ADAPTATION OF INK AND GLAZE PROPERTIES TO APPLICATION SYSTEMS AND DECORATING TECHNIQUES

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1. INTRODUCTION

The glaze application systems and decorating techniques used in ceramic tile manufacture have evolved greatly over the last few years as a result of different factors. The need to launch new products onto the market with new aesthetic finishes to broaden the product range and heighten corporate competitiveness has fostered the irruption of new decorating systems, enabling effects to be produced that had until recently been considered extremely difficult or impossible to achieve. Environmental constraints have also affected the development of new application systems or upgrading of existing ones, to make them cleaner or reduce the waste that they produce.

Finally, economic factors continuously drive the need to produce a variety of low-cost, high-quality products, which requires improving glazes and glaze application techniques within the production system, as well as the materials and systems used to decorate the tiles.

The operation of some of these new systems is based on different physical principles from those used in traditional methods. In other cases they have involved greater or lesser changes to the system. These changes in system operating principles have been accompanied by changes in the materials used (glazes, inks, etc.), not just with regard to composition, chemical nature, etc., but to their physical characteristics, and particularly their rheological conditioning. It has thus been and still is necessary to adapt the glaze suspensions and inks used in tile decoration to the new application systems that have recently appeared on the market. This adjustment has often led simultaneously to the implementation of new systems, with little time to fully understand the physical mass transfer mechanisms involved. Work is currently still ongoing to optimise the physical characteristics and rheological behaviour of the materials used in the application and decorating systems already implemented in the branch.

In view of the importance of the glazing and decorating stages in ceramic tile manufacture, it is vital to have a thorough understanding of the optimum glaze and ink preparation and application conditions to obtain technically and aesthetically high-quality products with the highest possible productivity. As new glazing and decorating systems keep appearing, it is useful to systematically set out the available knowledge in this regard, not just to obtain the greatest benefit from techniques that have been or are being implemented, but to enable tackling the start up of new systems, requiring the adaptation of glazes and inks to their peculiar characteristics with a greater likelihood of success.

The purpose of this paper is therefore to describe how the characteristics have evolved of the inks and glazes used to coat and decorate ceramic tiles, in their adaptation to the successively arising new glazing and decorating techniques in recent years, as well as to indicate the ink and glaze characteristics required with systems that will foreseeably be appearing on the market in forthcoming years. The focus will mainly lie on the most widespread application principle, the wet method, without however neglecting dry, traditional or innovative application systems, which though not so widespread, also continue evolving and are indispensable to making certain products.

2. GLAZING

This section will deal with the different glazing techniques and the most appropriate glaze suspension or dry glaze characteristics for optimum application.

2.1 TRADITIONAL SYSTEMS

Most traditional application systems are by the wet method. However the use of granulars as base glazes, though not so widespread, deserves to be noted especially for achieving certain effects or products.

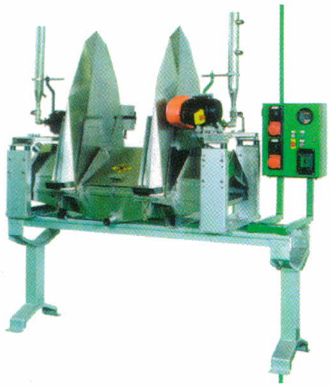


Figure 1. Discing machine.

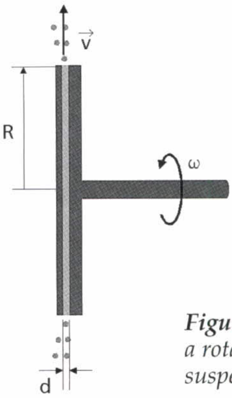


Figure 2. Schematic illustration of a rotating disc for glaze or engobe suspension application.

2.1.1 Application by the wet method

As is well known, the two traditional suspension application principles are spraying and waterfall application. Both have been historically used to glaze ceramic tiles by means of different machines, which have changed or evolved with time.

- *Spraying*

The spray application systems are based on the formation of droplets from a suspension, which are deposited on the ceramic tile surface next to each other, producing a continuous coating. The droplets can be formed by different methods, the most common being:

- Impelling the suspension by a centrifugal force.
- Forcing the suspension through a nozzle.

The first of these systems is used for applying certain engobes and glazes, especially the ones employed for coating floor tiles. Figures 1 and 2 depict an industrial facility that operates on this principle (booth with rotating discs), together with a schematic illustration of disc operation.

The systems based on the second procedure, known as airbrushing, are used to apply thin continuous coats as well as for the irregular deposition of small quantities of glaze, often coloured, with decorative effects. As this latter use is currently more common than the former, these systems and the characteristics of the suspensions involved will be dealt with in detail on the section on decoration.

