SURFACE TENSION OF GLAZE SUSPENSIONS

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ABSTRACT

In this study, two measurement methods have been fine-tuned. The first enables determining the surface tension of the aqueous phase in glaze and engobe suspensions, using the Wilhelmy plate. The second enables determining the stability of bubbles at the suspension surface.

The study addresses how constituents of these suspensions: kaolins and clays, deflocculants, adhesives, bactericides, common salt and ions from frit leaching, affect surface tension and bubble stability. The values of these two properties have also been determined for different types of industrial suspensions. This has allowed relating these properties to the appearance of certain problems in suspension application.

1. INTRODUCTION

In the ceramic tile manufacturing industry, the glazing stage involves applying fine layers of engobe and glaze onto a clay body. These coatings are generally applied as suspensions, since this enables obtaining homogeneous and reproducible layers.

The use of a liquid medium means that a series of surface defects can appear in the coatings caused by variations in density, rheological properties and/or surface tension of the suspensions. The first two properties are usually controlled for the application of ceramic suspensions. However, surface tension, which can lead to defects such as craters, dimples, material build-up at tile edges, crawling or bubbles, is usually not controlled.

In this study we have fine-tuned a method for measuring the surface tension of the aqueous phase of glaze and engobe suspensions, using the Wilhelmy plate method. The study has addressed how constituents of these suspensions: kaolins and clays, deflocculants, adhesives, bactericides, common salt and ions from frit leaching, affect surface tension and bubble stability. The determinations have been conducted in simple systems of water-one component, and also in more complex systems, analysing the possible effect of the interaction between suspension constituents.

The surface tension of the liquid has been determined in industrial glaze suspensions, and it has been attempted to relate the results obtained to the possible formation of defects. Finally, a method for the determination of bubble stability at the surface of ceramic suspensions has been fine-tuned.

1.1. SURFACE TENSION

1.1.1. Physico-chemical fundamentals

The molecules that form liquids interact with each other by means of attraction and repulsion forces (Van der Waals forces, electrostatic forces, chemical bonds, etc.) which are responsible for liquid cohesion^{[1],[2]}.

The molecules located inside the liquid are completely surrounded by other similar molecules, so that there is no resulting interaction (Figure 1). In contrast, the molecules located at the liquid-gas interface display an asymmetry in their interactions with neighbouring molecules, producing a resulting net force directed inwards into the interior of the liquid, perpendicular to the surface.

This surface force has an associated energy defined as the difference between the energy of all the molecules in the interface (gas molecules and liquid molecules) and the energy that they would have if they were inside their respective fluids. Surface energy is proportional to the free surface area of the liquid and represents the work needed to pull a molecule from the surface. The proportionality constant between surface energy and the free liquid surface is known as the liquid's *surface tension* (γ) and is expressed in the international system as newton/metre, although it is more convenient to use a submultiple (mN/m). Surface tension can be defined as the force per unit length that keeps the liquid molecules in contact at the liquid surface. At constant temperature, surface tension only depends on the nature of the contacting media.



Figure 1. Attraction forces between molecules at the surface and inside a liquid

The short-range attraction interactions that occur between molecules of the liquid can be of several types and intensities, depending on their molecular structure. The greater the intermolecular interaction force, the higher will the surface tension of the liquid be. A special case is water, which has a very high surface tension, due to the high forces caused by hydrogen bridging.

The surface tension of most liquids diminishes in a practically linear manner when temperature increases, and becomes very small in the critical temperature region, when the intermolecular cohesion forces are ineffective due to the high thermal agitation.

In a solution, the incorporation of a solute can increase or decrease surface tension depending on the nature of the solute. When solute molecules interact more strongly with solvent molecules than the solvent molecules with each other, the solute will be preferably surrounded by the greatest possible number of solvent molecules and keep away from the surface of the liquid where the number is smaller. In these cases, surface tension increases.

In contrast, certain solute molecules display weaker interactions with the solvent than those that take place between the solvent's own molecules. In this case, solute molecules will tend to locate themselves at the surface of the liquid, because in this zone there are fewer interactions with solvent molecules, reducing the system's surface tension.

Surfactants are molecules whose structure favours their adsorption at the liquid surface, reducing surface tension. These molecules generally have a bipolar structure. A part of the molecule exhibits little interaction with the solvent molecules, causing it to tend toward the liquid surface. The other part of the molecule displays an affinity for the solvent molecules, so that at the surface of the liquid, this part faces inwards into the liquid.

