

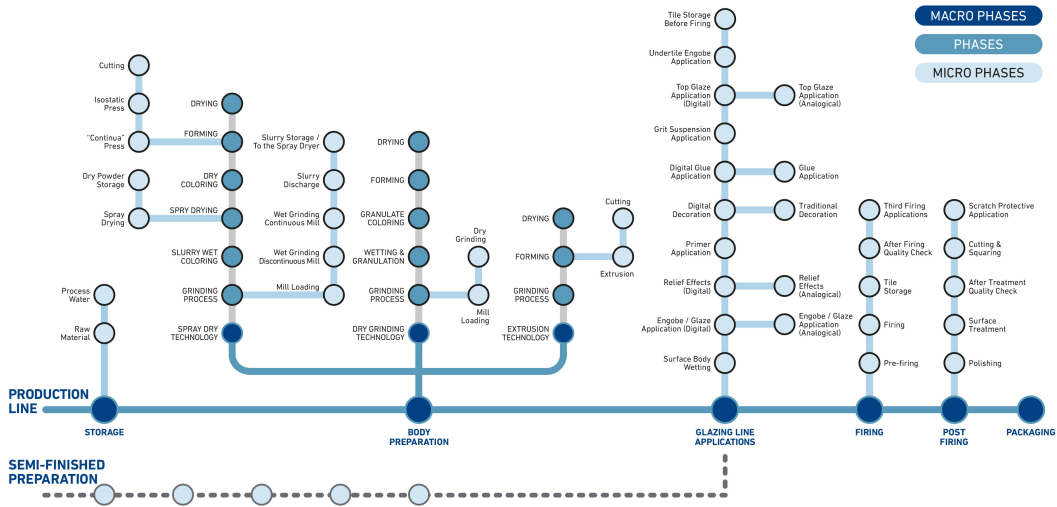


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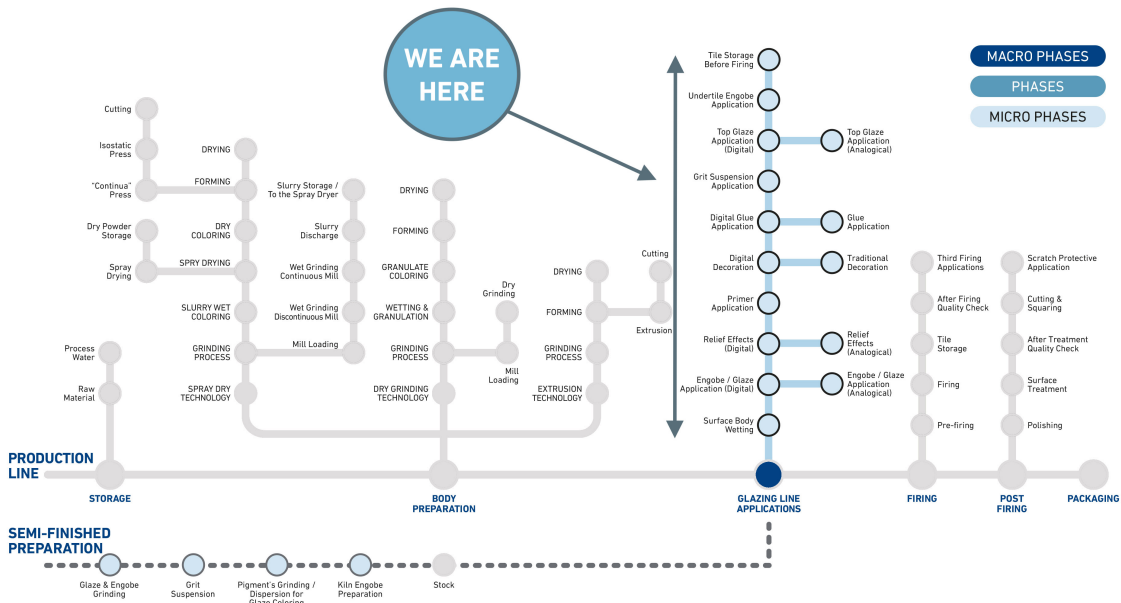
APPARENTLY INVISIBLE YET CONSTANTLY PRESENT

At every stage of the ceramic production process

A journey through problems & solutions



#40 GRIT AND GLAZE SUSPENSIONS: DIFFERENCES & SIMILARITIES





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1. FEATURES OF SUSPENSIONS

Suspensions, whether they are composed of grit or glaze, consist of a liquid part—usually made up of water and one or more rheological additives—and a dispersed solid component. An essential yet broadly proper description.

