Glaze Contraction

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1 Defect Morphology

This type of defect is quite common in sanitaryware production. Glaze contraction is easily detected. The defect is irregular in appearance, leaving the substrate/cast uncovered. It is as if that part of the surface has never been covered with glaze at all. The outer rim of the shrinking glaze is another element identifying this defect: the rim is rounded and thickened as a result of the action of surface tension (Fig. 1).

Glaze contraction usually occurs over concave areas of glazed surfaces because here the glaze layer is thicker. There are several causes for this defect. It is possible for glaze contraction to occur over different areas of the glazed surface.

Figs. 2 and 3 show typical examples of glaze contraction.

2 Mechanisms Causing Glaze Contraction

This section examines the processes and relevant laws of physics underlying glaze contraction in sanitaryware firing.

Generally a crack, i.e. an interruption in the layer of raw glaze covering the body, triggers the formation of this defect. Regardless of its origins (these are examined in the next section), such a discontinuity leads to glaze contraction as a result of the action of surface tension.

Therefore a cause of mechanical nature (discontinuity in the glaze thickness covering the substrate) triggers the formation of this defect while its driving power is surface tension. It is therefore necessary to define what surface tension is and which laws it follows.

2.1 Definition of Energy and Surface Tension

Studying the cohesive forces of liquids, Laplace developed a theory. According to this theory, two molecules of liquid, with mass m_1 and m_2 and a distance R between them, attract each other with a force
$$F = m_1 \, m_2 \, f(R).$$
f(R) cancels out when R is greater than a value _ equal to 0,005 µm. The sphere with a radius r is the sphere of molecular action, inside it the molecules of liquid attract each other.

If we consider the molecule m (Fig. 4) at a distance from the free surface greater than _, it is subjected to the attraction force of all the molecules included in the sphere of molecular action having the centre m and radius _. The resultant of the applied forces is zero, because of symmetry reasons all forces cancel each other out.

The situation is different for m_1; in this case action force is exerted by the molecules included in the sphere and positioned below the surface. Above the surface there are only gas molecules; these are much less numerous (lower density) and exert a modest action force compared to the one exerted by the liquid's molecule. Therefore the molecule m_1 is subjected to a resultant force directed perpendicular to the free surface towards the inside.

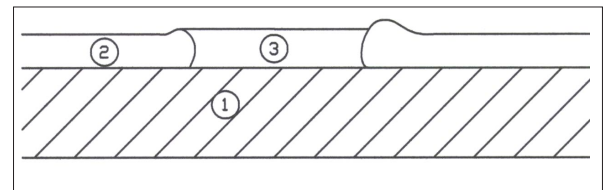In the case of molecule m_2, the resultant force is the maximum possible. So all the molecules of the liquid

Fig. 1 Section showing the glaze contraction defect
1: Substrate   2: Glaze
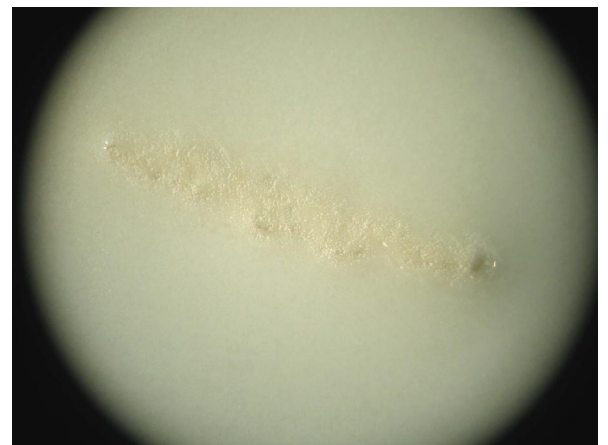3: Part of the body where the glaze has shrunk

Fig. 2 Photo showing the glaze contraction defect

positioned on the surface are subjected to a force perpendicular to the surface itself and directed towards the interior of the liquid. Increasing the liquid's surface means increasing the number of the surface molecules and therefore taking some molecules from the interior to the surface; a force F acts on all surface molecules. It is perpendicular to the surface and pushes the molecules inside to effectively oppose the surface increase. It is obvious that to increase the liquid's surface, work propor-