The migration of surfactant molecules to the surface of a liquid is not instantaneous, but involves a diffusion process towards the interface through the solution. In certain surface tension measurement methods, it is necessary to take into account the time required to complete the diffusion process.

1.1.2. Surface tension measurement techniques

Surface tension can be measured with static or dynamic methods^{[3],[4],[5]}. Static methods are run in equilibrium and use liquid surfaces at rest. In contrast, dynamic

methods are used to study the ageing of surfaces. The following static methods may be mentioned:

- Du Noüy ring method
- Wilhelmy plate method
- Method of capillary elevation of the liquid
- Pendant drop method
- Sessile drop method
- Spinning drop method

The du Noüy ring method and the Wilhelmy plate method are based on the determination of forces. When we make a solid body cross the surface of a liquid, the molecules of the liquid separate, creating an imbalance of forces between them, which translates into a non-zero resultant force (Figure 2a). Figure 2b schematically illustrates the molecules positioned in the wetting line, which present asymmetric interactions with the rest of the liquid molecules and undergo a resulting force tangent to the surface of the liquid. If the solid has a geometry that enables the forces which the molecules undergo in the wetting line to be summed when the solid is withdrawn from the liquid, we can measure this resulting force with a high-sensitivity balance. The difference between both methods lies in the shape of the solid immersed in the liquid.



Figure 2. (a) Imbalance of forces on attempting to modify a surface, (b) scheme of the force that liquid molecules undergo at the wetting surface

The four remaining methods are based on the determination of the dimensions of a drop or meniscus of the liquid. In order to obtain accurate results, good optical systems are required, given the small dimensions to be determined.

1.2. SURFACE TENSION OF THE AQUEOUS PHASE IN SUSPENSIONS

The interactions that take place between the molecules, which are responsible for the surface tension in liquids, occur at short range. These interactions only operate on a molecular level, so that the presence of solid particles will only affect surface tension when they are of colloid size^[6].

Solid particles larger than colloidal particles can affect surface tension, when:

- a surfactant initially present in the liquid is adsorbed by the solid, suppressing the effect of the surfactant,
- the addition of the solid releases ions into the liquid which thus modify surface tension.

The presence of large-size solids in a suspension can distort the surface tension measurement in the methods based on the determination of forces (drop weight method, Wilhelmy plate method, etc.), which is why such solids need to be eliminated (centrifugation, filtration, etc.) before making the measurement.

1.3. DEFECTS IN COATINGS

During the application of coatings, a series of defects can occur relating to variations in surface tension^{[7],[8],[9]}. Such defects include Bénard cells, craters, dimples, crawling and material build-up at the tile edges.

1.3.1. Bénard cells

Bénard cells are hexagonally shaped structures that appear at the surface of a coating due to the movement of the fluid caused by surface tension and/or density gradients.

When a coating dries, its density and surface tension change as these vary with temperature and composition. If there are surface tension or density gradients in the coating, convection currents are generated in the fluid that tends to accumulate material at certain points, removing this material from other areas and generating surface irregularities. The size of these zones is of the order of a few millimetres and the accumulation takes on the appearance of hexagonal cells (Figure 3).



Figure 3. Bénard cells

It has been experimentally shown that Bénard cells can be eliminated by reducing the thickness of the coating and increasing its viscosity. This phenomenon does not produce defects when ceramic suspensions dry, because of its limited occurrence and the tolerance of the materials used to the slight changes in composition that can arise.

1.3.2. Craters and dimples

Craters and dimples are depressions in the applied layer. They can be caused by regions of the body in which wetting is deficient, by bubbles that have burst without subsequently levelling, by the presence of a foreign body, or they may be due to surface regions in which the surface tension of the coating is smaller than in the surrounding areas. If this local surface tension gradient is sufficiently important to cause the fluid to flow, a crater will originate which may or may not disappear, depending on coating viscosity.

When a drop of liquid of smaller surface tension is deposited on a freshly applied coating, a surface tension gradient occurs that produces a crater. This grows rapidly in the first few seconds, after which its rate of growth decreases considerably as the crater area increases.

