T h e   P i n h o l i n g

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The pinholing is one of the most common glaze defects and, at the same time, the most difficult fault to be solved. It appears both in the fire-clay sanitaryware production and in the vitreous china one and it is due to many concomitant causes. They arise from the strict respect of those productive parameters (firing time, glaze fusibility, …) that don't allow for a change of the firing curve and/or the glaze characteristics or the body ones as you wish.

In our report we'll speak about the pinholing according to the following scheme:

°   morphological analysis;

°   characterization of its causes;

°   possible solutions.

We'll pay attention both to technological problems and the examination of physical laws that are at its basis.

Obviously, we cannot deal all the problems that are related to the fault, but we want only examine the most important ones.

Morphological analysis of the fault

Seeing the pinholed glaze surface with the naked eye or by a microscope, it will be possible to note dimples, different for size and depth (fig. 1).

Fig. 1 - Gas bubbles on the glaze coat [2]

They look like to the holes made by a pin's head. The name comes from this similarity. The name of the fault changes with dimple's dimension:

Average diameter of the dimple	Name of the defect [1]
400 – 800 μm	Blisters
200 – 400 μm	Orange peel
100 – 200 μm	Eggshell
80 – 100 μm	Bubbles

Usually, dimples 80 μm in diameter are difficult to see with naked eye and therefore they are not considered important defects. So, we can say that only gassy bubbles more than 80 μm in diameter can cause the pinholing.

If we cut our sample in the dimple area we note:

A. an almost spherical gassy bubble (from 80 to 800 μm in diameter) can be put between the body and the glaze coat, just under the dimple (fig. 2). The hole is therefore caused by double effects: the internal depression and the outside pressure, that occur during the glaze cooling process. The width of the dimple is directly proportional to the bubble's diameter, while its depth depends also by the distance of the gas bubble from the glaze surface: the nearer bubbles are to the surface, the more evident holes will be and vice versa.
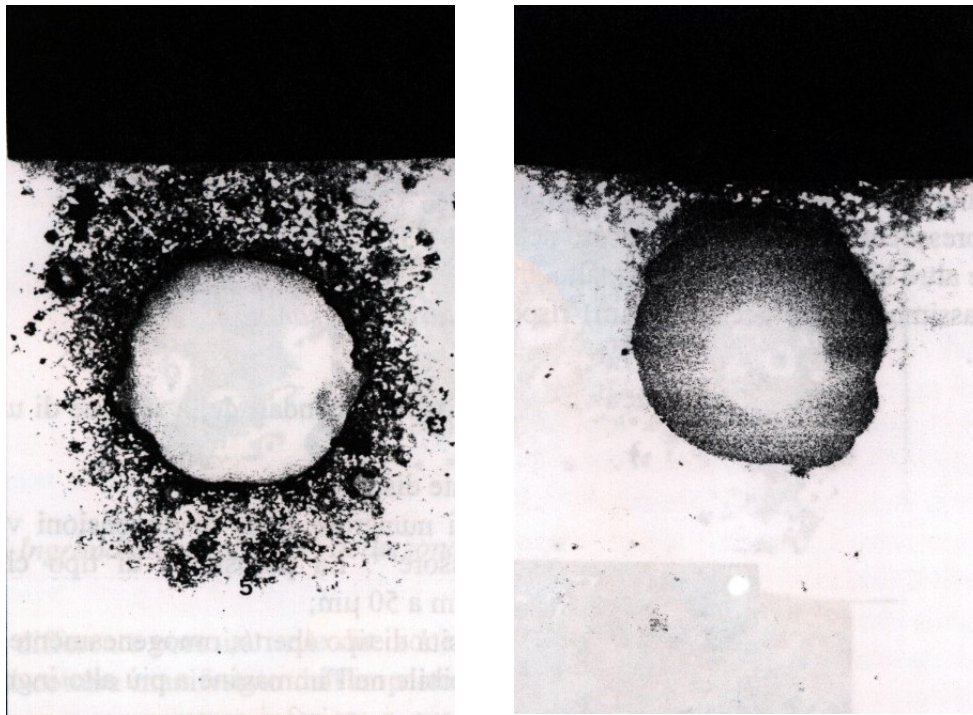

Fig. 2 - Case A: the oblique section of a dimple (optical microscope 100X) [3]

B.   The oblique section of the dimple is like a semi-spherical cavity or a small relief crater, opening on the glaze coat, with made round sides (fig. 3) [2]. In that case the defect is due to the outcrop and bursting of gas bubbles. If the glaze has a low viscosity at the molten state and/or the persistence to the firing temperature is sufficiently long, the crater can close again and disappear. Anyway it is rare in the sanitaryware production.
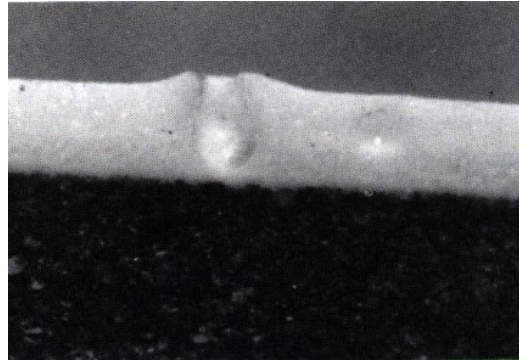

Fig. 3 – Case B: the oblique section of a dimple [14]

Some technological parameters, such as the maximum firing temperature and the persistence time, establish the case A or B. The glaze data, the glaze application, the glazed surface, the position of the piece on the kiln's trolley,…, are important, too.

Experimentally, it was clear that $CO_{(g)}$, $CH_{4(g)}$, sometimes $SO_{3(g)}$ and chiefly $CO_{2(g)}$ are responsible for the defect being examined. They come from the decomposition of some salts included, even by small percentages, in the body mixture [3]. They are carbonates and sulphates.

Very often the dimple core is black in colour as if it is dirty. Really it is just an optical effect due to the restraint of the reflection of light [4]. Many gassy bubbles, even small ones (below 80 µm in diameter), can impair the shining of the glaze coat.

The causes of the fault

We'll divide the paragraph in two parts:
-     analysis of the physical laws, that control the origin and the movement of gas bubbles in the molten glaze coat. It is very important to understand the influence of chemical-physical parameters (such as firing temperature, glaze viscosity, surface stress) on the beginning of gassy bubbles **(*)**.
-     analysis of the main factors we have to bear in mind while speaking about the source of gas bubbles (both in the glaze and in the body) **(**)**.

