

Review

Glaze surface Defects causes and Prevention Controls

E. Youssef^{1, 2}, N. Mostafa², J.E. Khoury², T. Merhej², R. Lteif^{*1}

¹Unité de Technologie et Valorisation Alimentaire, Centre d'Analyses et de Recherche, Université Saint-Joseph de Beyrouth, Faculté des sciences, Campus des Sciences et Technologies, Mar Roukos, Dekwaneh, B.P. 17 – 5208, Mar Mikhaël, Beirut, 1104 2020, Lebanon

²Lecico Egypt (S.A.E), P.O. Box 358, Alexandria, Egypt

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Abstract

Glaze defects adversely affect the quality of sanitaryware pieces and occur in form of pinholes, crawling or crazing. Pinholes are caused by the migration of gas from the body, which is either trapped by the glaze or released at a later stage during the firing process leaving the glaze insufficient time to heal. Several factors increase the development of glaze pinholes like high glaze viscosity during firing, high surface tension, and improper grain size distribution of raw materials. The choice of suitable materials and adjustment of the glaze formula combined with the optimum firing conditions contribute to minimizing pinholes. Crawling happens when the molten glaze withdraws from the ceramic body during firing leaving bare patches on the ceramic body. It is caused by high surface tension in the melting glaze. To prevent crawling, it is necessary to control all the measures that reduce surface tension. In the case of both crazing and peeling, the eradication of problems relies on matching the thermal expansion characteristics of the body and glaze. Crazing can occur when the body absorbs water and expands so the thermal expansion coefficient should be controlled. This work summarizes the reasons for glaze surface defects based on the recently published research and the suggested practical remedies.

Keywords: Ceramic, glaze defects, glaze pinholes, crawling, crazing

I. Introduction

In the sanitaryware industry, the glaze surface defines the quality of the production pieces, influencing the functionality of the product and its aesthetic properties. Glaze defects occurring in a finished glaze surface impair the quality of a product. The majority of these defects are seen only at the exit of the kiln regardless of whether their main cause is elsewhere in the manufacturing process. It is hard to characterize what causes a glaze defect in sanitaryware ¹.

In this study, we determine the origins of the occurrence of most generic defects in the ceramic industry. We focus on glaze surface defects like pinholes, crawling and crazing.

Glaze pinholes present as gassy bubbles from a visual perspective; they appear in the glaze surface as circular holes or pits with diameters greater than 80 microns and various depths, and are difficult to repair ^{2, 3}. Holes with a diameter smaller than 80 microns are difficult to see with the naked eye, and these are not considered significant defects ⁴. The gases that lead to bubbles, prompting the formation of pinholes, have numerous expected sources ¹. For example, gas from the decay of glaze components and gaseous emissions from external contaminants.

One common defect in the production of sanitaryware is glaze crawling. Crawling from a morphological perspective is a very regular deformity in ceramics production ⁴. The fault is a bare area in the glazed body, which is characterized as “the discontinuity of the glaze layer”. The size of the unglazed area can be small or large depending on the root cause of the fault. Around the fault, the glaze edge is smooth, rounded and thickened ⁵. It is instantly recognizable as the shrinkage of the glaze, although unpredictable in structure, forms small islands of glaze that leave the fired body exposed ⁶.

Crazing is more common than peeling in ceramic glazes. It is considered a serious problem in glazed wares ⁷. This is because the ceramic is a brittle material that exhibits higher resistance to compressive stresses than to tensile stresses. Crazing appears like a network of hairline cracks in the glaze surface ^{8, 9}, whereas peeling looks as if small parts of glaze have shrunk away from the surface. The thermal expansion mismatch between glaze and body lead to the formation of both these defects ⁴. Crazing can appear directly or shortly after the firing process, or after years of use ⁹.

As evident from the literature, several studies have been carried out and a number of main causes have been highlighted, such as variations in glaze application (method and techniques), impurities in glaze materials, thermal treatment of the glaze (overfiring, underfiring, and kiln atmo-

* Corresponding author: roger.lteif@usj.edu.lb

sphere) and retention of gases that come from the transformation and decomposition reactions of the raw material ¹.

The aim of this literature review is to provide a better understanding of the reasons behind the occurrence of glaze defects, that is pinholes, crawling, and crazing. This work will attempt to include some aspects concerning controlling the formation of glaze defects. Thus, understanding the factors that contribute to the formation of these defects is fundamental to effectively control them.