Fig. 3
Sectional view of the glaze contraction defect
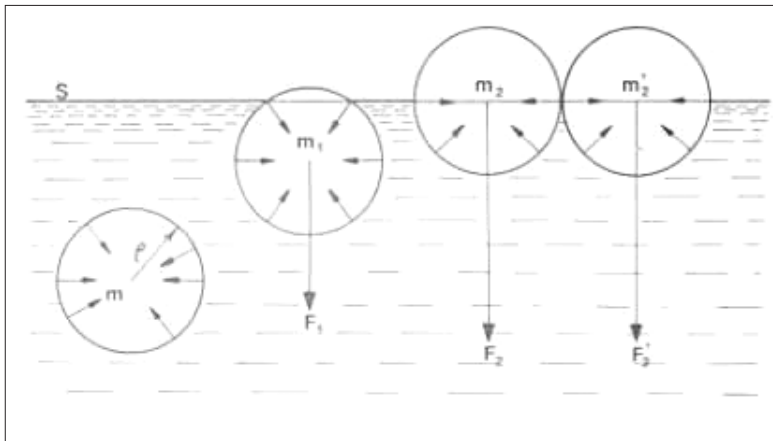
tional to the surface is necessary, according to the relation :

$$L = K S$$

where

L = work needed
K = specific constant of each liquid
S = amount of increased surface

The energy needed to generate the above-mentioned work is built up by the liquid's surface: this energy is known as surface energy.
The liquid's surface behaves like a flexible membrane aiming at minimizing the surface extension.
A film of liquid between two sliding threads (???), as shown in Fig. 5, is considered when defining surface tension.
To increase the liquid's surface, it is necessary to work with the force F applied to the sliding thread having length 1.
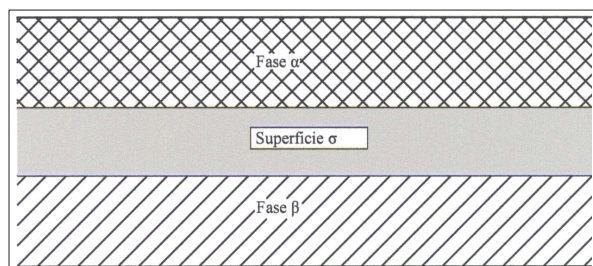The work needed to obtain a surface increase is equal to:

$$dL = F dx = 2 \_ l dx$$
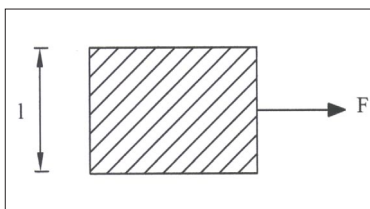
where:
dL = work increment
F = applied force
 = surface tension
l = application length of tension

Factor 2 appears only because the film of liquid has two surfaces. Consequently, surface tension _ can be defined as:

$$\_ = F / 2 l$$

It is therefore the force keeping the molecules of liquid's surface (in contact with each other oder with sonst etwas – ich verstehe diesen Satz nicht???) on a length equal to the unit. Surface tension is measured in dynes/cm.
Surface tension decreases when the temperature rises until it cancels out at the liquid's critical temperature (evaporation temperature).
In the case of liquids with a surface that acts like a flexible membrane, there is a concurrence between the surface tension and surface free energy (dynes/cm = ergs/cm^2). In the case of solids, work leading to surface growth causes a distortion in the solid itself. Consequently superficial stresses are generated. These can be compressive or traction stresses; in either case they are distinct from the surface tension.
It should be noted that the direction of surface tension is variable because it opposes the force trying to produce a break in the surface; it is always at a tangent to this surface whilst the liquid's cohesive force is always perpendicular to it.
That stated so far about the surface molecules of the liquid coming into contact with gas also apply to surface molecules in any phase. Interfacial tension is generated every time there is a parting surface between:
• two immiscible liquids