(*) The molten glass is a very viscous liquid. During firing we have an high development of gases, that dissolve in the molten glaze until the saturation. Undissolved gases can give rise to

bubbles in the liquid phase by the nucleation and the consequent creation of a liquid-gas interface. The bubble nucleation is impossible in an homogeneous liquid phase, but it is not our case. In the glaze, in fact, there are many cristalline particles that can act as nucleation's media [5]. Moreover, the porosity and surface irregularities of the body, which is in contact with the molten glaze, give rise to the best conditions for the chemisorption of gas molecules. The surface irregularity is also the easier area where find micro-bubbles, coming from the inside of the body. At last, we have to bear in mind that the glaze, after its application, consists of pores (40%) that during the subsequent sintering and melting can remain inside and give rise to micro-bubbles. The micro-bubbles will make possible the adsorption of gases developped during the firing.

Since their nucleation, gassy bubbles grow through the coalescence (union of small bubbles) and/or the adsorption of dissolved gases. The viscosity and the surface stress of the molten glaze are opposed to that growth. In fact, to enlarge a bubble means to increase the surface of the liquid-gas interface, that is to say to do a reversible work (L):

$$dL = \sigma \cdot dA \tag{1}$$

where σ is the surface tension.

This surface variation is in conformity with the one of the surface free energy (g_s):

$$dg_s = g \cdot dA \tag{2}$$

where g is the free energy's increase per unit of new made area.

Therefore, the surface tension is opposed to the development of bubbles. The higher the glaze viscosity is, the more difficult the movement (and the coalescence) of gas bubbles and molecules will be.

Anyway, both the viscosity and the surface stress are inversely proportional to the temperature. So, the increase of temperature can give rise to the growth of bubbles:

° the surface stress decreases about by 2% every 100°C

° the relationship between viscosity (ν) and temperature (T) is :

$$\log \nu = -A + B \cdot (T-T_o)^{-1} \tag{3}$$

where A, B and T_o are constants and change with the glaze [12]. Obviously, also the glaze surface stress changes with its composition.

A thermodynamic and kinetic analysis of gas bubbles'growth can emphasize the influence of the temperature.

From a thermodynamic point of view, we have to study the free energy variation (ΔG) [6]:

$$\Delta G = -\frac{4}{3}\pi R_b^3 \cdot \Delta g_v + 4\pi R_b^2 \cdot \Delta g_s \tag{4}$$

where R_b is the radius of the bubble.

It exists a special value of that radius (called critical radius, R_{bc}), starting from which we have a reduction of the total free energy in conformity with a dimensional increase and therefore a thermodinamically stable situation. Vice versa, bubbles with $R_b<R_{bc}$ are unstable and are intended to disappear. Only local increases in temperature can give to those bubbles the requisite energy to exceed the thermodynamic barrier. That is to say the $\Delta G_{cr} = \Delta G(R_{bc})$ [6].

From a kinetic point of view, we have to consider the kinetic barrier (ΔG_c) that is bound to the activation energy of molecules'diffusion. It is the barrier that must be surpassed in order to allow to gas molecules the necessary movements for gas bubbles'creation.

The activation energy is directly proportional to the molten glaze viscosity (ν) [7]:

$$E_{att} = f\,(ln\nu) \tag{5}$$

So, an increase in the temperature is responsible for a reduction of glaze viscosity and, at the same time, for the ones of E_{att} and ΔG_c, too.

In short, as regards what has been said above we can write the following formula [6]:

$$V_n = A \cdot \exp\left(-\frac{\Delta G_{cr} - \Delta G_c}{RT}\right) \tag{6}$$

where A is a independent constant from the temperature; ΔG_{cr} is the critical thermodynamic barrier; ΔG_c is the kinetic barrier and R is the gas constant. So the more the temperature (T) increases, the faster the bubbles'beginning will be.

What happens when bubbles increase in size? The equilibrium gas pressure (P), inside the bubble, is given to the following relationship [8]:

$$P = P_o + h\rho g + \frac{2}{R}\sigma \tag{7}$$

where P_o is the atmospheric pressure on the free glaze coat; σ is its surface stress; ρ is its density; g is the gravitational acceleration; h is the distance of the bubble from the free glaze coat and R_b is its radius. So, under the same conditions, if the bubble increases in size, we have a reduction of its internal pressure and an its self-growth. According to the Henry's law, the solubility of gases in a liquid is directly proportional to their pressure P (at uniform temperature):

$$C = H \cdot P \tag{8}$$

where C is the gas concentration in the liquid and H is the Henry's constant.

Therefore, if R_b increases we have a reduction both of the pressure and the solubility of the gas and its consequent release from the molten glaze. Those gases can contribute to increase the bubble in size.

Anyway, at uniform pressure, the solubility of a gas in the molten liquid depends on temperature and chemical composition of the glaze, too. In particular, it is inversely proportional to the temperature. See for example the following data sheet for CO_2 (that is the most spread gas in bubbles) (tab. 1). Note how the solubility decreases between 1100°C and 1200°C, that is to say

when the glaze is completing its vitrification process. At those temperature it will be possible a development of gases, that will stay in the impermeable glaze.

About the chemical composition, under the same temperature and SiO_2 content, we can note that the glass "A" (with a greater CaO/Na_2O than "C") can solve better CO_2. This is due to the higher viscosity of glass "A" than "C" at 1200°C [6].

Glass composition	T (°C)	Solubility (10^6 g CO_2/g glass)
(A) $Na_2O \cdot CaO \cdot 4.85\ SiO_2$	900	174
	1100	113
	1200	13.2
	1300	2.62
	1500	0.95
(B) $Na_2O \cdot 0.71\ CaO \cdot 3.72\ SiO_2$	900	95.2
	1100	25.2
	1300	4.73
	1500	2.68
(C) $Na_2O \cdot 0.71 CaO \cdot 4.85\ SiO_2$	900	249
	1200	5.78
	1300	1.12
	1500	1.02

Tab. 1 – Solubility of CO_2 [6]

At last, we have to bear in mind that during the firing some components of the body mixture (such as quartz) are dissolved in the molten glass. Their dissolution causes a change of the glass composition, in particular at the body-glaze interface, and the consequent reduction of the gas solubility. That phenomenon can produce a further growth of bubbles [10].