II. Glaze Pinholes

All glazes contain a few bubbles. Small bubbles have practically no impact upon the glaze quality and can be disregarded, especially if they are isolated from the outside surface of the glaze. However, when the bubbles get bigger or closer to the surface, they disturb the surface and present a non-conformity ¹⁰. According to D. Fortuna and A. Angeli, the formation of pinholes is a result of almost spherical gassy bubbles with a diameter larger than 80 µm between the body and glaze.

Two cases shape the pinhole under a microscope and they depend on several production parameters that present the formation of pits:

The first case: A spherical gas bubble under a very thin glaze layer with its dimension between 80:800 microns (Fig. 1). The bubble is shaped by two different pressures, the pressure inside the bubble and the external pressure, both of these due to the cooling process.



Fig. 1: Case 1 Cross-section of a pinhole.

The second case: A semi-spherical cavity on the surface of the glaze with a dimension between 80:800 microns (Fig. 2). A cavity in the glaze surface is shaped by a gassy bubble that has risen up to the surface and burst ¹¹.

Many studies have demonstrated how pinholes are induced by the decomposition of raw materials leading to a reaction within the glaze as this passes from a fluid state into a solid one in the cooling zone ¹. The majority of gases are released before the glaze melts over without generating any defects in the glaze surface ¹². During firing, the gas bubbles must overcome the melted glaze surface tension to escape from the glaze surface where they then burst ⁵. If the glaze is able to heal the surface, the bubbles leave the glaze without the presence of pinholes ⁵. Inadequate glaze fluidity severely affects the outgassing of the glaze or the body at high temperature, this affects the decomposition of raw materials, especially calcium carbonate, by releasing CO₂. At this stage, the burst gassy bubbles break the surface, creating pinholes. In general, melted glaze fills the craters but this might be more effective if the soaking pe-

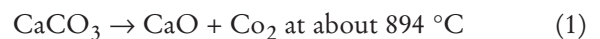
riod is excessively short or if the pinholes are generated at the end of the firing cycle. This problem can be solved by choosing adequate raw materials and optimum firing conditions to produce a glassy surface covering the body ¹. Another defect is pitting which is formed when the body has redundant thickness and double-glazed layers. Air becomes trapped especially during the firing cycle when gases cannot pass through the glaze before the glaze melting cycle has been completed.



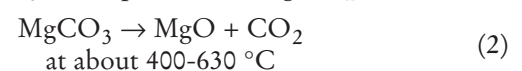
Fig. 2: Case 2 Cross-section of a pinhole.

The gases that fill bubbles come from at least one of a few sources:

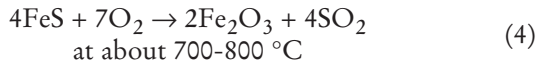
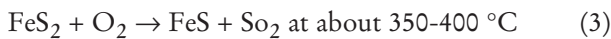
- Air entrapped between the particles of glaze owing to evaporation of the water accounts for about 40 % of the glaze volume ¹⁰. Water evaporation leaves small holes between the glaze grains. When the glaze grains are fine, the glaze pores will be minimal ¹¹.
- Air entrapped in the body pores ¹¹.
- Glaze spraying stage that generates bubbles due to excessive layers. Bubbles will surely occur if the first layer dries too fast, because the first layer will present surface porosity causing air leakage and bubble formation during application of the second glaze layer. It is necessary to ensure wetting of the first layer ¹¹.
- Inappropriate drying cycle of the cast pieces ¹⁰.
- Gas from the decomposition of glaze raw materials. Materials such as calcium and barium carbonates, china clay, talc, zirconium silicate and organic compounds are subject to gas development when these materials decompose during firing. Furthermore, quartz serves to increase retention of this gas ¹⁰, for example:
 - China clay: The kaolinite crystals are crashed between 460 °C and 550 °C and this causes the emission of steam, in what is referred to as the loss of constitution water.
 - Calcium carbonate: At about 894 °C, the decomposition of CaCO₃ leads to the release of CO₂:



Magnesium carbonate: At about 400 °C and 630 °C, MgCO₃ decomposes, releasing CO₂



- Dolomite This is a calcium and magnesium carbonate, and therefore decomposes as described above ¹¹.
- Breakdown of organic binders or glaze impurities that can cause gas include rust from preparation equipment and SiC, which is used in some kiln furniture ¹⁰.
- Gas from the decomposition of glaze contaminants that can get into the glaze during preparation, such as particles of silicon carbide, calcium carbonate, and plaster. Also, contamination of sodium and magnesium sulphate and the sulphur content from the kiln atmosphere ¹¹.
- Water vapour captured as a result of excessively fast melting and fixing of the glaze in fast firing processes ¹⁰.
- Specific body components. For instance, quartz can be dissolved on a large scale if the firing temperature is too low, causing a decrease in the gas solubility in the glaze, leading to the formation of bubbles and pinholes. Finally, the effect of gas leakage from the body can create pits. Steam can be formed as a result of the evaporation of residual humidity at about 150 °C and also between 460 °C and 550 °C from the evaporation of kaolinite constitution water that occurs in china clay and ball clay. Several factors are important and responsible in pinhole creation, like CO and sometimes SO₃ which are the result of the decomposition of certain salts in the body mixture such as carbonates and sulphates. The CO formation is due to the combustion of organic substances in ball clays at about 200 – 500 °C, and the evolution of SO₃ is due to the decomposition of sulphates such as ¹¹.