As Figure 2 shows, an axial duct leads to the rotating disc, which feeds the suspension to the centre part of the actual disc. Once inside the disc, disc rotation impels the suspension to the rim, thorough which it exits as little drops whose size depends on the rotating speed of the disc (ω) and the distance between the plates of which it is made (d). To increase the quantity of applied glaze several discs are normally used, linked together at their flat side. This application system can give rise to an accumulation of glaze on one side of the tile, as a result of the rotating direction of the disc. To avoid this problem, two groups of consecutive discs are generally used, spinning in opposite directions, so that the possible excess glaze provided by the first disc on one side of the tile is compensated by the next one.

There are different factors in this type of application, which can condition the characteristics of the suspensions used. It needs to be taken into account that the suspension must be forced through some very small openings, without any clogging, backups, etc. to hinder the application. To avoid this problem, glaze viscosity at the shear rates it undergoes on flowing through the openings (500 s-1) obviously needs to be relatively low. Moreover, suspended solids particle size must be sufficiently small to keep the foregoing problems from occurring. The proportion of particles in the suspension shall also not exceed a given value, as an excessive solids content, besides raising suspension apparent viscosity can of itself produce greater clogging at the outlet openings. Summing up, the application method used requires the suspension involved to exhibit a low solids content (density), fine particle sizes and low viscosities at working shear rates (on flowing through the openings).

However, working with suspensions characterised as above can produce further problems. One of these can occur in the glaze storage containers at mill discharge and with the containers in the glazing line prior to application, and involves the possible settling of the suspended particles. Thus, on having a relatively low proportion of particles, they have a high tendency to settle, as water (the medium in which they are dispersed) also has a low viscosity (1 cP). To avoid this problem, it is necessary for the suspension to exhibit high apparent viscosity when the suspension is at rest or subject to low shear rates, thus lowering the settling rate.

To meet the two working conditions described it is thus necessary to have suspensions with high viscosities at low shear rates (at rest or with slight stirring) and low viscosities at high shear rates (on flowing through the disc openings). In other words, it is necessary for this type of suspension to exhibit a pronounced pseudoplastic character with a high yield stress. This also conditions the behaviour of the drops after they are deposited on the tile surface, so that on remaining at rest, their viscosity will rise noticeably, suppressing the problems relating to excessive suspension flowability, such as dirtying the tile sides. The problem of dripping is also reduced on the booth walls where drops are always deposited owing to the scattering of the sprayed glaze, which, if they exhibit low viscosity, can drip and fall onto the tiles being glazed.

Figure 3 presents the typical rheological behaviour of a glaze suspension for disc application and Figure 4 gives its particle-size distribution. Table 1 briefly sets out the most important parameters for these types of suspensions. As can be observed, they exhibit clearly pseudoplastic behaviour, high yield stress, low density and fine particle size, to match the constraints of the application system. It may also be mentioned that when discing takes place on vertical surfaces, as happens with some types of extruded tiles, this pseudoplastic character needs to become even more pronounced to keep the glaze deposited on the surface from sliding down by the force of gravity and affecting the aesthetic finish. It is therefore necessary for glaze viscosity to be very high at shear rates such as those produced by the force of gravity, which are low and much smaller than those the suspension undergoes on spraying.

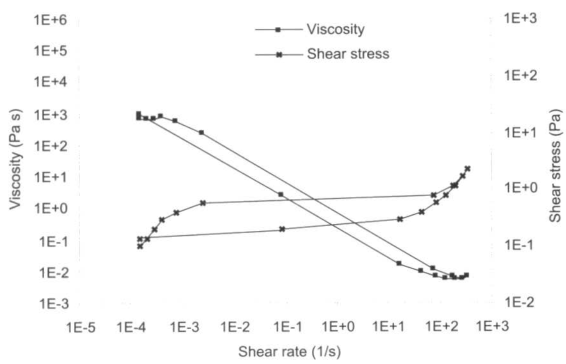


Figure 3. Suspension rheological behaviour for discing.

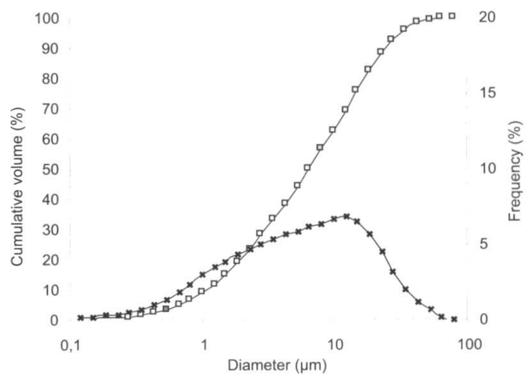


Figure 4. Particle-size distribution of a discing suspension.