In the molten glaze, gas bubbles are subjected to the Archimedean principle (that pushes them towards the free glaze surface), the Newtonian attraction and the friction force. When the balance of power is realized, the bubble's speed is constant and, in the laminar flow, it is defined by the Stoke's law:

$$V_t = \frac{(Ce - C)gD_B^2}{18v} \tag{8}$$

where V_t is the bubble's speed; Ce and v are respectively the density and the viscosity of the molten glaze; C is the density of the gas; g is the gravitational acceleration and D_B is the diameter of the bubble.

According to the Stoke's law, we have:

1. The higher ν is, the lower V_t will be. It means that an high viscosity prevents to gas bubbles the movements towards the glaze surface.

2. Under the same conditions, the bigger bubbles are, the faster they will be. In fact, $V_t \propto D^2_B$.

As regards what has been said above, in a glaze coat we can note bubbles that are bigger and bigger in size (100-800 µm) going from the bottom to the top. This phenomenon helps the pinholing's appearance. Therefore, the thiner the glaze coat is, the more difficult the beginning of big bubbles will be and vice versa. The correlation between trapped gases and glaze thickness is showed in fig. 4 [1].
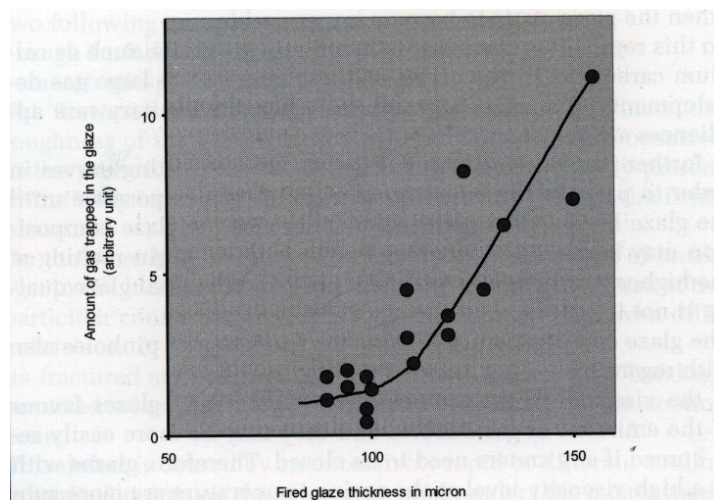

Fig. 4 – Relation between the glaze thickness and the air bubble amount [4]

Obviously, the best glaze thickness must be detected each time, according either to the glaze characteristics (viscosity, surface tension, vitrification temperature) and the body ones (quantity and typology of emitted gases) either to the firing curve. Anyway, 0.5 – 0.7 mm in thickness can be considered good values.

In the next pages we'll examine the fault from a technological point of view.

In succession, we shall have to consider the following points:

a. Gassy bubbles can be due to many reasons and the most influence of them are the following ones:

1. *Air in the glaze after its drying.*

Sanitaryware articles are wet glazed and about a forthy per cent water evaporates during the drying. That phenomenon gives origin to many small pores in the glaze coat (about by 40% in volume).

The thiner glaze particles are (extreme grinding), the smaller and the more numerous those pores will be and vice versa.

At the beginning pores are communicating, but during the vitrification phase they will be isolated and they'll turn into a closed micro-porosity. It can represent an important primer factor for the pinholing, because it behaves as an active center for big bubbles.

It is possible to reduce the micro-porosity by decreasing the amount of the water in the glaze (that is to say to increase its specific weight).

2. *Bubbles connected with the body porosity.*

If the body is too dry and shows a superficial porosity, the glaze can easily get into opened pores and expel the air inside. The air leaking causes the development of bubbles that can be trapped in the glaze coat. They can be isolated or joined by means of a tubular appendix to the body porosity (fig. 5). The appendix acts as a gas drum from the body to the bubble, so that it can continue its growth even until its explosion [4]. In order to reduce and/or eliminate the defect we have mentioned, it deems indispensable:

- • to avoid the removal of the thin layer of the finest clayey particles during the finishing, because it reduces the superficial porosity of raw articles. So, we must not use sponges too wet and we must not repeat the sponging more than necessary.

- • to moisten pieces before their glazing, so that it will be possible to fill up the superficial porosity with the water, in order to anticipate the air leaking.
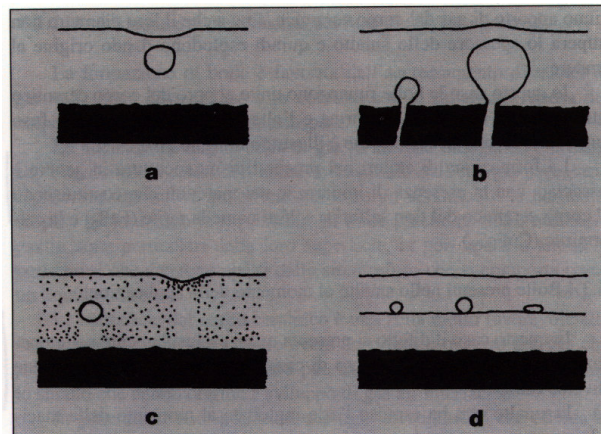

Fig. 5 – Different kinds of bubbles in the glaze [5]

3. *Bubbles due to the glazing.*

Usually, the glaze is put on the sanitaryware more than once. If the first layer dries up too quickly, surely we'll find the situation we have mentioned above. The first layer will have an internal and superficial porosity, where the getting of the second glaze can cause the air leaking and the subsequent development of bubbles.

Moreover, the irregularities between the first layer of the glaze and second one represent a preferential site for the nucleation and the growth of gassy bubbles.

It is obvious that now bubbles will be smaller in diameter, because we have half of the thickness of the glaze, but the risk of the pinholing will be smaller too. Anyway, they are a potential growth center and therefore it is better to decrease the risk for their formation. For this reason it is necessary to put the next glaze layer when the first one is still sufficiently wet.

Pratically, you must find:

- the best conditions among the first glazing and the others;
- the right amount of the glue in the glaze;
- the right amount of the water in the glaze;
- the best conditions for the spray gun (that is to say to find the right flow for the glaze and its polverization).