- Raw materials used in the body and glaze preparation or the dissolving water can contain many impurities such as soluble salts; this will be explained further later. If these are not removed before glazing, sulphates of alkali or alkaline-earth metals can react with the molten glaze and generate pinholes. In addition, calcium sulphates can be generated from the abrasion of plaster moulds and cause pinholing ¹¹.

(1) Soluble salts and organic substances

The holes in the glaze are brought about by the retention of gases that come from the transformation and disintegration of both glaze and body raw materials, as mentioned previously. While the hard raw materials used to accomplish fast cycles ordinarily contain just very small amounts of carbonates or sulphates, organic substances in clays and kaolin decay at 1 100 °C or above, which is well beyond thermodynamic equilibrium. According to D. Fortuna ², during clay firing, organic materials are trapped “carbons” (coarse mainly) transformed into carbon dioxide and carbon monoxide gases in the presence of oxygen. The reaction temperature starts from 600 °C and varies depending on certain factors like the kiln cycle length and temperatures, the form and quantity of carbon contamination, the kiln atmosphere (oxidation), and the piece shape configuration. If the reaction is not completed below 760 °C, this

causes incomplete degassing problems at higher temperature (approx. 1 000 – 1 100 °C) like glaze pinholes.

Gaseous substances migrate during the entire firing cycle. They pass through the body via interconnected pores and reach the interface with the glaze. In some cases, an engobe layer can be used to improve the chemical – physical interaction between the body and glaze.

As long as the glaze has not melted, all the gases are freely released. At the point when the glaze begins to melt, it becomes impenetrable to gases and their solubility in the glaze turns into the critical factor of the process ³.

Barium sulphates are the result of precipitation of sulphates salts in the slip after they react with the barium carbonate used as an additive in the slip ¹³. In the slip preparation process, this percentage is added to induce the precipitation of sulphate salts such as calcium sulphate coming from mould residue in the recycled slip, or sulphate salts coming from the contaminated water. Barium carbonate aids the deflocculation of the slip according to the following reaction ¹⁴:



Normally, the barium sulphates decompose at 1 500 °C, however, the temperature of the decomposition is different if silica is present in the mix. The decomposition of the slip begins at 1 000 °C and about 97.7 % of the barium sulphate is decomposed. Thus, it has been observed that the mixture of barium sulphates, alumina and carbon reacts at a temperature above 1 000 °C to produce aluminate of barium ¹⁵. The emission of sulphur oxides results from decomposition of barium sulphates, which starts at 1 000 °C and above, causing the formation of glaze bubbles ⁴.

In some cases, the gas bubbles escape as a result of the decay of soluble salts in body raw materials. The sulphate content ranges from about 0.01 % to 0.28 % in ball clay, 0.002 % to 0.015 % in china clay (dry basis) and up to 0.007 % in other materials (that is sand and feldspar). It has been found that during storage of ball clay (after mining and production) the soluble sulphate content is doubled owing to oxidation of the sulphur over six months ¹⁶.

Finally, the existence of salts like sulphates and carbonates coming from the body components, glaze raw materials, glaze additives and water used in the mill has a negative effect and leads to the formation of pinholes.

(2) Factors influencing the development of glaze pinholes

The factors that regulate the motion of gas bubbles through the melted glaze are glaze surface tension, viscosity of the melted glaze, the firing conditions and body thickness layer ⁵. The following factors control the rate at which gassy bubbles grow, rise, and burst ¹⁰.

(a) Glaze viscosity during firing

The high fluidity of the melted glaze ensures smooth movement of the gases resulting from the decomposition of materials and facilitates the release of the bubbles ^{5, 17, 18}. It also facilitates the curing of holes ⁵. Glaze viscosity is an important characteristic that mainly controls the glaze surface composition ^{18, 19}. It is affected by

two major factors: the composition of the raw materials and the firing cycle²⁰. Most of the studies have used hot stage microscopy (HSM) to measure the glaze viscosity^{17,19}. The measuring approach depends on the data of the glaze characteristics in the hot stage. The viscosity is calculated as a function of temperature¹⁷.