Density (g/cm^3)	1.4-1.6
$\eta_{\gamma=0.1s^{-1}}$(cP)	4000-7000
$\eta_{\gamma=500s^{-1}}$(cP)	≅10
D_{50}(µm)	6-7

Table 1. Characteristic values of a discing suspension.

To achieve this pseudoplastic behaviour with high shear stress, suspensions need to be prepared in such a way as to remain partially flocculated. When they are subject to high shear rates, the mechanical action applied separates the individual particles and lowers suspension apparent viscosity.

The partial flocculation of the suspension can be achieved by regulating the amount of deflocculant used, i.e., without reaching the minimum possible viscosity or adding a deflocculant. Materials with a high specific surface and extremely fine particle size can also be used, which on presenting considerable colloidal activity substantially contribute to raising apparent viscosity at low shear rates or at rest. Any of these actions or a combination of them provides glaze suspensions with suitable properties for application by spraying with a system of discs.

- *Continuous waterfall*

This is the most widely used method for obtaining very smooth surfaces. It has attained its most far-ranging application in wall tile glazing, in which smoothness is a highly valued characteristic. Suspension application by a continuous waterfall is a process that has long been used, not just in the ceramic sector, but also in other industrial sectors, and there are a great variety of facilities based on this system: "filera", "filera valenciana", bell glazing, etc.

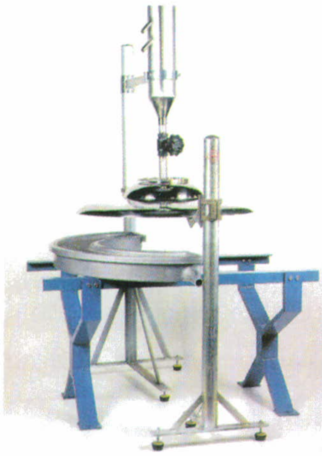


Figure 5. Bell application facility..

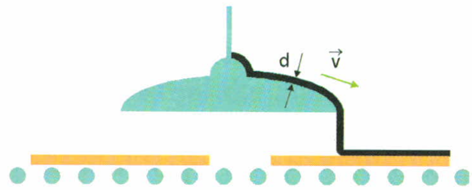


Figure 6. Schematic illustration of bell operation for glaze or engobe suspension application..

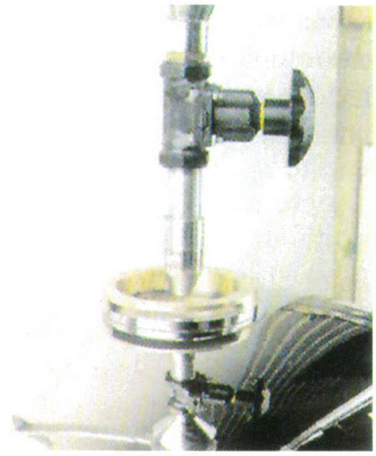


Figure 7. Detail of the bell glazing facility..

Amongst the waterfall application methods mentioned, bell glazing has become the most widespread system in the ceramic tile branch in recent years, as an alternative to discing to improve the surface texture of the glazed layer, making it much smoother and free of irregularities.

Figures 5 and 6 depict an industrial bell glazing facility and a schematic illustration of its operating mechanism. It can be observed that after pumping the suspension to the vertical pipe at the top of the system, it flows down inside the pipe by gravity. The suspension flow rate can be regulated by the corresponding valve (Figure 7). The suspension flows from the pipe through a vessel from which it overflows onto the top of the bell surface, freely sliding down to the bell rim from which it drops as a continuous waterfall.

A system is currently being developed and fine-tuned for a self-regulating flow rate of the suspension over the bell. This works using a sufficiently accurate flowrate meter, which continuously measures the flow of the applied suspension and depending on its value, sends the corresponding signal to a flowrate regulating valve. The valve is considerably more accurate than the one currently used in bells and enables the quantity of glaze or engobe to be adjusted with great accuracy.

The characteristics of this application system are obviously quite different from those of the discs. Suitable suspensions will therefore also need to have quite different behaviour. In the first place, as there are no openings for the suspension to flow through, there is no possibility of clogging. Rather, the fact that the suspension falls by gravity makes it advisable for suspension viscosity to be relatively high, to avoid problems of swings in the flow of the curtain, which could produce non-homogeneity in the glaze layer. This in turn allows using high densities, unlike the discing suspensions.

It is therefore necessary to make up suspensions with high solids contents as well as high viscosities at the shear rates the suspension undergoes on leaving the bell (1000-1500 s^{-1}). Unless it is completely deflocculated, a suspension with these characteristics exhibits high yield stress and thixotropic behaviour, i.e., its viscosity tends to rise considerably when at rest or subject to low shear rates, such as those produced by the force of gravity.