4. *Gases coming from the components of the glaze.*

Some components of the glaze emit gases. Such as:

♣ China clay: it emits steam in consequence of the kaolinite crystals' destruction. It is the so-called loss of constitution water, that happens between 460°C and 550°C.

♣ Calcium carbonate: $CaCO_3$ decomposes and releases CO_2 at about 894°C.

♣ Magnesium carbonate: $MgCO_3$ decomposes and releases CO_2 at about 400°C and 630°C according to the carbonate.

♣ Dolomite: it is a calcium and magnesium carbonate and therefore it shows the two decompositions we have just said above.

♣ Talc: the $3 \, MgO \cdot 4SiO_2 \cdot H_2O$ loses the combination water in consequence of the increase of the temperature.

Obviously, above mentioned temperatures are concerning the pure raw materials. In reality, those temperatures can change in relation to the:

- mineralogical composition of raw materials;
- quantity and type of additional materials (that can act as catalysts or not);
- particles size of raw materials.

In order to eliminate the gases' production in the glaze, it is habit to change the calcium carbonate with the wollastonite (calcium silicate) (because it does not produce gases) and the magnesium carbonate with the talc (that emits less gases than the other).

5. *Gases coming from soluble salts.*

In the ceramic world, the soluble salts are chiefly sulphates of alkali metals or alkaline-earth ones. They can be as impurities in raw materials or in the water we use to prepare the body or the glaze.

Moreover, the calcium sulphate is always in the mixture as residue, even if it is in different content. It comes from the erosion/abrasion or dissolution of plaster moulds. If the total amount of those sulphates is too big, it is possible their appearance on the pieces' surface during the drying of sanitarywares. Their surfacing is due to the evaporation of the water in which their are solved.

If sulphates are not carefully removed before glazing, they can dissociate or act with the molten glass and give rise to gassy bubbles.

The calcium sulphate is the most harmful of them. In fact, as anhydride, it has an high stability to the temperature (even more than 1180°C) and therefore it acts during the most critical time of glaze maturity.

6. *Gas coming from the contamination of the glaze.*

Sometimes, the glaze can be subject to a fortuitous pollution. It is usually due to some contaminants that are in raw materials. Other times, they can be subject to a superficial pollution. It can be due to the contaminants coming from the outside or from some components of the kiln (such as fire-supports, bars of carbide, burners, …).

In the sanitaryware production, we can find as contaminants:

♣ Silicon carbide particles, that give rise to the following reaction:

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2 \qquad [1].$$
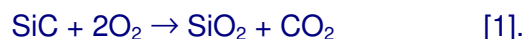
Less than 0,5% of SiC can cause a located pinholing.

♣ Plaster inclusions: less than 1% of them can cause big gassy bubbles [6].

♣ Granules of $CaCO_3$: they can produce big and located bubbles. Experimentally, it was clear that the Ca amount around a bubble is more than in the remaining glaze. It means, therefore, that its located increase is due to those granules.

♣ Sodium and magnesium sulphates: they decompose and develop SO_3 [6].

A particular contamination is due to the absorption of gases, that are in the kiln, by the molten glaze. During the firing, in fact, there is a continuos change of gases between bubbles in the glaze and the glaze itself and between the liquid and the kiln atmosphere.

Therefore, if we use a fuel with an high content of sulphur, we can have a glaze contamination due to the sulfur dioxide coming from the kiln atmosphere. It can act with the calcium oxide and give rise to the development of calcium sulphate, that can provoke gases or located shadiness of the glaze.

7. *Bubbles due to the dissolution of some components of the body.*

During the firing, we have the formation of a layer between the body and the glaze. It contributes to increase the adherence of the glaze on the support. Anyway, in that phase, even if the firing is too slow (that is to say a prolonged persistence to an high temperature), it is possible

an excessive dissolution of some components of the body, such as the quartz. They can decrease the solubility of gases in the glaze and provoke bubbles and the pinholing, even in a very thin glaze coat, where normally we have not the fault [5].

8. *Bubbles due to the leak of some gases from the body.*

Normally, mixtures for sanitarywares, both in vitreous-china and in fire-clay, give rise to the following gases:

- Steam, due to the getting rid of the remaining humidity (until about 150°C).
- Steam, due to the getting rid of the constitution water of the kaolinite. It is both in the ball clays and in china clays (between 460°C and 550°C). Its elimination can continue until 650°C according to the raw material and the temperature gradient.
- Carbon dioxide, due to the organic substances' combustion in ball clays (200°C – 500°C).

To tell the truth, the combustion can continue until ≈ 1100°C, even if the speed of the heating is high (as we normally have in a modern kiln) and if the organic substances are in the form of coke in small granules [7].

Experimentally, it was evident the presence of CO_2 in the electric kiln atmosphere. It was heated with 300°C/h and used for the firing of a vitreous-china mixture. In an electric kiln, over 1000°C, the CO_2 can be due only by the combustion of organic substances [3].

Another study showed carbon inclusions 10 μm in diameter in some fired and glazed sanitarywares (fig. 6) [2].
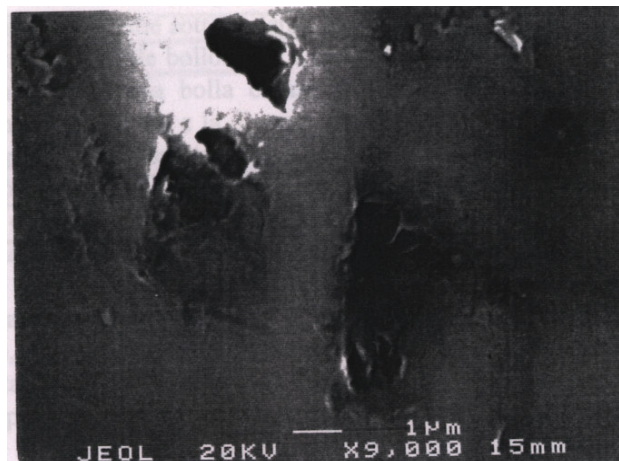

Fig. 6 – Carbon inclusions [6]

It is evident that the above mentioned combustion can happen during the complete firing cycle and it represents therefore the most dangerous source of gases for the pinholing.