(b) *Glaze surface tension*

If the melted glaze has high surface tension, the gassy bubbles cannot escape easily. On the other hand, a low-surface-tension glaze allows the delayed gases to escape during the cooling stage when glaze solidification starts so the holes cannot heal^{5, 18}.

Many factors are responsible for the occurrence of pinholes, such as overfired glaze, which leads to the decay of raw materials, generating small gassy bubbles⁵.

High surface tension offers protection from the initial development of large gas bubbles and thus from pinholing. This is because a high surface pressure advances the dissolution of small gas bubbles, blocking their coalescence. In addition, regardless of whether huge gas bubbles develop, high surface tension diminishes the hollow space in the glaze zone over the pinholes, decreasing the impact of the defect. Basically, the surface tension of a glaze can be increased by²:

- Increasing the fineness of the glaze particles by means of more intensive grinding.
- Increasing the content of oxides with a high surface tension².

(c) *Grain size distribution of the glaze raw materials*

Adjustment of the glaze grain size is used as a modification method to control the glaze surface properties. Most studies conclude that decreasing the glaze grain size (by a limited amount) leads to a decrease in the glaze viscosity, which ensures gas bubbles can escape easily.

On the other hand, if the size of the glaze particles is decreased excessively, air absorption of the glaze suspension will increase during the spraying process and cause porosity in the glaze layer, which in turn leads to bubble formation²¹.

(3) *Prevention measures and suggested remedies*

The reduction or elimination of bubble defects entails various changes in preparation of the glaze such as expanding the heat-over temperature, selection of suitable raw materials to reduce volatiles, and the use of defloculants. Many bubble elements can influence this development, including a proper application procedure, minimal and even glaze thickness with a good surface, complete drying before firing, and firing at an optimum temperature and with an ideal firing curve that allows adequate time for the emission of gases before the glaze seals over¹⁰. Use of an appropriate formulation of the glaze to increase its viscosity and its melting temperature by substituting Na₂O with Al₂O₃, K₂O and/or CaO and the use of wollastonite instead of calcium carbonate. Use of clays and kaolin with low LOI, and granulometric distributions that are not overly fine, in order to avoid surface densification phenomena: 40 to 41 % of particles larger than 1 micron is by all accounts a good compromise³.

The choice of raw materials should meet some important criteria. It is better:

- To use ball clays with a low organic substance content and additionally with the smallest average dimensions for carbon particles. Clearly, some organic substances have to be added to improve and balance out the rheological attributes of the body, so it is vital to reach a compromise. It is not recommended to exceed 2 % carbon.
- To select raw materials free of components that emit gases at high temperatures (above 1 000 °C), such as:
 - Chalcopyrite (CuFeS₂)
 - Granules of calcium carbonate
 - Pyrite (FeS₂)
 - Sulphates and other soluble salts
- To choose raw materials that are not excessively compact as these can slow down or even prevent gas leakage from the body as the glaze surface becomes impermeable.
- To avoid some impurities or some minor components, such as calcium carbonate or magnesium and/or talc as these can have two detrimental effects:
 - Their decay causes the development of carbon dioxide (due to CaCO₃ and/or MgCO₃) and water vapour (due to talc), leading to an increase in gases.
 - They act as catalysts for the vitrification of the body; thus, they cause a decrease in its porosity at lower temperatures than would otherwise be the case. The body offers more significant protection from gas leakage, which, therefore, only begins at higher temperatures. It has been regularly observed that this move towards higher temperatures is enough to make the glaze impermeable and consequently to cause bubbles².

To prevent pinholes, many vital factors should be taken into consideration. First, the body porosity should be sufficiently open to allow the release of gaseous flows. Next, the kiln firing must have an excess oxygen level to enable oxidation because various volatile compositions of carbon and hydrogen need to oxidize. Then, the responsible factor influencing the growth of pits is sulphur. The content of sulphur must be low for available oxygen, so sulphur can react hardly with carbon and hydrogen. At the end, the glaze must not melt too early because gases will become trapped under the viscous glaze. Moreover, if the glaze is too thick, any released gases will have a longer way to migrate, provoking the formation of pinholes.

In order to minimize pinholes, it is necessary to proceed as follows:

- Choose raw materials to ensure minimum gas leakage during firing (vitrification), i.e. introduce a specific oxide into a glaze such as wollastonite (CaSiO₃) instead of calcium carbonate, talc instead of magnesium carbonate and/or dolomite.
- Choose raw materials with particle dimensions that are not overly fine. This is especially significant for quartz and feldspars. Their high fineness reduces the underlying vitrification temperature of the glaze; it delays gas leakage from the body, thus increasing the risk of pinholing.