• a liquid and a gas
• a gas and a solid
• a liquid and a solid.
A multicomponent system should be taken into account when defining surface tension according to thermodynamics (Fig. 6)
According to the first and second law of thermodynamics, the variation of internal energy (E) and Gibbs' free energy (G) in the system showed in Fig. 6 are expressed by:

$$dE = TdS - pdV + \_dA + \_ \_i n_i$$
$$dG = SdT + VdP + \_dA + \_ \_i n_i$$

In relation to the system internal energy E and free energy G, the surface tension can be defined as: (???) Formel????
i.e.:
• the increment of system's internal energy equivalent to a unit increment of the surface, with entropy S, volume V and species number ni of the constants' system.
• the increment of system's free energy equivalent to a unit increment of the surface, with temperature T, pressure P and species number n_i of the constants' system.
Interfaces between two phases are characterized by interfacial energy equivalent to the energy needed to create a new unit area interface in the system. This interface energy is always smaller than the sum of each surface energy of two phases, which is why there is always some kind of attraction energy between the phases.

2.2 Study of the Behaviour of a Drop of Liquid on a Solid Surface

This section examines the behaviour of a drop of liquid on a solid surface, keeping in mind the physical laws that govern it; the importance of such an analysis is fundamental to understanding the defect of glaze contraction, because glaze in a molten state behaves like a liquid placed on a solid (body).
A drop of molten glaze on a solid surface has three existing interfacial tensions and they are:

$\_{LG}$ = surface tension liquid - gas
$\_{SG}$ = surface tension solid - gas
$\_{LS}$ = surface tension liquid - solid

To understand the behaviour of the drop of liquid, the cohesive force and adherence force must be

defined as a function of the interfacial tensions.

• Cohesive force

By breaking a column of liquid with a section measuring 1 cm², two liquid/gas interfaces can be obtained: with reference to above, the work needed to create these two forces is:

$$L_{LG} = 2 \, _{LG}$$

The work needed to break cohesive forces is termed cohesive work.

• Adherence force

Removing part of the liquid to uncover 1 cm² of solid surface creates a 1 cm² gas/liquid interface and a 1 cm² gas/solid interface; but a 1 cm² liquid-gas interface is eliminated. The work needed to remove this portion of liquid is equal to:

$$L_A = \, _{LG} + \, _{SG} - \, _{SL}$$

This work takes into account the energy needed to separate 1 cm² of liquid from a solid and is termed adherence work. In defining adherence work, we assume that the pressure remains constant, there is no liquid viscosity, the surface of the solid is perfectly clean and there is no relation between the solid and the liquid.

To return to the drop of molten glaze on solid surface, the end-point between the different interfacial tensions is defined by the following relation:

$$_{SG} = \, _{LS} + \, _{LG} \cos \_$$

In the relation of adherence

$$_{SG} = L_A - \, _{LG} + \, _{SL}$$

replacing in previous relation:

$$L_A = \, _{LG} (1 + \cos \_)$$

Considering the relation of cohesive work, the expression can also be written as:

$$L_A = L_{LG} (1 + \cos \_) / 2$$

The conditions under which a liquid wets a solid substrate can be defined.
Back to the equilibrium relation:

$$_{SG} = \, _{LS} + \, _{LG} \cos \_$$

with

$$\cos \_ = (\, _{SG} - \, _{LS}) / \, _{LG}$$

there are the following possibilities (Fig. 7):

• if $_{SG} > \, _{LS}$, cos _ is positive and _ is smaller than 90°; therefore the liquid wets the solid
• if $_{SG} < \, _{LS}$, cos _ is negative and _ is larger than 90°; therefore the liquid does not wet the solid
• if $_{SG} - \, _{LS} = \, _{LG}$, cos _ = 1 and _ = 0; therefore the liquid spreads perfectly over the solid.