A possible explanation for the persistence of organic substances over 1000°C is the slowing down of the kinetics of their decomposition. The slackening off is caused both to the high speed of the heating and to the low speed of the oxygen diffusion inside the ceramic body.
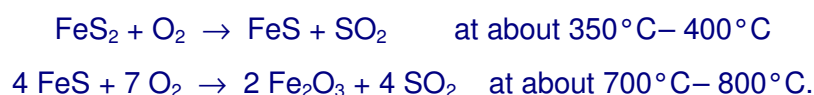
As far as the speed of the heating is concerning, we can say that it provokes a temperature gradient between the outside of the piece and its inside. Consequently, some chemical changes in the piece happen at higher temperatures than the theoretical ones.

About the oxygen diffusion, you must note that it is controlled both by its partial pressure (and therefore by the oxiding atmosphere of the kiln) and by the resistance of the medium (body).

By the way, it is important to say that the resistance increases during the firing, owing to the shrinkage and the vitrification. They reduce, in fact, the indispensable porosity for the diffusion.

- The mica, that is in ball clays, loses its constitution water between 700°C and 800°C.
- SiF_4/HF, due to the decomposition of fluorine compounds (800 – 900°C).
- SO_3, due to the decomposition of sulphates that are, as impurities, in ball clays and/or china clays and/or sulfides (pyrite FeS_2 or chalcopyrite $CuFeS_2$).

For example we can have:

$$FeS_2 + O_2 \rightarrow FeS + SO_2 \qquad \text{at about } 350°C - 400°C$$
$$4\,FeS + 7\,O_2 \rightarrow 2\,Fe_2O_3 + 4\,SO_2 \quad \text{at about } 700°C - 800°C.$$

About the point **b.**, we can image the glaze coat, after drying and before glazing, as a layer with a thick plot of little pipes that are communicating. Corresponding to an opened porosity by 40%, they are made by the water evaporation after the glaze application. The latter keeps that structure even also the firing and until the vitrification temperature, that is to say until 1080°C – 1120°C, according to the composition and the particles size of the glaze.

So until 1000°C – 1050°C, the glaze is fully permeable and can easily expel gases, coming from its inside or from the body.

It is obvious that most gases cannot cause the pinholing under 1000°C. When the glaze gets to the vitrification temperature, the shrinkage of the porosity starts and we have a closed porosity. During the firing the glaze melts and it becomes a very dense liquid, characterized by many closed pores. Since the vitrification temperature, therefore, the glaze is not permeable and it traps gases in the form of bubbles.

Got to know why the gas is trapped in the molten glaze, it is simple to understand what are the most dangerous causes for the fault we are speaking.

In fact, all causes that provoke gases' leaking under 1000°C are not so important like the ones descripted at points 5, 6, 7, 8. Anyway, speaking from experience we can come to the conclusion that the main cause for the pinholing is the gas leaking from the body, with particular

reference to the combustion of organic substances, but sometimes fortuitous pollution (point 6) is important, too. In fact:

• the fault intensifies when the sanitaryware is glazed on both sides. This phenomenon happens because, in order to escape, gases must pass through the glaze coat. So, if only one side of the surface is not glazed, it represents the preferential way for gases.

• if we use the engobe between the body and the glaze, the fault decreases noticeably. It is particularly true with the fine fire clay mixture and the fire clay one. If the pinholing does not depend on the gas emitted by the support, the engobe will have no effect on it.

In reality, the engobe acts as a filter and it has a double effect:

° it restricts the gas diffusion towards the glaze;

° it distributes and makes uniform the remaining gas by its plot of small holes and therefore it prevents the development of big bubbles.

Before analysing the best remedies for the pinholing, we want to specify that all next instructions are quite detailed, but always general. It is not possible, in fact, to give here the solution for single cases, because many variables come into them.

For our convenience in analysing and setting forth the arguments, we shall divide them into five groups:

I. The sorting of raw materials and methods for the preparation of the body.

II. The sorting of raw materials and methods for the preparation of the glaze.

III. Methods for the glazing.

IV. Management of the firing.

V. Glaze composition.

I. *The sorting of raw materials and methods for the preparation of the body.*

The choice of raw materials involves some important criterions to follow. It is better:

° To use ball clays with a low content of organic substances and/or with the smallest average dimensions for coal particles. It is obvious that some organic substances contribute to improve and to stabilize the rheological characteristics of the body, hence it is indispensable to arrive at a compromise. Anyway it is not advantageous to exceed the limit of 2% in coal.

° To select raw materials free from those components that can emit gases at high temperature (beyond 1000°C), such as:

♣ chalcopyrite ($CuFeS_2$)   ♣ granules of calcium carbonate

♣ pyrite (FeS_2)   ♣ sulphates and other soluble salts

° To choose opportunely particle size distribution for raw materials, in order to avoid packing phenomena in the thickness and at the body-mould interface. In fact, if they are too

compact, the leak of gases from the body will be slowed down and consequently their leak from the glaze could be not possible, because, in the meanwhile, the glaze surface could be become impermeable.

° To avoid some pollutants, (impurities or minor components of the body), such as calcium carbonate or magnesium and/or talc. They involve two disadvantages:

♣ their decomposition causes carbon dioxide (due to $CaCO_3$ and/or $MgCO_3$) and water vapor (due to talc), that is to say an increase in the amount of gases;

♣ they act as catalysts for the vitrification of the body, hence they cause a decrease of its porosity at lower temperatures than the ones we have without them. In other words the body offers a greater resistance to the leak of gases, which, consequently, starts at higher temperature. That displacement towards higher temperatures is often sufficient to make the glaze impermeable and therefore to cause the fault.

Table 6 shows the results of a specific research on the matter. Obviously, the same glaze and firing cycle were used in the tests.

	C from organic materials	C from carbonates	Sulphur	Fluorine	Glaze surface
Mix A without talc	100 ppm	100 ppm	50 ppm	350 ppm	Not pinholed
Mix B with talc	100 ppm	100 ppm	50 ppm	100 ppm	Pinholed

Table 2 – Comparison between two different mixture

To note that the mixture B, though with less substances that can originate gases, causes the fault in the glaze.