It should be remembered that there are numerous causes for the bubbles, and consequently the correct management of the firing process, especially vitrification, is essential, however, not necessarily enough to eliminate pinholing. An exorbitant value or a delayed exposure to the highest temperature can cause pinholing-reboiling in the glaze due to:

- Evaporation of alkali (sodium) in the body;
- Evaporation of alkali (sodium) in the glaze;
- Decrease of viscosity and surface tension in the molten glaze with maximizing of coalescence phenomena and subsequent explosion of gassy bubbles².

III. Crawling

When crawling happens, irregularly shaped zones that are either unglazed or only semi-covered ruin the consistency of the fired glaze. This non-conformity can range from one small uncovered region of the ceramic body to beading of the glaze or could be influenced by glaze surface tension²².

Another indication of this imperfection comes from the external edges of the retracted glaze, which are adjusted after the action of the surface tension. Typically, shrinkage of the glaze happens in the curved zone of the surface to be glazed, since here the glaze layer tends to be thicker⁴. Generally, the development of this defect is a crack⁶ (Fig. 3), shown as an interruption in the glaze covering the body. The reason for this can be of a mechanical nature, such as irregularity in the thickness of the glaze covering the body, leading to the formation of this defect, which has its rationale force in the surface tension⁴ (Figs. 4 & 5). Crawling is caused by:

- An interruption in the continuity of the thickness of the glaze;
- The progressive activity of the surface tension, which determines the shrinkage level of the glaze during firing

The reasons for the interruption in the thickness of the glaze are:

- Fast shrinkage of the glaze during drying. The drying conditions must be changed so that cracks in the weak coating do not occur^{22,23}. Tragically, many drying cracks are so small that they cannot be seen prior to firing. During firing, the material pulls back because of surface tension, inducing crawling. Shrinkage issues can likewise emerge from applying a subsequent wet coating layer before the primary layer is dry²². Magnesia may contribute to glaze crawling because it causes glaze dryness²⁴.

Excessive shrinkage of the glaze after it is applied can be brought about by unnecessary fineness of the particles that make up the glaze; thicker glaze particularly in the concave regions of the product, which will generally assimilate a higher quantity of glaze; presence of dust or granules in the surface of the body that can prompt shrinkage in the glaze^{4,5,25}.

- Poor grip between the glaze and the body caused by the presence of dust on the body which prevents good binding; inadequate wetting of the body by the glaze; incorrect application of the glaze; the aggregation of soluble salts on the surface of the body getting between the body and the glaze, which can cause the glaze to lift

during firing, soluble salts from the body can collect on the body surface. These salts can lift the glaze from the body, prompting crawling^{4,22,26}.

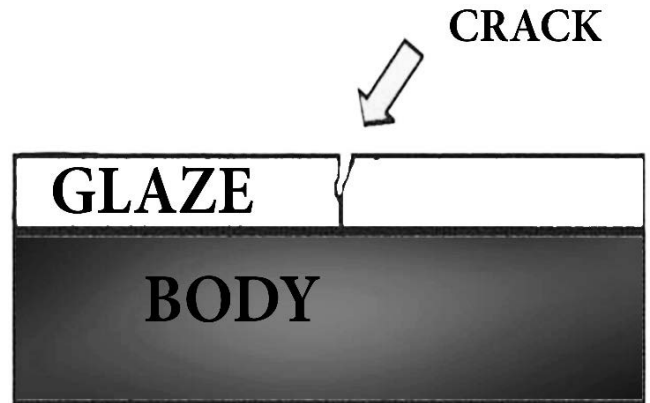


Fig. 3: Cracked glaze layer.

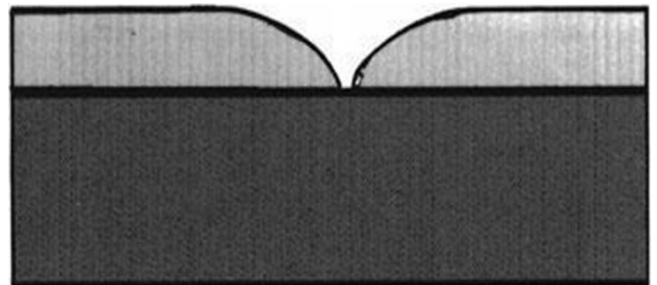


Fig. 4: Surface tension pulls the crack edges.