When _ = 0 and cos _ = 1, in the relation linking adherence work to cohesive work there is

$$L_A = L_{LG} (1 + 1) / 2$$

When adherence work is equal to cohesive work, the liquid spreads perfectly over the solid.
The spreading coefficient can be also defined (3):

$$S_{LS} = \, _{SG} - (\, _{LG} + \, _{LS})$$

There is spreading when S_{LS} is positive and so $_{SG} > (\, _{LG} + \, _{LS})$.
In conclusion, low surface tension of liquid is necessary for spreading of the liquid itself, but it is not sufficient; Fig. 8 shows that a liquid with low surface tension can also cause low wettability (poor spreading).

3 Causes of Glaze Contraction

3.1 Introduction

The defect of glaze contraction is essentially caused by:
• an initial interruption in the continuity of glaze thickness
• the subsequent action of surface tension that determines glaze contraction during firing, making the defect more or less obvious
A detailed analysis of the causes of glaze contraction follows.

3.2 Causes Triggering an Interruption in the Continuity of Glaze Thickness

Causes of discontinuity in glaze thickness include:
1) Excessive shrinking of the glaze following its application. Excessive shrinking can lead to the formation of cracks; this shrinking can be caused by:
• excessive thickness of the particles composing the glaze; therefore the glaze is too fine, or it contains too many components characterized by morphology of particles such as zirconium silicate, talc, etc.
• excessive thickness of the glaze layer; such a phenomenon is usually
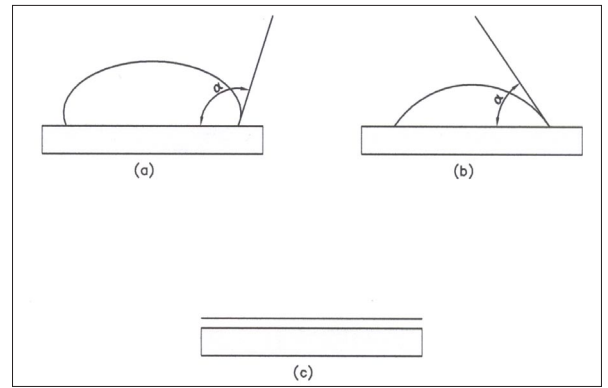
most noticeable in concave areas of sanitaryware because these areas soak up a larger quantity of glaze.
• the presence of components characterized by high raw material shrinkage (plastic kaolin or clay/bentonite) in the composition of glaze
• a high content of zinc oxide in the composition; zinc oxide is usually characterized by very thin particles. In water zinc oxide undergoes hydration with attendant formation of a hydrate layer around each particle. Consequently, each particle increases its diameter. During subsequent dehydration, i.e. while the applied glaze is drying, every particle suffers high shrinkage, this can trigger crack formation in the glaze layer.
• excessive preheating speed in wet sanitaryware
• presence of irregularities on the body surface (such as granules). These can cause non-uniform shrinking of the glaze thickness.

2) Poor adhesion between glaze and body

Poor adhesion between glaze and body can cause detachment and/or interruption in the glaze layer. The main causes of such a defect are:
• the presence of powder on the body: powder positioned between glaze and body prevents good binding thus enabling the detachment of small areas of glaze
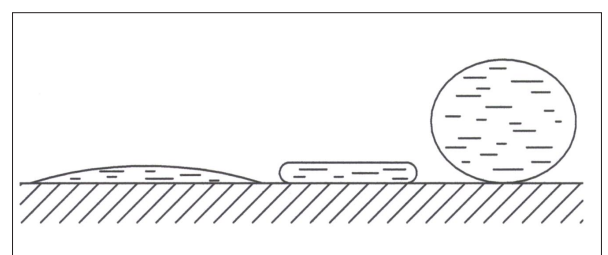
- the presence of oil and grease spots, which has the same effect as described for powder above
- the presence of casting spots; this problem, caused by the casting methods and slip features , leads to the formation of body areas that are more impermeable (less porous) than others; on these areas the glaze cannot bond as well as on other areas of the body
- the re-absorption of ambient humidity by part of the (already dried) glaze layer. This leads to a slight expansion of the layer itself, whilst body does not expand, resulting in the glaze becoming detached from the body.
- incorrect application of glaze: if the first glaze is not applied properly, granules of powdery glaze will form in some parts of the piece to be glazed; such glaze dust causes the same problems as the presence of powder, thus leading to micro-detachments of the glaze
- deposition of soluble salts (almost always sulphate salts) on the body. Such salts situated between body and glaze can cause a raising of the glaze. The more a glaze is pulverized and the more kaolin it contains, the more probable such a defect becomes (soluble salts being equal). In this case, the glaze thickness is more compact and it can prevent the passage of soluble salts from the body to the glaze surface.
- insufficient quantity of bonding agent added to liquid glaze, or excessive ageing and respective degradation of bonding agent itself; in both cases, the glaze tends to powder easily, which causes glaze detachment. An insufficient quantity of bonding agent (or its deterioration) reduces the mechanical resistance of the glaze layer, increasing the possibility of cracking in the layer itself.