A description that might suggest a great similarity between the two types of suspension.

Grit and glaze suspension in comparison: most important differences

Grit	Glaze
Vitreous material	Mix of frits and raw materials
High percentage of frits	Percentage of frits that ranges according the chosen application
Low content of raw materials (or even none)	It usually does not contain raw materials, even in high concentration (up to 90%)
High grain size (up to 0,2mm)	Low grain size (much lower than 0,1mm)

- **A) SOLID CONTENT**

However, if we delve deeper and check more closely the characteristics of these two categories of suspensions, we immediately notice their differences, which, in terms of the solid component, can be quite important.

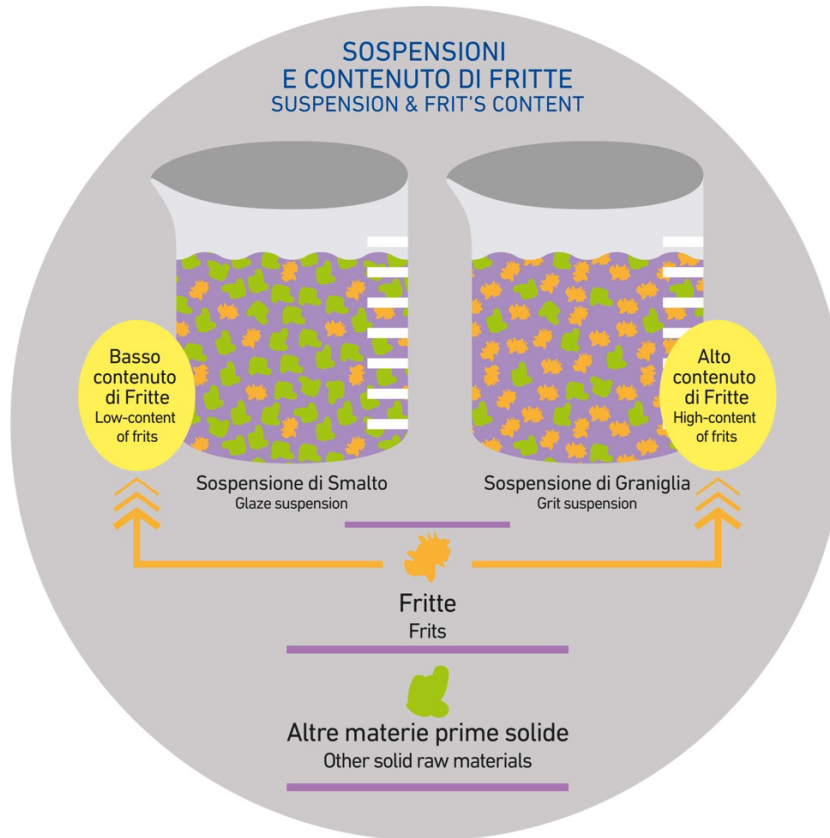
Grit is a vitreous material whose composition is more "refined" compared to a traditional glaze. It is usually applied as the last or penultimate layer, and after firing, it becomes the material exposed to the environment when the ceramic tiles have been laid. For this reason, in addition to meeting specific aesthetic requirements, the finished tile must also meet specific values of mechanical, stain, and chemical resistance. This also applies to glaze, which, even if they are marked by a different quality, must provide the same (or at least similar) chemical and mechanical properties.