As the suspension only flows by the force of gravity in the feeding system to the bell and when it slides over the bell, it is very dangerous for its viscosity to rise too much, as it could be held up at any point in the process. If this occurs, the break in flow will immediately produce faults in the glaze coat. Moreover, the retained part of the suspension can subsequently become detached, be drawn along by the rest of the suspension and drop onto the tile, deteriorating the surface.

To avoid such problems, it is therefore necessary for suspension viscosity at low shear rates not to be much higher than at the shear rates arising when the suspension drops from the bell rim. The suspension shall also not be very thixotropic, to keep viscosity from rising with standing time, which would contribute to material retention if the suspension stopped flowing. This is the same as saying that the suspension shall have the most Newtonian possible behaviour and have low yield stress for it to flow easily.

Figure 8 depicts the typical rheological behaviour of a suspension conditioned for bell application, and Figure 9 shows its particle-size distribution. Table 2 presents the values of the most significant parameters of this type of suspension. It can be observed that the yield stress is low, that the viscosity at medium and low shear rates (10-1000 s^{-1}) is not very different (revealing its eminently Newtonian character), and that there is a small thixotropic area. If these are compared to the data corresponding to the disc application, the suspensions are observed to exhibit high density and viscosity values (at high shear rates), as indicated above.

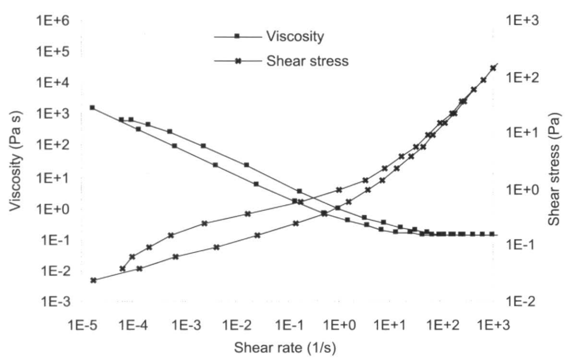


Figure 8. *Rheological behaviour of a suspension for bell application.*

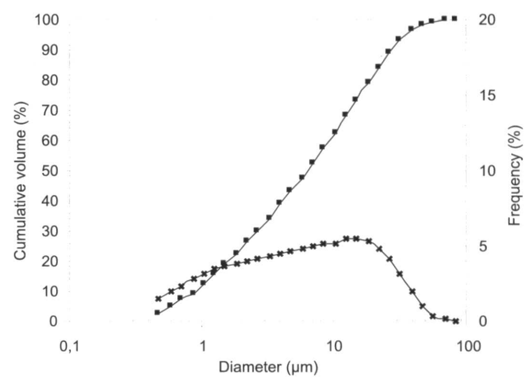


Figure 9. *Particle-size distribution of a suspension for bell application.*

Density (g/cm^3)	1.8-1.9
$\eta_{\gamma=0.1s^{-1}}$(cP)	2000-4000
$\eta_{\gamma=1000s^{-1}}$(cP)	100-200
D_{50}(μm)	6-7

Table 2. *Characteristic values of a suspension for bell application.*

These application conditions make it essential for the suspension to be well deflocculated, as the particles are then deagglomerated at low shear rates, exhibiting lower apparent viscosity. This means that deflocculation needs to be very strictly regulated, to ensure the lowest possible viscosities at all shear rates, working at solids contents (densities) that are as high as the process allows. For this reason, continuous waterfall applications generally require a greater level of attention and care than spraying applications.

The characteristics described also allow the suspensions, on being deposited onto the tile, to spread readily over the tile to ensure the sought-after smooth finish, however without surface waviness or dirtying of the tile edges. Furthermore, the resulting unfired glaze layer is not very porous and highly compact, owing to the low water retention between the glaze particles, as a result of low particle agglomeration when the particles are deposited on the tiles. This makes the drying rate of these glaze layers slow and gives them low permeability, compared to the coats formed from sprayed suspensions, as these are more porous and permeable owing to their low density and partially flocculated state.

Finally, a typical waterfall application problem may be mentioned here, which can considerably impair the quality of the resulting coat: bubbles produced and retained in the suspension. The origin of the bubbles is usually entrained air from mechanical conveying actions, stirring, pumping, etc. If the bubbles are not removed before application, they produce irregularities in the waterfall curtain and can become a glaze fault after the tile has been fired (pinholing, dunts, etc.). As the viscosity of these suspensions is relatively high, it is difficult to remove the bubbles, as they can only rise with difficulty to the surface of the containers in which the suspensions are stored. From this point of view, it is advisable to produce as few bubbles as possible, analysing the points in the process at which they could form and reducing their frequency. From a strictly rheological standpoint, working with deflocculated suspensions with high densities is also beneficial, as these conditions most facilitate bubble removal.