If a solid particle is deposited on the coating, the coating may wet or repel it. In the case of wetting, the particle may be absorbed into the coating or remain as a lump, depending on its size. If the coating does not wet the particle, a crater will form.

1.3.3. Material build-up at the edges

This defect consists of an accumulation of material on the tile edges and can be due to two causes: surface tension gradients in the coating or the combined effect of surface tension and the geometry of the substrate itself.

When a coating is applied, the coat dries more rapidly at the edges of the substrate. This can give rise to temperature gradients that produce differences in surface tension. If the temperature at the tile edge is lower, surface tension will be higher, so that the liquid will tend to flow towards the edges, transporting and building up material on the edges.

1.3.4. Crawling

If a surface tension gradient originates during the application of a coating, material flow can occur that produces rupture of the coating layer, baring the surface of the substrate (Figure 4), so-called crawling.



Figure 4. Crawling

1.4. BUBBLE STABILITY

Bubbles are gaseous inclusions bounded by a gas/liquid interface. The generation of a bubble involves the formation of a new surface and is not a

thermodynamically favourable process because it entails an energy contribution. More energy will be required to produce bubbles (new surfaces) as liquid surface tension rises. Consequently, liquids with a greater surface tension will display more difficulties because they facilitate bubble formation.

The incorporation of air into a suspension generally occurs because of turbulence in suspension milling, transfer, stirring and/or application processes. Generally, bubble formation cannot be completely avoided in suspensions, so that it is desirable that bubbles should be readily eliminated.

The bubble elimination process consists first of migration to the surface, followed by bursting. Bubble migration is driven by the difference in density of the two media and is governed by Stokes' law. The bubble ascent rate is proportional to bubble radius and inversely proportional to the viscosity of the medium. The largest bubbles reach the surface more quickly. In addition, the most viscous media retain bubbles in their interior longer, in some cases preventing them from escaping.

Once the bubble reaches the surface, the system will tend to diminish its surface energy, minimising the gas/liquid interface, releasing the gas from the bubble into the atmosphere, while the surface of the liquid recovers its horizontal shape. If this does not occur in a matter of seconds, it is because of the presence of a stabilising element in the liquid, generally surfactant molecules.

When the bubble is at the surface, a lamella develops, shown in Figure 5, in which surfactant molecules are positioned at the gas/liquid interface. Both the force of gravity and surface tension favour the draining of the lamella, causing it to narrow until reaching a critical thicknesses (50-100 Å) when it can rupture spontaneously.



Figure 5. Illustration of a bubble at the surface of a liquid stabilised by the presence of surfactant molecules

The presence of surfactant molecules can slow the draining of the lamella and prolong mean bubble life. The surfactant molecules on the surface of the lamella provide it with elastic behaviour. If the lamella stretches, the surfactant concentration at the surface decreases, raising surface tension at the stretched points, as schematically illustrated in Figure 6. The arising surface tension gradient produces liquid flow towards the area of greatest surface tension, which tends to equalise the thickness of the liquid film, countering stretching. The additives that encourage bubble elimination are divided into two groups, based on the mechanism involved:

- De-airers: they facilitate bubble coalescence inside the liquid, favouring bubble ascent to the surface.
- Defoamers: they favour draining of the surface lamella, causing bubble rupture.



Figure 6. Surface elasticity

2. MATERIALS AND METHOD

2.1. MATERIALS

Aqueous solutions/suspensions were used with the usual glaze suspension components. For this, the glaze in Table 1 was used as a base composition, and solutions/suspensions were prepared of the individual constituents. The proportions of each constituent used are set out in Table 1, expressed in terms of solids dry weight basis (for example, 8g kaolin) relative to water (32g of water). Several types of given constituents (glue, kaolin) were tested, as detailed in the corresponding results sections. Suspensions of crystalline raw materials typically used in the glaze compositions were also tested (quartz, zircon, feldspars, etc.).

| Raw material | | Dry wt % | Total wt % |
|--------------|------------------|----------|--------------|
| | Crystalline frit | 92 % | |
| | Kaolin A | 8 % | |
| Solids | Glue A | 0.3 % | FO 64 |
| | NaTPP | 0.3 % | 72 % |
| | NaCl | 0.05% | |
| | Bactericide A | 0.05% | |
| Liquid | Distilled water | | 28 % |

Table 1. Glaze composition used as a base composition in this study.