As far as the body preparation is concerned, we have to reduce organic substances and in particular way the biggest ones (ø > 100 µm). So, we suggest the following procedure:

1. to dose ball clays;
2. to dissolve ball clays with the greatest amount of water (and relative deflocculants). It allows an easy sieving with nets by 180 MESH, in order to eliminate the most part of impurities, normally present in the ball clays, and particularly the granules of carbonaceous substances;
3. to sieve with nets by 160 - 180 MESH;
4. to mix china clays and hard components in the argillaceous suspension.

The other operations will be made as usual.

II. *The sorting of raw materials and methods for the preparation of the glaze.*

In order to minimize the fault we are speaking, it is necessary to consider the following directions.

a. To choose those raw materials that give rise to the lowest leak of gases during the firing, in order to bring a specific oxide in a glaze.

For example:

♣ in order to bring CaO, use wollastonite ($CaSiO_3$) instead of calcium carbonate and, among various wollastonites, you have to prefer the ones with the smallest firing loss;

♣ in order to bring MgO, use talc instead of magnesium carbonate and/or dolomite.

Table 7 shows the results of a research [13] that tests the changes of the fault, under the same conditions, substituting $CaCO_3$ with two different kinds of wollastonite.

	Firing time		
Glaze with:	**4h 20 min**	**3h 20 min**	**3h**
CaCO₃	Pinholed	Greatly pinholed/blister	Greatly pinholed/blister
Wollastonite type A	Pinholed	Pinholed	Pinholed
Wollastonite type B	Not very pinholed	Not very pinholed	Not very pinholed

Table 3 – Changes of the pinholing with the glaze composition [13]

To note how the pinholing decreases substituting $CaCO_3$ with wollastonite, particularly if it is used the type B (L.I. 1.4%) instead of the type A (L.I. 2.1%).

Obviously, the replacement of the calcium carbonate with the wollastonite it is not sufficient to avoid the pinholing, because the glaze composition is only one of its cause.

b. To choose raw materials with not too fine particle dimensions; this is particularly true for quartz and feldspars (normally the main components of a ceramic glaze). Their high fineness, in fact, decreases the initial vitrification temperature (T_{iv}) of the glaze; it opposes the leak of gases coming from the body and consequently it increases the risk of the pinholing.

Table 4 shows the particle size of a quartz and a feldspar [13].

Raw materials	**Particle size**	**Ø < 2 µm in %**	**Ø in µm at 50%**	**Ø < 20 µm in %**	**Ø$_{max}$ in µm**
Quartz	Industrial	7	10.5	84	50
	Finer	28	3.6	100	20
Feldspar	Industrial	8.5	19.5	51	100
	Finer	33.5	3.2	100	20

Table 4 – Particle size distribution of a quartz and a feldspar [13]

Using one of finest raw materials or both of them, it has got a more remarkable pinholing on samples.

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As it is well known, ceramic glazes are obtained by the wet grinding of raw materials. It is an important phase of the production process, because if the grinding is excessive, we'll have the just said case: a high fineness of the glaze particles causes a quickning of the reaction kinetics, a decrease in the vitrification temperature of the glaze surface and hence an increase of the pinholing. Moreover, a high fineness causes an increase of the glaze surface stress, that has an effect on the fault we are speaking.

If the grinding is insufficient, instead, the glaze will be opaque and bad melted.

So, it is very important to select a right particle size distribution for the glaze and to determine the most suitable grinding procedures (grinding time and ball mill charge) to be followed in achievement of the required distribution. It is necessary to pay a great attention in the preventing any change of the grinding in the long run, too.

Every time the ball mill is used, in fact, its grinding medium wears itself out according to the materials and their hardness (for example the sintered alumina wears itself out less than porcelain). So, by the passing time and the use, the amount of grinding media decreases and their dimensional distribution changes.

In the long run the amount of media with the smallest diameter increases in consequence of the reduction in the volume, due to the consumption for abrasion. A greater amount of small spheres will be therefore in the ball mill grinding charge. It involves a shifting of the grinded particle size distribution towards finer parts and a gradual development of the fault. For this reason, it is necessary to examine constantly the grinding media of the ball mill.

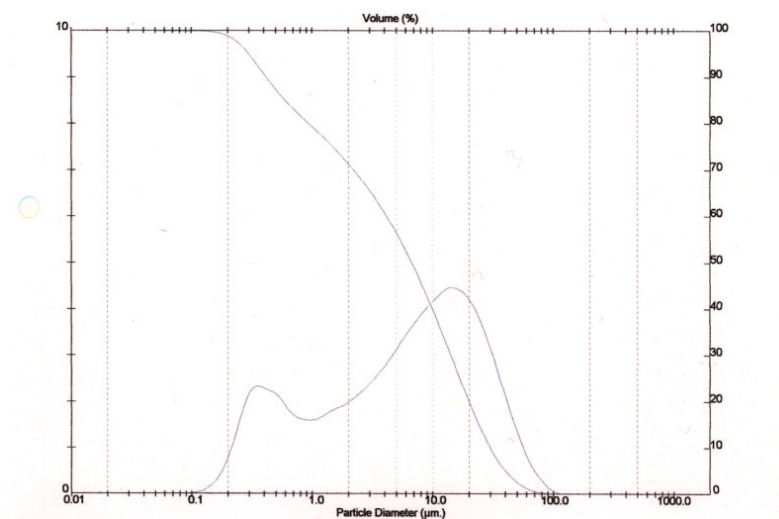Figure 7 and table 5 show a typical particle size curve for a ceramic glaze.

Fig. 7 – A glaze particle size distribution made by laser equipment

Size (µm)	Volume Over %	Size (µm)	Volume Over %	Size (µm)	Volume Over %
0.100	99.28	15.00	28.18	63.00	1.03
0.250	97.21	20.00	19.96	75.00	0.42

0.500	87.36		25.00	14.14		90.00	0.10
1.00	79.32		30.00	10.04		105.00	0.01
5.00	56.41		35.00	7.14		125.00	0.00
10.00	39.74		45.00	3.62		150.00	0.00

Table 5 - A glaze particle size distribution made by laser equipment.

III. *Methods for glazing.*

As it is well known, the glazing can cause the pinholing.

It is important, therefore, to follow the next instructions:

a. To avoid to apply the glaze on a dried glazed surface. In that case, in fact, it will be possible the formation of a plot of micro-bubbles at the interface between the first and the second layer of glaze. Those micro-bubbles can operate as nucleation centers for bigger bubbles and hence it can promote the fault.