2.1.2. Dry application

In general, dry glaze application is done to achieve decorative effects or to protect the base glazes, so that it appeared more suitable to deal with this in the section on decorating. However, there is at least one type of glaze that is applied dry to produce a continuous glaze coat, and which has recently become quite popular: the so-called "polishable glazes". For this reason, the characteristics of some glazes that are applied dry will be briefly discussed here.

These glazes are usually found as granulars, a product obtained by dry milling the frits to different particle-size distributions depending on the targeted type of effect. A great variety of granular sizes are currently marketed: 0.1-0.3 mm, 0.2-0.6 mm, 0.2-1.2 mm, etc. The tendency has been for their average sizes to decrease as market characteristics have evolved.

Figure 10 depicts an industrial granular application facility for decorative effects or continuous coating. The appropriateness of the application is clearly conditioned by the flowability of the material to be applied, a property that relates to particle-size distribution and shape. To improve flowability, products have been developed with rounded shapes by granulation or by thermal softening, which allow the glazes to be

Figure 11. *Rectilinear continuous waterfall application facility.*

Figure 10. Granular application machine.

applied faster with better control. These types of products are now commercially available and represent an alternative, with their advantages and disadvantages, to the traditional granulars.

2.2 NEW SYSTEMS

Some of the new application techniques that have appeared on the market and which are still being optimised for definitive implementation will be dealt with in this section. A brief description is also included of some alternatives to the traditional systems, which although they may at present appear difficult to adapt to ceramic products, deserve to be considered as future options.

2.2.1. Wet application

The most significant recent innovations basically refer to the continuous waterfall application and the appearance of a new system based on mass transfer by contact, using a principle similar to that of rotogravure.

- *Continuous waterfall*

One of the traditional continuous waterfall applications was the so-called "filera", in which the suspension flowed by gravity through split between two flat vertical sheets, which could be moved closer together or separated. This system, which had not been used for years, has recently been revived in a machine based on the same operating principle, but in which the suspension flows under pressure to ensure a constant application flow rate. Figure 11 depicts such a machine. The suspension is pumped to the top of the machine and fed under pressure into the gap between two vertical sheets that form the actual application system. It then flows through the opening between these at the bottom, which can be regulated by a micrometric system. The machine is also fitted with a flowrate meter to continually measure suspension flow, thus allowing the applied quantity to be regulated, and if variations are detected, enable making the appropriate adjustments by acting on the feeding pump. These adjustments need to be performed manually.

The use of pressure means that in principle, one of the inherent problems of the traditional "filera", namely swings in suspension flow, can be noticeably reduced. Moreover, as flow takes place under pressure, the suspension is subject to relatively high shear rates, which should allow working with relatively pseudoplastic suspensions without the risk of flow retention as a result of excessive viscosity. This therefore involves the possibility of working at high densities, so that although for this reason, even though the suspension is well deflocculated, it can exhibit high viscosities at low shear rates, on undergoing forced flow it will flow appropriately. In other words, only the viscosity at high shear rates will limit the application possibility and condition the suspension solids content.

The other factor that also needs to be closely controlled and adjusted is particle-size distribution, as the glaze must pass through a relatively narrow gap. To avoid clogging, the particles in the solution therefore need to be sufficiently fine to keep this from occurring.

Summing up, this system requires using suspensions with a fine particle size, high density and optimum deflocculation. The particles can then be individualised as much as possible. Thus, although they tend to agglomerate at low shear rates or at rest (which should not be an important problem, given application system characteristics), the force applied to the suspension will be enough to deagglomerate them and reduce their apparent density to working limits.

This application system is currently being optimised with regard to the most appropriate suspensions to be used as well as to the machine itself.

- *Contact transfer*

This is a technique that is being developed for glaze application, although it is already quite widely implemented for producing decorative effects, as will be discussed below. The system is based on the rotogravure technique and is shown in Figure 12. It consists of two rolls that turn in opposite directions, arranged one behind the other according to the travelling direction of the tiles to be glazed (Figure 13). The surface of the first roll, which turns in the same direction as tile advance contains a series of small cavities (with an average diameter of between 100 and 400 μm), arranged next to each other with a minimum spacing. The glaze suspension is fed in at the top of the roll, and spread by a squeegee, helped by roll rotation, so that it enters the cavities. The surplus material is removed by the distributing squeegee. Thus, when the roll enters into contact with the tile to be glazed, the glaze is held in the surface cavities, transferred by contact to the tile and deposited on the tile surface. Given the great number of points marked on the roll, when the glaze

Figure 12. *Rotogravure glazing system.*

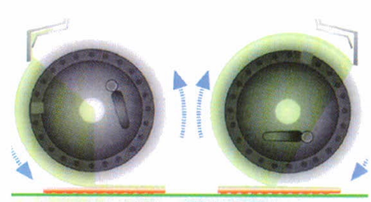


Figure 13. *Schematic illustration of the rotogravure.*

held in the cavities is transferred to the tile, a practically continuous glaze layer forms.