In order to assure homogeneity the solutions/suspensions, these were prepared using blade stirrers and a high-performance concentric ring disperser. Two preparations were made of each suspension, obtaining the same results in the measurements.

To determine the possible effect on surface tension of ions leached from the frit, solutions were prepared with chlorides of the cations present in the frit. Two solutions were prepared, one corresponding to a single-fire frit and the other to a double-fire frit. The starting data were the values obtained for the solubility of these frits in aqueous suspensions with 60% solids content. The cation concentrations are detailed in Table 2.

| Cation | Single-fire frit | Double-fire frit | | |
|--------|--|------------------|--|--|
| Cation | Concentration ·10 ³ (mol/l) | | | |
| Na | | 9.76 | | |
| K | 2.84 | 7.41 | | |
| Са | 3.54 | 0.91 | | |
| Mg | 2.30 | 0.15 | | |
| Zn | 0.81 | | | |

Table 2. Cation concentrations in the test solutions.

Solutions/suspensions were also prepared with mixtures of two of the glaze constituents to study their possible interactions. Finally, industrial glaze suspensions and engobes were tested.

2.2. EXPERIMENTAL METHOD

2.2.1. Determination of surface tension

Surface tension was determined with a KRÜSS K12 tensiometer, keeping the sample thermostatted at 25.0 ± 0.1 °C. The Wilhelmy plate method was used, in which the measuring element is a platinum plate of known dimensions with a rough surface to ensure wetting.

The presence of solids will affect the value obtained with the measurement method, even when this does not affect surface tension. A procedure has therefore been fine-tuned for measuring suspension liquid surface tension. For this, the solids were removed, centrifuging at 2800 rpm for 30 minutes. The supernatant liquid was then filtered using a cellulose nitrate membrane filter of 8 μ m pore diameter.

As the method is very sensitive to impurities, at least five determinations were run for each sample, meticulously cleaning the measuring accessories between each determination. In order to achieve good reproducibility (error around $\pm 1 \text{ mN/m}$), it is necessary to empty and clean the receptacle after each determination, and then refill it with liquid homogenised by stirring.

2.2.2. Determination of mean bubble life

For the study of bubble stability in the ceramic suspensions, an assembly has been used that consists of a vertically suspended plastic container holding the suspension. Air was pumped in through the bottom of the container with a syringe, as shown in Figure 7.

This produces a bubble that ascends towards the surface of the suspension, where it bursts. To determine bubble stability, the time it took for the bubble to disintegrate was timed from the moment it reached the surface of the suspension. The life of twenty bubbles was measured for each suspension, calculating the mean value. Between the generation of each bubble it was necessary to refresh the surface of the suspension, by stirring vigorously.



Figure 7. Scheme of the arrangement used to determine bubble stability.

3. **RESULTS**

3.1. INFLUENCE OF GLAZE CONSTITUENTS ON SURFACE TENSION

As indicated in the introduction, surface tension directly influences the development of different defects in coatings. In order to establish the influence of the different glaze constituents on this property, it was first necessary to study how each constituent affected surface tension by preparing aqueous suspensions/solutions with the individual constituents. This was followed by a study of the complete glaze composition.

The following constituents were studied: water, deflocculant, glues, clays, kaolins and bactericides. First, surface tension was determined of four water samples of different origin: decalcified water, well water, potable water and osmosis water. Table 3 lists the results obtained:

In two of the studied samples, the surface tension value found was considerably lower than that for pure water (72.8 mN/m). In fact, these two samples developed beds of algae with time. The presence of organic matter could

be the cause of this reduction in surface tension. As a first control step for avoiding the presence of surface defects in the glaze layers related to low surface tension, with the ensuing greater tendency to bubble formation, it is recommended to analyse the water used.

| Sample | Surface tension (mN/m) | | |
|---------------------|------------------------|--|--|
| Decalcified water-1 | 68 ± 2 | | |
| Well water-2 | 65 ± 3 | | |
| Potable water-3 | 72 ± 1 | | |
| Osmosis water-4 | 72.4 ± 0.1 | | |

Table 3. Surface tension values of four water samples

The influence of the glaze constituents on the surface tension of the water was studied by preparing the corresponding solutions or suspensions of each type of constituent in distilled water^{[10],[11]}. The sample preparation percentages were close to the ones generally used in glazes. The resulting surface tension values are given in Table 4.

