holes or pinholes.

The use of DEFOAMERS to counteract the foam promoted by the surfactant can therefore partially or totally solve the problem, but the balance is sometimes rather unstable.

On the one hand, we fight against the surfactant's foaming by using a defoamer, and on the other hand, we must also face the action of the defoamer that, in high dosage, can produce depressions and holes due to its water-insolubility.

Despite this scenario, it does not mean that in ceramics surfactants and defoamers cannot be used in combination. This is what frequently happens, but the combo must be carefully checked until a perfect balance is achieved with a tailored solution.



DISPERSANTS & SUSPENDING AGENTS

Suspending and dispersant are true glaze correctives.

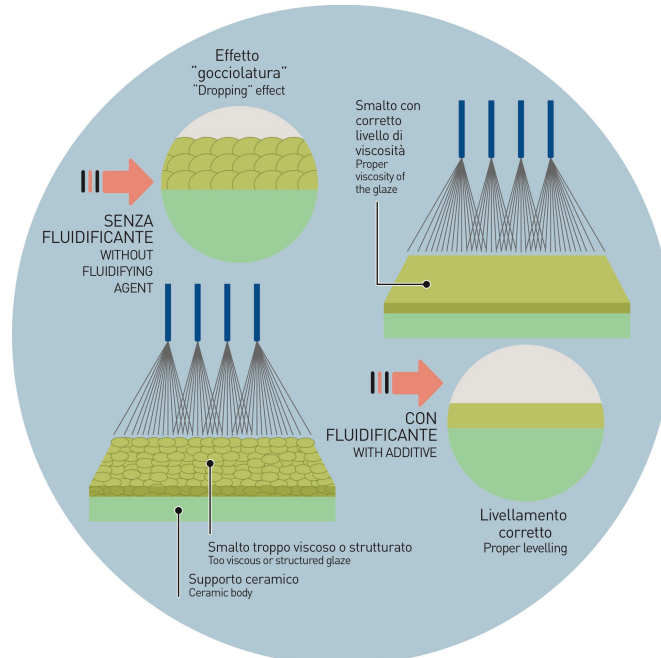
DISPERSANTS

The glaze fluidization of a glaze is particularly important when it is too plastic and therefore when it is unable to properly level on the ceramic support. Dispersants are involved to change the structure of the aqueous system, to deconstruct it.



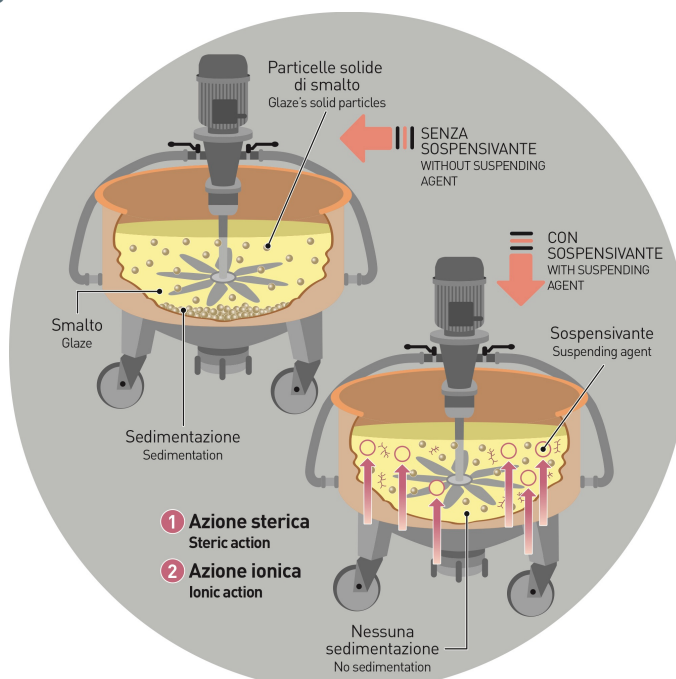
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Just like dispersants used in the grinding step, they succeed in lowering the suspension's viscosity by keeping separate the solid particles suspended within the liquid phase. This action leads to the right viscosity value required by the chosen application system, allowing a proper leveling of the glaze.

SUSPENDING AGENTS





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Suspending agents act on possible sedimentation phenomena that may occur in some of the application tools, such as, for example, the stirring tanks.

As the name clearly explains, they keep the glaze's solid parts in suspension within the system.

How do they do it?

IN THE SIMPLEST POSSIBLE TERMS, **they can act on a steric level**, by producing a grid in the system, thanks to the use of polymers that prevent and stop the particles' agglomeration process, counteracting the gravitational force that would bring these solid parts to fall in the lowest part of the container.

Suspending agents **can also act on an ionic charge level** by increasing some ions that have the possibility to saturate the water, thus giving structure to the system.

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