To achieve a smoother, more compact layer, the second roll with a smooth surface, turning in the opposite direction to the first one, lightly presses the material applied as dots so that their shape vanishes completely. As a similar system is being used to decorate tiles, it will be dealt with in further detail below. However, the importance is to be noted of some of its elements, such as the shape and dimensions of the cavities on the roll, or the adjustment and shape of the squeegee, as well as its hardness and contact angle. With regard to the first of these factors, this is especially critical for a good application of a glaze layer of considerable thickness, since the cavities need to be sufficiently deep to hold an appreciable quantity of suspension, and their shape subsequently needs to encourage transfer of all this material to the tile when the roll enters into contact with the tile. As to the squeegee, it needs to be well adjusted to wipe the material that has not entered the cavities off the surface of the roll, to prevent uncontrolled amounts of suspension from being added.

This system is not currently being used industrially, having only been built for some types of mosaic tiles. For this reason, the optimum conditions for the suspensions involved are not exactly known for correct application with this technique. However, given system characteristics, and in view of the first results obtained with the system, a series of considerations can be made regarding required glaze behaviour for rotogravure application.

While the suspensions are held in the roll cavities, they are at rest or subject to very low shear rates. They also need to enter and leave the cavities easily, on contact with the tile body. Finally the smoothing action of the second roll shall readily deform the portions of suspension deposited in the form of points by the first roll. In this sense, it is also convenient for suspension viscosity to be such as to allow the suspension to spread slightly by itself on being deposited on the tile, thus facilitating the formation of a continuous layer.

The above suggests that in general, the viscosity of these suspensions should not be too high, to permit suitable cavity filling and allow the material to leave the cavity just by adhering to the body. In other words, their yield stress should not be high and the variation of viscosity with shear rate should therefore not be too pronounced. The suspensions should not be thixotropic either, to avoid excessive rises in viscosity when the suspension is at rest in the cavities or on the tile surface. As the solids content needs to be high, to reduce the quantity of water contributed to the tile and hence the drying rate of the applied layer, the only way to achieve this behaviour is by deflocculating the suspension to the minimum possible viscosity. Thus, the characteristics of the suspension to be applied by rotogravure will resemble those used in bell glazing: high densities and optimum deflocculation, which from a rheological viewpoint means Newtonian-like behaviour in the working range with low yield stress.

As will be discussed further below, this is the rheological behaviour of the inks used in rotogravure for decorative purposes, albeit with certain peculiarities. However, although in this case daily practice appears to confirm the theoretical assumptions, the same cannot yet be said of glaze application, given the absence of an industrial implementation. It will therefore be necessary to wait for this to happen to verify the theoretically appropriate operation of the suspensions with the foregoing properties.

2.2.2. Dry application

The alternative dry glaze application methods to the traditional procedures make use of techniques employed in other industrial sectors, seeking to adapt these to the needs and characteristics of ceramic products. To be highlighted amongst these, having already obtained results on a semi-industrial scale, is the electrostatic application.

This technique is based on spraying dry glaze particles with a certain electric charge onto the surface to be coated, which has been given an electric charge of the opposite sign. The sprayed particles are then deposited on the surface owing to the arising electric attraction between the two components.

The difficulty of the procedure lies precisely in the need to charge ceramic materials, which have a very low electrical conductivity. This requires using additives in the glaze powder, which can be readily charged and provide the whole material with the necessary properties. On the other hand, the particle size needs to be very fine, to be easily put through the nozzle of the spraying gun without clogging. Moreover, electrostatic application, whose main advantage lies in the total elimination of water from the glazing process, exhibits a further series of problems not directly related to the purpose of this study, which need to be resolved to allow its use to spread: consistency of the formed layer, green bonding, removal of the additives used without generating waste, etc. Nevertheless, this technique deserves to be considered for future use as an alternative to the existing application systems, and it could be interesting to develop it further.

3. DECORATION

Decorating systems are described below together with the characteristics of the suspensions used.

3.1 TRADITIONAL SYSTEMS

The most widespread ceramic tile decorating methods involve wet applications, although a few dry application methods are used which will also be discussed.

3.1.1 Wet application

Screen printing is the most common wet decorating technique, in flat or rotary

Figure 14. Flat screen printing machine.