The solid part of grit suspensions is, in many cases, composed of a very high percentage of frits, while the solid component of glaze suspensions varies depending on the application and always contains a certain percentage of raw materials (clays, feldspars, etc.), which changes based on the desired aesthetic results and the type of application used.



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FOCUS_CERAMIC FRITS

Frits are materials widely used in the production of ceramic tiles. They can be defined as artificial glasses characterized by well-defined chemical compositions that, after melting, undergo a quenching process (rapid cooling) followed by grinding. There are frits with a wide variety of compositions for all types of glazes. Frits are used extensively because they offer numerous advantages compared to using only raw materials. Among the most important benefits are improved fusibility during firing, greater reproducibility of behaviour between production batches, limited gas emissions during the firing phase (resulting in higher glass quality). These characteristics allow for the creation of surfaces with superior technical and aesthetic properties, making it possible to develop formulations that cannot be achieved using only raw materials.

Their production involves melting a powdered mixture of raw materials in melting furnaces that can reach temperatures exceeding 1400°C (significantly higher than the 1180-1280°C typically found in standard tunnel kilns). The molten mixture is then subjected to a sudden cooling process using water, producing vitreous flakes about one millimetre thick. The frit, once reduced to flakes, is ground in special dry mills to obtain a very fine powder or dispersed in an aqueous suspension to create liquid glaze.

Clearly, the formulation of the frit influences and defines the physical, chemical, and rheological properties of the glaze or grit suspension.



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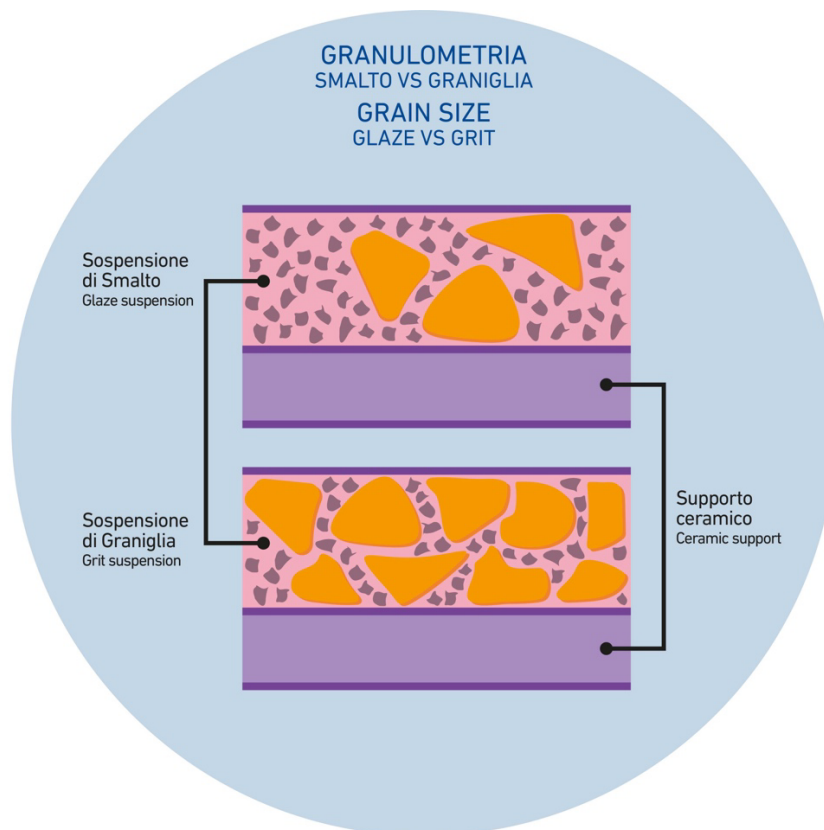
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- **B) GRAIN SIZE**

Grit suspensions and glaze suspensions can be different not only in the amounts of frits they contain but also in the particle size of the solid components.

Although the inorganic elements present in both suspensions are similar (albeit in different proportions), in general, it can be said that grit suspensions are characterized by larger solid particles, which, in turn, can contribute to improve technical-aesthetic performance.