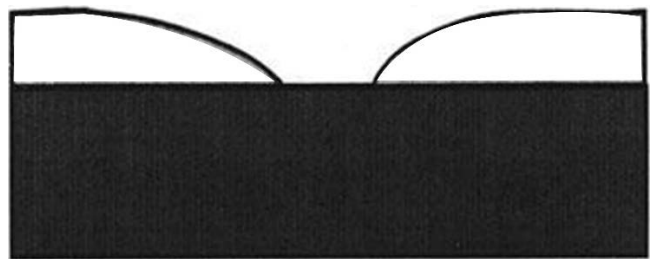


Fig. 5: Body left with bare area.

An increase in the firing temperature can lead to an increase in the glaze fluidity so that glaze may fill the crater again.

(1) The impact of glaze particle size

An increase in the surface tension is caused by increased fineness of the glaze as a result of extended grinding in the ball mill, which leads to many overly fine particles and ultimately to crawling^{27,28}.

The impact of glaze particles and thickness on crawling could be due to:

- A particle size of the glaze less than 1 micron, which can cause the glaze to become turbid or even crawl^{27,29}.
- An increase in the thickness of the glaze, which generally aggravates crawling²⁷.

(2) Impact of surface tension on crawling

High surface tension of the glaze is a major factor causing glaze crawling^{5,26}. This problem occurs when the

glaze contains a high amount of clay, an excessive amount of potassium [$K_2O \cdot Al_2O_3 \cdot 6SiO_2$] and calcium carbonate^{1,28}. At this level, $MgCO_3$, Al_2O_3 and $CaCO_3$ have a significant effect on the surface tension by increasing it²⁸. Furthermore, changing the chemical composition of the glaze may increase the high-surface-tension oxides, e.g. if magnesium oxide is replaced with barium oxide or alumina is increased and silicon oxide is reduced. Glaze pigmented with natural oxides can also suffer crawling³⁰. Such behaviour by the glaze is exactly that which, starting with a discontinuity of the covering layer, leads to glaze crawling^{4,27}.

Glaze crawling may also be caused by several accompanying reasons^{5,27}:

- An excessively thick glaze layer.
- Excessively fine glaze particles.
- Excessively high viscosity of the melted glaze.
- Too much alumina introduced into the glaze.
- Presence of soluble salts in the glaze or the body^{26,27}.
- A long cycle with a low temperature and a slow cooling process that does not allow the glaze to dissolve completely results in glaze crawling²⁸.

(3) Preventative measures

To reduce glaze crawling, it is necessary to consider the following measures:

- An inappropriate slip composition leads to crawling during firing. Glaze crawling might arise from shrinkage cracks. A slip with low shrinkage and high dry strength creates excellent resistance to crawling^{4,31}.
- Reduction of plastic materials in the glaze. Keep the clay content of the glaze as low as is reliable by substituting it with calcined kaolin to decrease shrinkage of the glaze while it dries. Avoid the use of ball clays and other highly plastic components, unless in low amounts because these materials increase the risk of crawling^{4,22}.
- Reduce the content of components consisting of very fine particles⁴.
- Avoid overgrinding the glaze slip. A finer particle size increases surface tension and likelihood of crawling^{4,22}.
- Minimize the levels of opacifiers used because opacifiers promote crawling²².
- Apply an adequate thickness of glaze particularly to concave surfaces. Keep the coating thickness to a minimum while ensuring acceptable coverage. Thicker glazes are more apt to crawl^{4,22}.
- Limit the presence of sulphates by adding a reasonable level of barium carbonate to the water as this makes them insoluble as per the following reaction⁴:



- Wipe the surface of the ceramic piece to remove any dust, oil or other impurities that could cause the glaze to lift off the surface.
- Reduce the heating rate in the pre-heating process.
- Prevent the development of dry glaze powders in any region of a sprayed piece during the glaze spraying of the first layer⁴.

- To combat the propensity to crawl, add a limited quantity of binder to the glaze. This hardens the green covering, preventing cracks that could become tears during firing²².

IV. Crazing and Peeling

Crazing and peeling are common defects in sanitaryware. The two faults are caused by significant differences between the expansion coefficient of the body and that of the glaze. If the glaze expansion coefficient is higher than the body expansion coefficient, this will cause tension in the glaze surface, leading to hairline cracks known as crazing. On the other hand, if the expansion coefficient of the body is higher than that of the glaze, this will cause compressive stress in the glaze surface, leading to the fracture of multiple glaze chips, a defect known as peeling^{5,8,32,33,34}.