| FLOCCULANTS AND DEFLOCCULANTS | NaCl 1% | Double-fire frit solubility | Single-fire frit solubility | NaTPP 1% | | | |
|-------------------------------------|------------------------|--------------------------------|--------------------------------|-------------------|-----------------|-----------------|-----------------|
| $\gamma (mN/m)$ | 72.7 ± 0.3 | 71 ± 1 | 71 ± 1 | 72 ± 1 | | | |
| GLUES | Glue A 1% | Glue B 1% | Glue C 1% | Glue D 1% | Glue E 1% | | |
| γ (mN/m) | 46 ± 1 | 56 ± 3 | 59 ± 4 | 56 ± 3 | 64 ± 1 | | |
| KAOLINS AND CLAYS | Kaolin A 18.7% | Kaolin B 18.7% | Kaolin C 18.7% | Kaolin D 18.7% | Clay A 18.7% | Clay B 18.7% | Clay C 18.7% |
| γ (mN/m) | 66 ± 2 | 61 ± 3 | 64 ± 3 | 65 ± 2 | 68 ± 1 | 58 ± 1 | 61 ± 1 |
| BACTERICIDE | Bactericide A 0.03% | | | | | | |
| $\gamma (mN/m)$ | 60 ± 5 | | | | | | |

Table 4. Surface tension values of solutions or suspensions of a raw material in distilled water

For the tested concentrations, no significant variations were observed in the surface tension of the distilled water when salt or sodium tripolyphosphate was dissolved (NaTPP). The same occurred when the cation concentrations arising from the solubility of different types of frits was simulated.

In contrast, the solution of the different samples of glues in distilled water produced an important drop in surface tension value, which ranged from 64 to 46 mN/m, depending on the sample. The highest of these values corresponded to solutions of glues with the greatest molecular weight (glues C and E).

The liquid obtained on removing the solids from the suspensions of kaolins and clays in every case displayed lower surface tension values than that of the distilled

water. This reduction in surface tension, from 72.8 mN/m to values between 58 and 68 mN/m, could be caused by rests of organic matter initially present on the particle surface.

The solution of the studied bactericide sample caused a reduction in surface tension of the water by around ten units.

Summarising, it may be said that when the different constituents making up the ceramic glaze compositions are dissolved, the water can modify suspension surface tension to a greater or lesser extent, either because of the constituents themselves or because of the presence of impurities.

However, the mixture of the different glaze suspension constituents can give rise to interactions between the constituents, reflected in variations of surface tension of the medium. This therefore makes it necessary to verify the effect of a constituent when it is not the only ingredient in the suspension, but is encountered together with other glaze constituents. For this, a reference glaze suspension (STD) was prepared in addition to other suspensions in which one of the constituents was changed or withdrawn, in order to study its effect on the surface tension of the medium. Table 5 lists the results.

| Raw materials | STD glaze | Glaze 2 | Glaze 3 |
|------------------|-----------|---------|---------|
| Crystalline frit | 92 % | 92 % | 100 % |
| Kaolin A | 8 % | 8 % | |
| NaTPP | 0.3 % | 0.3 % | 0.3 % |
| Glue A* | 0.3 % | | 0.3 % |
| Glue C* | | 0.3 % | |
| γ (mN/m) | 39 ± 3 | 47 ± 3 | 41 ± 3 |

* percentage in respect of total frit and kaolin content

Table 5. Glaze suspension compositions and their corresponding surface tension values

Comparison of the STD glaze and glaze 2 data shows the effect of different types of glues. When the glaze suspension is prepared with glue A, which causes a greater reduction in surface tension of the water (Table 4), the same tendency to reduce surface tension in the glaze suspension is observed.

In contrast, the effect of kaolin is not noticeable in these samples, when it is the only suspension constituent that reduces surface tension (Table 4). Table 5 shows that STD glaze surface tension values and those of the glaze without kaolin (glaze 3) are similar, suggesting that the kaolin sample used does not appear to contribute to the low surface tension value of the glazes.

3.2. EFFECT OF GLAZE CONSTITUENTS ON BUBBLE STABILITY

Bubble formation in liquids is encouraged when the surface tension of the medium is low. When the bubbles reach the surface, their elimination depends on numerous factors. In addition to determining surface tension it is therefore necessary

to study the influence of the different glaze suspension constituents on bubble stability at the suspension surface.