3.3 Elements Increasing the Surface Tension Value

As pointed out in the previous sections, with a rising glaze surface tension, there is an increasing tendency of the glaze not to wet the substrate and consequently to shrink in the form of a droplet. It is evident that such behaviour, which is triggered by a discontinuity in the glaze coating, leads to glaze contraction.

Therefore it is important to establish what causes an increase in glaze surface tension.
According to Chapter 1, section 5.2 (????), there are two ways to increase surface tension (_):
- increasing glazes thickness by grinding raw materials. According to the definition of surface tension, increasing glaze thickness leads to an increase of the total surface and consequently of the surface tension value. Figs. 10 and 11 show two different granulometric curves for the same glaze; these result from the use of two different grinding methods. Glaze characterized by thinner granulometry exhibits a tendency towards glaze contraction. The same defect is totally absent in glazes with coarser particles.
- varying the chemical composition of the glaze and increasing oxides with a high surface tension, e.g. by using magnesia instead of barium oxide or increasing alumina at the expense of silicate oxide.

4 Measures to Counter Glaze Contraction

The following measures can be effective in countering glaze contraction:
- Always use the same glaze together with the body, this glaze having been modified appropriately; non-wettability of glaze depends on gas-solid and solid-liquid interfacial tensions. These tensions vary according to the ceramic body type. Each body has its own surface porosity and raw porosity. All these characteristics can affect (the glaze being the same in each case) the bond quality of glaze-body layer and consequently the possibility of discontinuities in glaze thickness.
- Reduce the quantity of plastic raw materials in the glaze by replacing them with calcined kaolin. This helps reduce glaze shrinkage during drying.
- Reduce the content of glaze components with very fine particles, e.g. zirconium, talc etc, or replace them with components with larger particle sizes.
- Prevent excessive grinding of glaze and maintain constant control of the glaze grading curve; this is why it is essential to check for the uniform particle size distribution of

the raw materials, the grinding time and uniformity of the grinding charge
- Apply the correct thickness of glaze and avoid excessive deposition, particularly on concave surfaces because they absorb more glaze
- For each glaze type, measure the type and quantity of bonding agent. This helps to avoid low mechanical strength of the raw glaze, which leads to powdering of the glaze and its detachment from the substrate. Bonding agent slows down glaze drying, prevents powders forming and improves the adherence of the glaze to the substrate.
- When possible, limit the problem caused by the presence of sulphates by adding an appropriate quantity of barium carbonate to the water, as this makes the sulphates insoluble as shown in the following reaction (e.g. calcium sulphate):

$$CaSO_4 + BaCO_3$$
$$-> CaCO_3 + BaSO_4$$
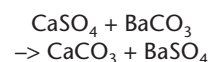
- Remove any powder, grease and oil residues, and any other contaminants from the surface of the pieces to be glazed. These can all cause glaze detachment.
- Carefully wash the surfaces to be glazed so as to clean and damp them
- Reduce the heating rate during preheating
- Make sure that no dry glaze powder is formed after application of the first glaze to the sanitaryware.

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