Ceramics materials are brittle materials, with high resistance to compression. But they fail easily under tension. For that reason, crazing is the most common fault because it occurs when the ceramic materials face excessive tensile stress due to the mismatch of the thermal expansion coefficients of the body and the glaze^{4,18,22,23}. The thermal expansion coefficient is not the only cause of crazing, there are many other influencing factors⁷, such as the particle size distribution of the glaze³⁵. In general, crazing and peeling occur when the forces generated in the glaze (tension/compression) exceed the mechanical strength of the glaze^{4,7}.

During firing, an intermediate layer forms between glaze and body that has direct impact on the appearance of crazing and peeling. The composition of the intermediate layer depends on the body and glaze composition and the glaze properties during firing like the molten glaze viscosity and surface tension. In addition, it depends on the firing temperature and firing curve (highest temperature and dwell time at this temperature)⁴.

Many studies have been conducted to measure the strain between glazes and bodies of sanitaryware pieces. Measuring the strain is useful to prevent crazing, as the glaze and body composition can be adjusted depending on the measurement result, to ensure enough compression strain without crazing or peeling caused by excessive compression^{36,37}.

Varying glaze layer thickness has a significant effect on the surface of sanitaryware, resulting mainly in crazing. However, a minimum layer thickness is needed to cover the colour of the body in order to achieve a uniform colour surface. And there is a maximum permissible glaze layer thickness as otherwise the piece would present crawling or crazing^{4,37}.

During re-firing (heat treatment), the crazing appears when the thermal expansion of the glaze is lower than that of the body. Small cracks are exposed as the glaze shrinks during the cooling stage. In contrast, peeling occurs when the thermal expansion of the glaze is higher than that of the body.

In general, a glaze with a lower thermal expansion coefficient is better than one with a higher coefficient of thermal expansion. A ceramic glaze can withstand compressive stress better than tensile stress³⁸.

(1) Delayed crazing

In some cases, the glaze and body have matching thermal expansion and crazing does not occur during processing. Sometimes crazing happens in sanitaryware during storage or even after installation³⁹. This delayed crazing is caused by expansion of the body due to the absorption of water from humidity or of water during usage, this is called “moisture crazing”^{4,7,40,41}.

Another type of delayed crazing is frost crazing. This type of crazing is caused by two factors. The first factor is thermal shock of the ceramic piece when it is exposed to hot steam after its temperature has been very low during its previous service, in other words the ceramic piece is exposed to a sudden temperature change. The second factor is due to small changes in the size of the body when it is saturated with water during use and the weather turns cold, the water volume increasing as it turns to ice^{40, 42}.

The thermal shock crazing can generally be prevented by guaranteeing that the glaze is under sufficiently high compression to resist this type of crazing. The water absorption of the ceramic body does not affect resistance to thermal shock crazing directly but a high silica content in the body formula can improve its resistance to this type of crazing⁴⁰.

(a) Methods to prevent delayed crazing

1. Increase the maximum firing temperature to reduce water absorption^{4, 43}.
2. Change the glaze/body composition to adjust their coefficient of thermal expansion³⁹ and get a better match
3. Eliminate the unglazed areas in contact with water during design of the sanitaryware product⁴.

(2) Coefficient of expansion factors

Crazing and peeling of the glaze is related directly to the coefficients of expansion of the glaze and the body⁴². The factors that cause the internal tensile stress and strain in the glaze are:

1. Temperature differences between the body and the glaze during cooling or heating stages. When the cooling/heating rate is high, the tensile stress increases and vice versa^{4,39}. Crazing is considered to be a repeated process that happens during cooling depending on stress, strain, and temperature³⁴.
2. Difference in expansion coefficient between the body and glaze
3. High modulus of elasticity for the body and glaze increases the stresses in the glaze or body.
4. Differences in glaze thickness (non-homogeneous thickness) or higher glaze thickness forms higher stresses in the glaze (tension/compression)^{4, 37, 43}.

The Steger Tensiometer is an instrument that measures and calculates the tension in the glaze. This instrument gives a quantitative curve of the force that is generated in the glaze and allows you to recognize the type of stress (tensile or compressive) and evaluate its intensity⁴.

(a) Methods for measuring the coefficient of expansion

Measurement of the coefficient of expansion is a difficult process due to many factors that can affect the measured

value, for example material homogeneity, the firing conditions, and error of the measuring instruments³³. The coefficients of expansion can also be calculated based on the empirical formula calculation for raw materials, for example using Mayer and Havas factors. Other methods are used to evaluate the coefficients of expansion such as chemical analysis or testing techniques⁴⁴. The following are the most common techniques used to determine the coefficient of expansion⁴:

- Measuring method using a dilatometer applied directly on a fired sample (glazed ceramic cylinder measuring 5 cm in length). This technique does not directly return the value of the coefficient but gives information that can be used to calculate it.
- Calculation method using the Mayer-Havas coefficient for the individual oxides. The glaze coefficient is a result of summation of the coefficient of the oxides multiplied by their weight percentage or mole in the glaze composition.
- Calculation method using Hall's or Appen factors of linear thermal expansion. Hall's method depends on multiplying the percentage weight of individual oxide factors. Appen's method uses the mole percentage instead of weight percentage⁴.