Once melted, the glass-ceramic derived from a grit suspension becomes more transparent and shows fewer imperfections. In fact, vitreous grit is characterized by better fusibility during firing compared to glaze. Additionally, due to the fritting process, which has already started the vitrification process, there is less gas release from the grit during the firing phase. Greater fusibility and reduced gas release result in a higher quality glass compared to glaze, despite the larger particle size of the grit.



The solid component of glaze suspensions, on the other hand, not only includes a certain amount of raw materials (and therefore a lower percentage of refined material) but is also generally more finely ground, resulting in smaller particle sizes. This means that these suspensions, aside from often being more cost-effective due to the use of less expensive raw materials, will be marked by performances with different and sometimes lower technical features.

This does not mean that glaze suspensions promote poor or inadequate performance, but it does highlight that, despite their similarities, the two types of suspensions also present several differences.



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Additionally, it is important to note a significant detail that justifies the use of two different particle sizes: the smaller size of the glaze particles facilitates the sintering and vitrification processes that occur and develop inside the kilns. The smaller the glaze particles, the higher their reactivity during firing. It is crucial to understand that during firing, glaze particles undergo physical transformations and chemical reactions, producing a certain amount of gas that can negatively affect the final outcome.

It is also good to remember that, due to the fast-firing times, the melting and vitrification of the glaze components may be incomplete. The particle size of the frit, having already undergone a pre-vitrification process, can be larger and, consequently, yield superior results, often better than those achieved with a glaze suspension.

In grit suspensions, thanks to the preliminary pre-vitrification process of the frits, it is possible to use ceramic glass formulations that would otherwise require higher firing temperatures than those typically used in standard industrial firing cycles.

In grit suspensions, the glass is basically already formed, while in glaze suspensions, the vitrification process occurs entirely during the firing phase. This is why it is important for glaze suspensions to include raw materials and frits that facilitate the development of the ceramic glass.

- **C) RAW MATERIALS**

Raw materials can also differ depending on the type of suspension chosen, and, in general, it can be stated that in grit suspensions, there is a tendency to reduce or limit the clay content. Clay can, in various ways, compromise the final result after firing. For example, it can affect transparency or cause colour shifts.

- **D) THE POINT OF VIEW OF PHYSICS**

Beyond the various components that make up the two different types of suspensions, what are the differences from a physical perspective?

Without getting into overly detailed scenarios, we can simply say that a larger mass corresponds to a greater gravitational force (grit suspensions), while a smaller mass corresponds to a lesser gravitational force (glaze suspensions). What does this mean?

It means that the solid components of the suspensions are affected by different gravitational forces (or, in our specific case, a force of attraction toward the bottom) depending on their mass. This statement indicates that larger particles are subject to a greater force of attraction that pulls them downward, showing a tendency to settle more quickly.

- **E) PREPARATION OF SUSPENSIONS**

The processes involved in the preparation of glaze and grit suspensions are definitely different. For glaze suspensions, the raw materials, water, and rheological additives are usually loaded into a mill, initiating a grinding process that not only ensures perfect mixing of the various components but also reduces the particle size of the suspension to the desired dimension.

On the other hand, the preparation of grit suspensions is, in some ways, simpler and faster: the grit is merely dispersed in water with the help of specific rheological additives, saving time and energy compared to the previous process. What do we mean by that?