It must be carefully checked:

° The rheological characteristics of the glaze and hence the dosage of the glue. It is responsible for the water holdup time and consequently for the drying speed of the first layer of the glaze.

° The specific weight of the glaze. The higher it is, the lower the amount of the water in the glaze will be and, consequently, the faster the drying of the glaze will be, too.

° The pulverization degree of the glaze in the spray gun and hence the value of the flow and the pressure of the vaporization air.

° The time between the first and the second application of the glaze.

b. To determine the optimum thickness for the glaze and to respect that value during the glazing. Usually it must be 0.6 - 0.8 mm after firing, in order to avoid the outbreak of the pinholing (greater thickness) or an incomplete covering of the support (finer thickness), especially in the case of sanitarywares in fine fire clay.

The glaze thickness depends on:

° the time of the total application;

° its specific weight;

° the amount of the glue;

° the porosity of the support to be glazed;

° the temperature and the degree of humidity of the support to be glazed;

° the flow of glaze in the spray gun.

IV. *Management of the firing.*

During the firing, it is supplied, both to the body and the glaze, the thermal energy that is necessary to start and to complete those chemical reactions that give the final characteristics to the fired pieces. The kinetic of those reactions depends on:

- ° the mineralogical composition of raw materials;
- ° the particle size distribution;
- ° the body and glaze composition;
- ° the firing curve, hence it depends on the supply of thermal energy. The higher the body thickness before firing is, the more important that parameter will be important. In fact, a high thickness determine a temperature gradient between the outside and the inside of pieces, hence a displacement between the theoretical and the real temperature of reactions (such as, for example, the combustion of organic substances).

It is therefore very important to determine a heating rate in order to obtain optimum conditions in the development of chemical reactions and hence to decrease the risk of the pinholing.

It has already been said that the temperature affects the viscosity and the surface stress of a molten glaze. It has already been said that a surplus of the temperature (or an excess of the persistance to the highest firing temperature) can cause a reboiling of the glaze and the consequent formation of blisters, too.

The surface stress and the viscosity are bound by the following relation, called flow factor:

$$\sigma \propto \log\eta$$

that depends on the firing cycle more than on the glaze composition [18].

Suitable instructions are given in the following lines in order to determinate:

1. the pre-heating curve;
2. the highest firing temperature in order to minimize the pinholing.

Anyway, we have to keep in our mind that there are many causes for the fault and hence a right management of the firing can be necessary but not sufficient to eliminate the pinholing.

1. The pre-heating curve is called that area of the firing curve that starts with the beginning of the cycle until the downright firing zone, that is to say up to 1200°C.

Most of gases, coming both from the body and the glaze, develop in the range 800°C – 1100°C. This happens because, as it has already said, a displacement between the theoretical and the real temperature occurs toward higher values.

We have to pay attention to this part of the pre-heating curve.

In order to put in evidence which is the best management for the pre-heating phase, the results of a research [13] on the matter are showed in table 6. They show the influence of the pre-heating curve on the development of the pinholing on the same glaze, applied on four different bodies. In table 7 the different bodies are showed. They differ on their composition: three of them

(bodies I-III) contain different amount of raw materials generating gases and the last one contains talc (IV).

Materials generating gases (ppm on fired product)	Bodies			
	I	II	III	IV
C from organic substances	100	100	7000	100
C from carbonates	100	100	500	100
Sulphur	50	50	500	50
Fluorine	350	100	100	100

Table 6 - Tests on different bodies

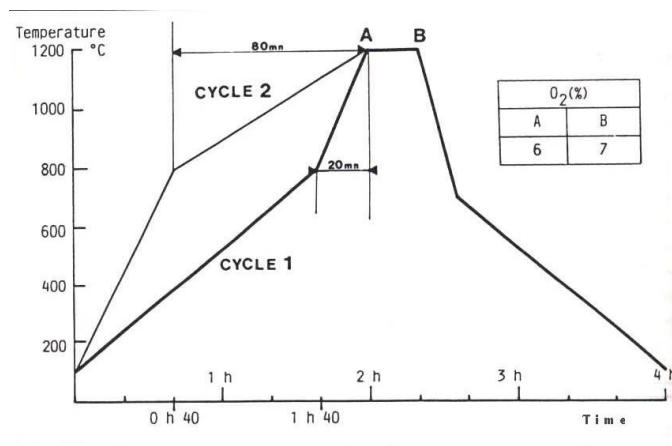Glazed samples of those bodies were fired with two different firing curves, that are showed in figure 8.

Fig. 8 – Two different firing curves

Firing cycle	Bodies			
	I	II	III	IV
Cycle 1	Pinholed	Pinholed	Pinholed very much /blisters	Pinholed very much
Cycle 2	Not pinholed	Not pinholed	Not much pinholed	Pinholed

Table 7

As you can note the thermal gradient in the range 800 – 1200°C is gone from 1200°C/h of the 1st cycle to 300°C/h of the 2nd one. The heating rate is therefore decreased, allowing a more complete outgassing before the glaze becomes impermeable. So, it was possible (see table 6) to eliminate the pinholing for two bodies and to decrease it for the body III, that had many components generating gases.

The results are not good for the body IV because the talc was present. The talc, in fact, catalyzes the vitrification of the body decreasing, at lower temperature, its porosity and hence

slowing down the outgassing from the body. It means that the outgassing is not still completed when the glaze will be not more permeable.

The pre-heating curve must be made in order to prolong the persistence of the bodies in the range between 800°C and the beginning of the firing.

2. About the highest firing temperature, it has been already said that an its excessive value (or a high persistence at the highest temperature) can cause a pinholing-reboiling in the glaze due to:

- volatilization of alkali (sodium) in the body;
- volatilization of alkali (sodium) in the glaze;
- decrease of the viscosity and surface stress of the molten glaze with maximing of coalescence phenomena and subsequent explosion of gassy bubbles.

It is therefore necessary to determine the best firing temperature (and the persistence time) for every pair of body/glaze, basing our choices on the following instructions:

a. the best firing temperature for a body corresponds to the intermediate temperature of the of the greification curve, that is equivalent to the stability zone of the water absorption curve and the shrinkage one;

b. the best firing temperature of a glaze with zirconium is the one that gives a viscosity equivalent to about $10^4 - 10^{4.5}$ Poises to the molten glaze. It is necessary to keep a high viscosity because the glaze with zirconium are inclined to develop the pinholing.