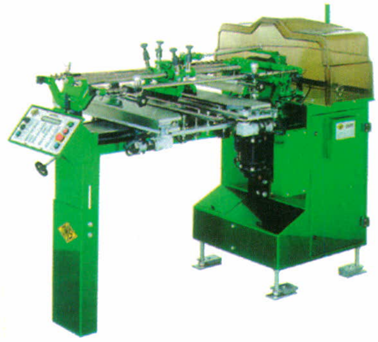


Figure 15. Rotary screen printing machine..

versions, based on mass transfer by contact. Airbrushing is also used for decorative effects, which is a system with quite a concomitance, with regard to the suspensions to be used, with the disc application described above.

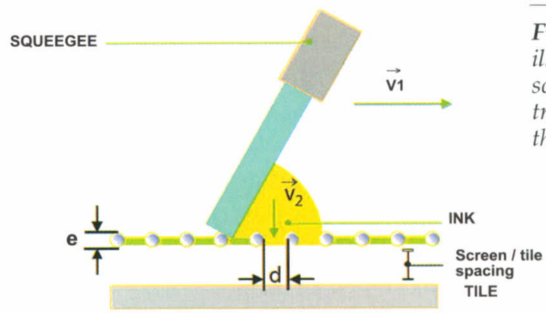


Figure 16. Schematic illustration of the screen printing ink transfer mechanism through a screen.

- *Screen printing*

Screen printing involves forcing a paste or ink through the holes of a screen, which form a pattern or design, by means of a mechanical system known as a squeegee. The screen can be flat or curved. Figures 14 and 15 respectively depict a flat and rotating industrial screen printing machine. The screen printing ink is deposited on one side of the flat screen surface, spread across the screen, and when the tile lies below the screen the squeegee presses the ink through the screen openings, depositing it on the tile. Figure 16 presents a schematic illustration of this transfer mechanism. In the case of the curved screens, the cylinder turns and the squeegee stands still, though the end effect is the same with the material being forced through the openings and deposited on the tile surface.

There has been a progressive tendency to use ever-smaller size openings to achieve more complicated decorating effects with greater sharpness. This has led to an important evolution in screen printing ink preparation in order to obtain rheologically well conditioned materials with fine, controlled particle sizes, free of agglomerates.

Particle size is critical to keeping part of the ink from being held back on the screen, on not passing through the openings. If this occurs, the screen needs to be regularly cleaned, and the resulting aesthetic effect will not be the desired one, owing to part of the material being left behind on the screen. It is therefore necessary to adjust particle size, especially the larger sizes to the mesh aperture. This requires suitably milling the ink components (frits, pigments, etc.), reducing their size below 40 μm, and after mixing them with the corresponding screen printing vehicles, ensuring agglomerates do not form, and if they do, breaking them up.

Specially designed systems are currently marketed for deagglomeration, which force the ink between pressing cylinders that eliminate any lumps. To have the appropriate effectivity, starting solids particle size in the ink must be sufficiently fine. If this is not the case, it is necessary to mill the ink by milling systems that allow reducing particle size in viscous suspensions such as screen printing inks. Different fine milling systems are available. The most widespread one in the ceramic industry is the so-called bead mill, involving the use of very small beads (1-2 mm) as grinding media. The ink is poured into the gap, which also contains the beads, between a central rotor and a fixed outer wall. When the rotor turns, the ink undergoes vigorous shear owing to the rotating motion and the beads in the ink, producing particle comminution.

Besides the foregoing, the screen printing ink also needs to be suitably prepared from a rheological point of view. In the first place it is necessary to consider the very high shear rate that the ink undergoes when it crosses through screen openings, around 10.000 s^{-1}, and under these conditions ink viscosity shall be quite low to avoid clogging. At the same time, on being deposited on the screen, before being forced through the openings, ink viscosity needs to be high to keep from flowing through the openings too soon. Furthermore, when the ink is deposited on the tile, it also needs high viscosity so as not to lose sharpness. And finally, suspension apparent viscosity shall drop very quickly when the squeegee is applied to the ink to force it through the screen openings.

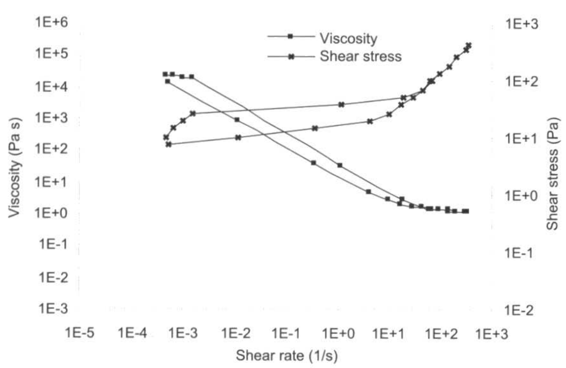


Figure 17. Rheological behaviour of a screen printing ink..