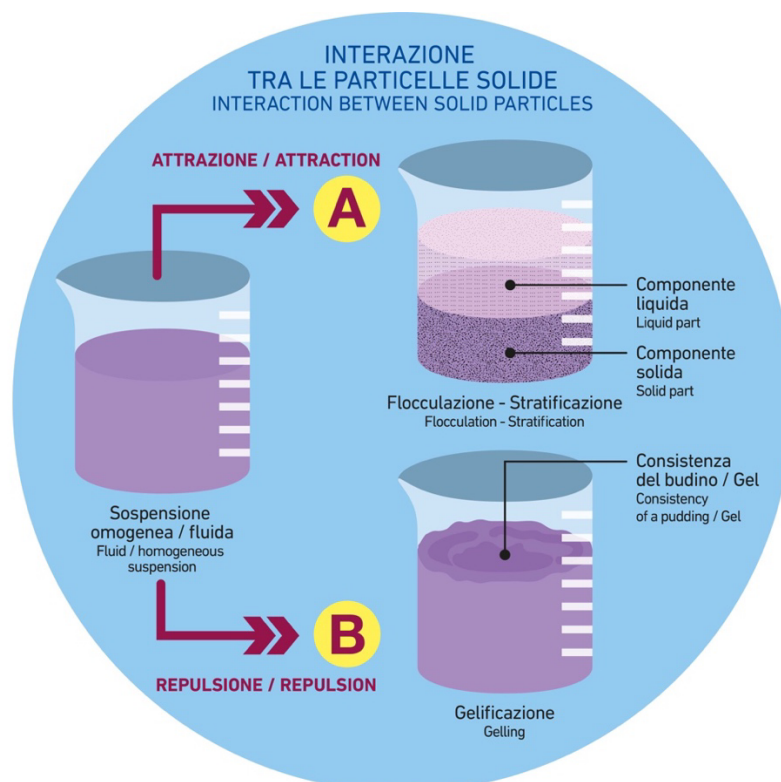
2. SEDIMENTATION & AGGLOMERATION PHENOMENA

Once the main differences have been identified, it becomes clear that the two categories of suspensions require chemicals with different properties capable of handling various scenarios. First of all, the most evident aspect is the multiple and ever-changing **suspending properties of the additives** called into action by the masses/particle sizes involved. Without oversimplifying, we can say that the properties of the additive must be calibrated according to the parameters characterizing the suspension, and among these, particle size plays a significant role.

Another aspect to consider is that the smaller the particles, the greater their interaction surface area. A smaller particle size corresponds to a larger surface area, and the greater the surface area, the higher the probability of **interactions (attractive or repulsive)** occurring between particles. This is not always good.

Depending on the type of interaction, when it is not desired, several problems may arise. An attractive interaction, which often occurs in the presence of divalent or trivalent cations, can lead to phenomena of separation and flocculation. When particles come into improper contact, they tend to agglomerate, separating from the solvent and increasing the rate of sedimentation. To prevent this, the use of deflocculating additives capable of triggering one of the three main deflocculation (or deagglomeration) mechanisms is certainly the most immediate and effective solution [for further details, see episode #23].

On the other hand, an excessively repulsive interaction could, in some cases, lead to sudden gelation, compromising the condition of the semi-finished product.





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In fact, the ideal condition is achieved when there is just the right repulsive force to keep the particles at a proper distance, creating a useful and necessary balance for the proper progression of the process.

To manage these phenomena correctly and restore the appropriate stability to the suspension, it is essential to consider the various scenarios and the heterogeneous components of glaze and grit suspensions. This requires not only different families of additives but also additives within the same category marked by properties tailored to the specific requirements. For each type of suspension, a different additive is needed.

3. CHEMICALS

First of all, binders, which are almost always present within the suspension, play a crucial role in promoting the homogeneity of the mixture both during application and afterward. They also ensure the cohesion of the solid part applied to the substrate once the liquid component has evaporated or drained into the lower layers of the ceramic body. Although the term "binder" might suggest only a sticking effect, the action of binders used in ceramics is, in some ways, more versatile or less rigid, encompassing concepts like homogeneity, cohesion, and sedimentation.

Given this, it is not difficult to understand that a binder intended for a glaze suspension must have very different rheological properties compared to those of a binder additive used in a grit suspension. Although both act on the level of cohesion, the rheological properties that should be provided to the different suspensions are clearly different

In short, to achieve the same hypothetical rheological behavior that allows for proper application, chemicals need to have different properties due to their different interactions with the solid component.