So, we have to choose the body and glaze recipes with the same maximum firing temperature and the same maturity cycle and to check that those conditions are followed in the industrial firing process.

In the firing os sanitarywares there are other variables that influence, more or less, under the same conditions, the surface stress of a glaze and as it has an important role in the beginning and development of the pinholing it is evident that we have to pay attention to them. The most important of them are:

° the kiln atmosphere, that is usually oxidizing for the firing of sanitarywares. Anyway, the not correct functioning of a burner and/or its bad regulation can cause a decrease of the amount of oxygen till to generate locally some reducing areas. They provoke an increase of the surface stress of the glaze by 20-25% [17].

° Water vapour (H_2O_v), sulfur dioxide (SO_2), ammonia (NH_3) and hydrochloric acid (HCl) decrease the surface stress of a glaze and it can help the pinholing. On the solid surface, in fact, a thin layer of gases is always chemisorpted and it will be replaced to the molten liquid. It is therefore obvious that the kind of gas influences the wetting angle of the liquid according the more or less great stability of the gassy layer.

V. *The glaze compositions.*

If a glaze composition is changed, its characteristics change, too. The most important of them to which we have to pay attention are:
- the glaze waterproofing temperature (vitrification temperature T_{iv});
- its surface stress (σ);
- its viscosity (η).

In order to avoid the pinholing as much as it is possible, we have to regulate them as follows.

- *Vitrification temperature (T_{iv})*

The T_{iv} must be the highest that is possible in order to allow to the gases coming both from the body and the glaze can pass through the glaze layer and to avoid their trapping into it.

It is obvious that a high T_{iv} usually involves glazes with higher maturity temperatures and hence less brilliant and with not very smoothed down surfaces. In order to avoid that the solution of a fault (the pinholing) can cause an other one, sometimes more evident (not very sheen glazes), it is common to use glazes based on particular eutectics. It is usual, in fact, to use glazes characterized by remaining permeable (that is to say not vitrified) till high temperatures (1150-1180°C) and by melting quickly and completely at eutectonic temperature. These glazes are similar in the final appearance to the low-firing glazes.

- *Surface stress (σ)*

We have already said that an its high value offers resistance to the beginning of big gassy bubbles and hence to the pinholing. This is because a high σ helps the dissolution of small gassy bubbles, hampering their coalescence. Besides, even if a big gassy bubbles develops, a high value of the surface stress decreases the hollow that is in the glaze area put on the bubble. That is to say that it decreases the effect of the fault.

Essentially, the surface stress of a glaze can be increased:
- ° rising the fineness (and hence the grinding) of the particles of a glaze;
- ° increasing the amount of oxides with a high σ.

It has been verified, in fact, that the surface stress of a glaze is a linear function of its composition:

$$\sigma = \Sigma \, (\sigma_j \cdot \rho_j)/100 \qquad [dynes/cm]$$

where σ_j is the surface stress coefficient for the component j expressed in dynes/cm and ρ_j is the molar percentage of the component j.

Mr. Appen has divided oxides into three groups:

° the first group gatheres together the oxides with constant values for σ_j, independently from their percentage of use. All values are expressed in dynes/cm at 1300°C.

TiO$_2$	250	BeO	390	Li$_2$O	450	CaO	510
SiO$_2$	290	MnO	390	ZnO	450	MgO	520
Na$_2$O	295	NiO	400	BaO	470	Al$_2$O$_3$	580
ZrO$_2$	(350)	CdO	430	FeO	490	La$_2$O$_3$	610
SnO$_2$	350	CoO	430	SrO	490		

° the second group assembles the oxides that are inclined to decrease the surface stress and with σ_j depending on their percentage of use. Sometimes it can happen that σ_j are negative. Some oxides of this group are the following ones:

K$_2$O   Rb$_2$O   Cs$_2$O   Tl$_2$O   B$_2$O$_3$ PbO   Sb$_2$O$_3$ Bi$_2$O$_3$ P2O$_5$

It is possible to take a medium value for the most common oxides. For example:

K$_2$O   10   B$_2$O$_3$ 80   PbO   120

° the third group includes the oxides that are not very soluble in the molten glaze and with σ_j depending on their percentage of use. Those oxides are like surface-active agents that decrease very much the surface stress.

As$_2$O$_3$ V$_2$O$_5$ WO$_3$ MoO$_3$ Cr$_2$O$_3$ SO$_3$

The surface stress of a molten glaze is inversely proportioned at the temperature: it is possible to consider that σ rises by 4 dynes/cm every fall in firing temperature by 100°C.

- *Viscosity (η)*

A high viscosity value of a molten glaze, as already said, prevents the gassy bubbles development of big gassy bubbles and their motion towards the glaze surface. In that way a high viscosity decreases the pinholing risk.

We have already said that the η decreases greatly with the growth of the temperature and depends on its composition, too. In fact:

° substituting CaO and/or BaO with MgO, η increases;

° decreasing the % of Na$_2$O, K$_2$O, Li$_2$O in favour of earthy-alkaline oxides, η increases;

° increasing Al$_2$O$_3$, η increases.

According to what we have just above said, it is not easy to hamper the pinholing by changing the glaze composition (in order to change its T_{iv}, its σ and its η). We have to consider, in fact, that the glaze has to respect very important rules:

- a good dilatometric agreement with the body;

- a good brilliance and result during the glazing;

- the lack of other faults (such as the glaze shrinkage due to an excessive surface stress).

It is necessary, therefore, to arrive at a compromise, often very difficult to find, in consequence of many variables we have.

When we have not other solutions to fight the pinholing, we can use the engobe (above all on fire clay sanitarywares). It is almost always resolutive, but it involves a further working phase (the engobe application) with an increase of the production costs.

The engobe is often used with the fire clay also to decrease the faults due to appearance of grains of chamotte on the glaze surface. It increases, in fact, the covering of the glaze, in particular way where are the corners.

Rarely the engobe is used in the vitreous sanitaryware production in order to eliminate a fault of pinholing, that was difficult to eliminate by other systems.

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