Using the experimental assembly described above it was verified that bubbles were not stable in the distilled water used for preparing the solutions/suspensions in this study, but burst on reaching the surface. Testing of the four water samples, whose surface tension was detailed in Table 3, resulted in the bubble stability times listed in Table 6.

| Sample | Bubble stability (s) | | |
|---------------------|----------------------|--|--|
| Decalcified water-1 | 20 ± 2 | | |
| Well water-2 | 11 ± 1 | | |
| Potable water-3 | 11 ± 2 | | |
| Osmosis water-4 | 2 ± 1 | | |

Table 6. Bubble stability in the four water samples of Table 3.

It can be observed that water samples 1 and 2, whose surface tension values were low, display a certain bubble stability at their surface. It can further be observed that the water sample with a surface tension value closest to that of pure water (water 3) exhibits slight bubble stability. This is because, as mentioned previously, surface tension is not the only factor that affects bubble life.

Table 7 details bubble stability times at the surface of suspensions of the individual constituents of the studied glaze suspensions. The table includes the mean particle diameter (d_{50}) of the tested quartzes and zirconium silicates.

| MATERIALS | PERCENTAGES | MATERIALS | PERCENTAGES |
|------------------|-------------|----------------------------------|-------------|
| PLASTIC MATERIAL | 20% | NON-PLASTIC MATERIAL | 10% |
| Clay A | 0 ± 1 | Zircon (d ₅₀ =1.84µm) | 16 ± 3 |
| Clay B | 0 ± 1 | Zircon ($d_{50}=5\mu m$) | 1 ± 1 |
| | 8% | Floated potassium feldspar | 23 ± 7 |
| Kaolin A | 0 ± 1 | Sodium feldspar | 13 ± 2 |
| Kaolin D | 2 ± 1 | Quartz (d ₅₀ =3.40µm) | 0 ± 1 |
| GLUES | 0.40% | Quartz (d ₅₀ =27.6µm) | 22 ± 8 |
| Glue A | 24 ± 8 | Talc | 0 ± 1 |
| Glue D | 10 ± 3 | | |
| THICKENERS | 0.5% | BACTERICIDES | 0.5% |
| Starch | 21 ± 5 | Bactericide A | 0 ± 1 |
| Sodium bentonite | 0 ± 1 | Bactericide B | 3 ± 2 |

Table 7. Bubble stability in aqueous suspensions of the glaze constituents

Table 7 shows that the aqueous suspensions of the tested plastic raw materials do not favour bubble stabilisation. In contrast, due to the organic nature of the glues, they act as stabilising molecules of the arising bubbles, when they are in an aqueous solution. Of the two thickeners tested in this work, only starch (of an organic nature) favours bubble stabilisation in the water.

Of both studied zirconium silicates, the one with the smaller particle size encourages bubble stabilisation in the aqueous suspension. In the other tested non-plastic materials, the two feldspars and coarse quartz stabilise the bubbles when they are in aqueous suspension. This stabilisation can stem from the type of beneficiation undergone by these materials. The present flotation techniques for beneficiating feldspars and quartzes are based on the use of surfactants. Surfactant rests can remain adhered to the surface of the particles, and when put into suspension again, they will favour stabilisation of the bubbles arising in the medium.

The studied bactericides hardly stabilise the bubbles in aqueous medium.

As the value of surface tension or bubble stability in the glaze or engobe suspensions is influenced by the interactions that can occur between the different suspension constituents, we conducted a study of both properties with different combinations of the two constituents in aqueous medium. The results obtained are set out in Table 8.