Grit

Heavy and big particles → little surface area and few interactions between particles:

- counteract the high sedimentation
- promote the homogeneity of the suspension throughout all phases of wet application
- allow for good levelling and achieve cohesion after drying

Glaze

Smaller grain size of the particles and presence of raw materials:

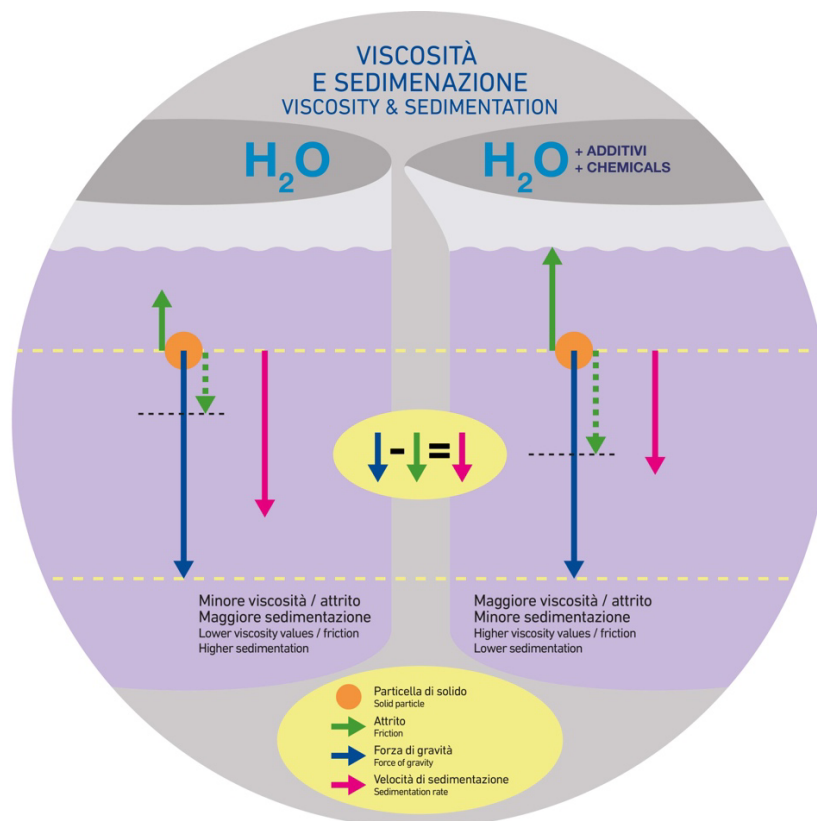
- the suspending properties can be less strong, and it will be necessary to strongly counteract the interaction effects caused by the high number of fine particles in suspension
- once again, it is essential to promote good leveling and achieve cohesion after drying

Despite their name, binders generally act on multiple fronts. They can function, for example, both as adhesive and suspending agent: some of them show stronger action in one direction rather than the other, often affecting the viscosity values of the system.

Binders, in fact, help make the liquid part of the system more viscous, and due to this thickening action, they can counteract sedimentation phenomena that may develop over time. On a physical level, the increase in viscosity values helps counteract the effect of gravity or, more precisely, slows



down the sedimentation time. In reality, the sedimentation process of these types of suspensions (if we ideally considered endless time) is inevitable and difficult to counteract. However, efforts can be made to minimize the likelihood of this process occurring during operation, along production lines.



BINDERS & SUSPENDING AGENTS FOR GLAZES & GRITS: DIFFERENCES & SIMILARITIES

Since suspensions are characterized by different values and properties, binders and suspending agents (and, more generally, chemicals) must necessarily take these differences into account. As is well known, there are several variables involved (always in a state of mutual balance), so the list of properties could be quite extensive and, in some respects, approximate. However, with the same level of approximation, it is possible to focus on certain specific aspects.

The most important difference between binders for grit and binders for glazes lies in their suspending action or the actions that can help reduce sedimentation phenomena. This difference is crucial from a rheological standpoint. Based on the particle size, it is clear that a glaze suspension is naturally less prone to sedimentation, so the suspending action must be present but not always very strong. This principle, which may seem trivial, also reveals a difference in the chemical nature of the substances involved in the different systems.