All these methods give estimated values that are valid in certain cases. Appen's calculation is more valid for glaze that contains zinc oxide and Hall's calculation is suitable in the case of melting alkaline. However, both techniques are not valid for glaze compositions with a high content of calcium oxide. Moreover, testing methods are available to evaluate the crazing resistance of the ceramics, such as the Harkort autoclave test and the glazed rings method. Generally, the calculated thermal expansion coefficient is higher than the actual value obtained in experiments, which varies with the temperature⁴.

The autoclave is used to test ceramic pieces that have been exposed to moisture crazing or crazing due to body expansion in general. This is considered the best method in the international standards to determine crazing resistance in ceramic manufacturing, for example in the ISO standard for the ceramic specifications⁷. The glazed samples are placed in an autoclave and steam pressure is applied at a rate 150:175 lbf/in² for an hour⁴¹.

(3) Preventative measures

The elimination of crazing and peeling depends on controlling the root causes of the defect. The first step is to choose the suitable glaze and body coefficient of expansion and then to consider the delayed body expansion after firing and during the lifecycle of the pieces⁴. Lowering body porosity decreases its tendency to craze⁴³. Methods to improve crazing resistance (conversely peeling resistance)³⁵:

1. Decrease the thermal expansion coefficient of the glaze.
2. Use glaze with a high setting point, as higher-firing glazes usually have a lower thermal expansion coefficient.
3. Decrease the glaze thickness⁴³.
4. Increase the body thermal expansion coefficient by changing the body composition³⁹.
5. Grind the sand in the body²²

6. Use less plastic clay in the body, but more sandy clay³⁹.
7. Maintain the glaze particle size by adjusting the grinding weight ratio of material to grinding pebbles and the grinding duration³⁵.

Generally, to reduce crazing, it is necessary to modify the glaze formula as per Dr Seger⁴³. It is important when developing procedures to prevent crazing to consider the glaze composition so that it fits with the body composition, because the interfacial layer that is formed during firing between the body and glaze changes depending on the composition of the two components. The error in the expansion calculation should also be taken into consideration⁴⁵.

A perfect match between the glaze and body prevents crazing by maintaining the compression stress in the glaze in order for it to work safely. In other words, the preferred glaze thermal expansion coefficient is lower than that of the body. The compressive stress changes depending on many factors like the glaze mechanical strength and modulus of elasticity, the firing conditions, and the intermediate layer between glaze/body, body composition and body porosity (water absorption)^{4,7}.

An old rule to reduce crazing by increasing the silica content is not applicable in all cases. The ratio between the alumina and silica is important to prevent the formation of lower-alumina glazes, which lower the glaze tension stress but increase crazing because they also reduce glaze elasticity⁴⁵. In the case of glaze compositions containing zirconium oxide as an opacifier, the crazing resistance can be improved by using a high percentage of magnesium oxide⁴⁶. When soda feldspar and potash feldspar are used in a glaze composition and crazing occurs, the ratio between the feldspars must be optimized⁴⁷. Other studies have been performed on glaze with a high clay content and they conclude that zinc oxide and feldspar can improve crazing resistance. On the other hand, in this type of glaze the magnesium oxide, barium oxide, and calcium oxide may decrease the glaze crazing resistance. In general, glaze that contains magnesium oxide does not tend to craze, but in the extreme case when glaze contains 0.40 eq. MgO, the opposite effect has been observed³⁹.

V. Conclusions

Glaze defects occur during the manufacturing process. Each defect appears due to a combination of factors, and to eliminate the defect, all the factors must be considered before manufacturing. Glaze formula must be selected carefully based on consideration of the purity and type of materials used in order to prevent the harmful gases that cause glaze pinholes during firing. In addition, the glaze formula must allow for glaze shrinkage to reduce and eliminate glaze crawling. On the other hand, to ensure that the ceramic piece is not exposed to crazing or peeling, a glaze composition should be selected to match the thermal coefficient of expansion of the ceramic body.

This review provides a comprehensive study of the morphology of glaze surface defects, the factors that cause the defects during production and practical measures to eliminate such defects.

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