| BUBBLE STABILITY (s) | | | | | | |
|----------------------|------------------------|--------------|--------------|--------------|--------------|--------------|
| | (SURFACE TENSION mN/m) | | | | | |
| Aqueous medium | Frit cations | NaTPP | Glue A | Bacter. A | Kaolin A | Clay B |
| Frit cations | 0 ± 1 | 7 ± 2 | 38 ± 3 | 24 ± 3 | 0 ± 1 | 0 ± 1 |
| | (72 ± 1) | (54 ± 1) | (48 ± 1) | (59 ± 1) | (50 ± 1) | (51 ± 1) |
| NaTPP | | 12 ± 2 | 4 ± 1 | 3 ± 1 | 25 ± 3 | 16 ± 3 |
| INATII | | (72 ± 1) | (50 ± 1) | (55 ± 5) | (54 ± 2) | (55 ± 2) |
| Clue A | | | 24 ± 8 | 23 ± 6 | 30 ± 5 | 29 ± 6 |
| Olde A | | | (46 ± 1) | (52 ± 2) | (57 ± 1) | (62 ± 1) |
| Bacter. A | | | | 0 ± 1 | 22 ± 3 | 21 ± 2 |
| | | | | (63 ± 1) | (64 ± 1) | (61 ± 1) |
| TC 11 A | | | | | 0 ± 1 | |
| Kaulin A | | | | | (66 ± 2) | |
| Clay B | | | | | | 0 ± 1 |
| City D | | | | | | (58 ± 1) |

Table 8. Values of bubble stability (and surface tension) in suspensions or dissolutions of one or two raw materials in water.

It can be observed that the salt and tripolyphosphate solutions, in the tested proportions, have the same surface tension as water. However, when one of these constituents is mixed in aqueous medium with any of the studied raw materials that reduce surface tension, this can strengthen the effect of the latter.

Pure water and the solutions of salts in water do not allow stable bubble formation. The presence of other raw materials, generally those of an organic nature, can encourage bubble stabilisation.

Glue A and bactericide A, which contain molecules of an organic nature, tend to reduce water surface tension when they are dissolved separately in water. When one of the other raw materials is added to the glue solution, surface tension of the medium increases, however without ever reaching the value of water. Adding any of the other tested raw materials to the bactericide A solution slightly reduces surface tension.

When the two studied plastic raw materials, kaolin A and clay B, are in suspension, they reduce water surface tension. In the case of the kaolin suspension, the addition of any other raw material favours this decrease. The presence of another raw material in the clay B suspension can increase or reduce initial suspension surface tension, without however ever reaching the water surface tension value.

In the aqueous suspensions of the tested plastic materials, the bubbles are practically unstable. When molecules are added that are susceptible of adsorbing onto the surface of the particles in any of these suspensions (NaTPP Glue A or Bactericide A), the bubbles in the medium are clearly observed to stabilise.

3.3. INDUSTRIAL SUSPENSIONS

Finally, surface tension and bubble stability were measured in six industrially prepared glaze suspensions with a view to determining whether these properties would allow a priori rejection of a suspension that could originate defects in production. Table 9 sets out the results, and includes the defects that occurred when the suspensions were applied industrially.

| Suspension | Surface tension (mN/m) | Mean bubble life time (s) | Defects |
|------------|------------------------|---------------------------|--|
| А | 46 ± 1 | 24 ± 5 | Bubbles and dimples |
| В | 34 ± 1 | 60 ± 6 | Bubbles and dimples |
| С | 49 ± 2 | 1 ± 0.2 | |
| D | 49 ± 2 | 1 ± 0.2 | |
| Е | 49 ± 2 | 0 | |
| F | 50 ± 2 | 38 ± 7 | Slight tendency to form bubbles and dimples |

Table 9. Properties of different industrial glaze suspensions

It can be observed that the two suspensions (A and B) which display a greater tendency to cause bubble and dimple defects are those that have the lowest surface

tension values. When this tendency is smaller, as is the case of suspension F, no clear difference is observed with the suspension surface tension values that do not cause any defects.

On the other hand, bubble stability values are highest for the three suspensions that exhibit defects in production. The suspensions for which application defects are not detected display very low bubble stability values.

4. CONCLUSIONS

The study allows drawing the following conclusions:

- The surface properties of industrial glaze suspensions are responsible for numerous defects that appear during their application.
- Measurement methods have been fine-tuned for the determination of the surface tension of the suspending liquid and the stability of the bubbles at the surface of solutions or suspensions.
- The individual and combined effect of the different constituents has been verified, which can be a very useful tool in selecting these constituents. In fact, it has been verified that the same type of raw material can cause important variations in surface tension and bubble stability, depending on its characteristics and origin.
- The relation has been confirmed between the appearance of certain surface defects in the applied glaze suspensions and the modification of properties such as surface tension and bubble stability in the corresponding suspensions. It is therefore recommended to determine these properties as a control method for industrial suspensions prior to suspension use in production lines.

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