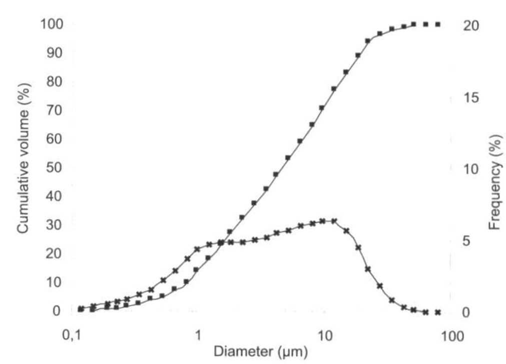


Figure 18. Particle-size distribution of a screen printing ink.

Mesh aperture (thread count)	36	68	77
Density (g/cm^3)	1.7-1.9	1.6-1.7	1.6-1.7
$\eta_{\gamma=0.1s^{-1}}$ (cP)	$\cong 10^5$	10^4-10^5	10^4-10^5
$\eta_{\gamma=1000s^{-1}}$ (cP)	$\cong 10^3$	$\cong 10^3$	$\cong 10^3$
D_{50}(µm)	4.5-5.5	4.5-5.5	4.5-5.5

Table 3. Screen printing ink characteristic values.

All these conditions mean that screen printing inks need to exhibit pseudoplastic behaviour, with high yield stress, as shown in Figure 17, which corresponds to the rheological behaviour of one of these materials. Figure 18 presents the particle-size distribution of the same ink, and Table 3 lists the values of the most significant parameters for this type of suspension.

If these values are compared to those of suspensions for bell application, a noticeable difference can be observed from a rheological viewpoint. Although inks usually have a slightly lower solids content, ink viscosity is much greater across the whole range of shear rates, as befits the application. Such behaviour is a direct consequence of dispersing a high concentration of very fine solids in a liquid. Although this liquid (the screen printing vehicle) should hardly interact with these solid particles, the water it contains does so to a certain extent, contributing to particle agglomeration especially at low shear rates, thus substantially raising the yield stress and pseudoplastic character of the resulting suspension. In the case of the suspensions used in bell applications, deflocculant additions lower suspension pseudoplastic behaviour, making it more Newtonian; in screen printing inks, as the first behaviour is required, deflocculant additions are not required for correct application.

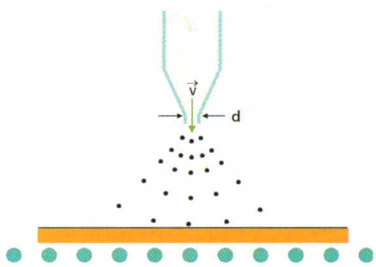
On the other hand, the fact of using screens with very small mesh apertures basically leads to a slight reduction in suspension solids content, which helps avoid clogging of the screen openings during use. This also reduces apparent viscosity at low shear rates as a result of less particle agglomeration, although after individualising them by the corresponding mechanical action, the resulting viscosity at high shear rates exhibits no great differences.

- *Airbrushing*

Airbrushing involves spraying the suspensions by forcing them through a nozzle (Figure 19). Spraying can take place by using pressurised air (Venturi effect), or by impelling the suspension through the nozzle by a pump. The former procedure, which was extensively used for many years, causes spraying by generating a multitude of droplets (aerosol effect), which besides being deposited on the tile surface are also widely scattered in the ambient. However, the latter procedure sprays the suspension without contributing additional air. This focuses the droplets that are produced mainly in the direction in which they exit the nozzle, appreciably lowering ambient scattering. This is a significant example of system modification directly affecting ambient conditions in the workplace, besides involving an important technical improvement.

For these reasons, traditional airbrushes are fitted in a booth that holds the nozzle (Figure 20), to contain ambient scatter of the arising drops.

Figure 19. Schematic illustration of the airbrush operation.



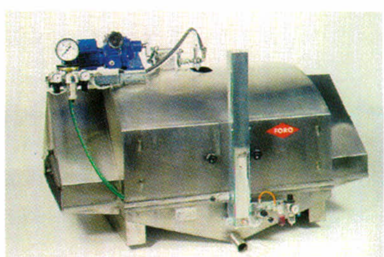


Figure 20. Airbrushing equipment.

The characteristics of the suspensions to be applied by airbrushing are very similar to those applied by discing, given the obvious similarity between both systems.

The particle size also needs to be fine to avoid clogging the nozzle and have a low solids content, while the suspensions shall exhibit pseudoplastic behaviour with a high yield stress to avoid settling in the storage containers or producing faults in the glazed tile. This all involves rheological conditioning similar to that described on dealing with discing. What was said there is generally valid for this case. It should be highlighted however that it is very important to keep lumps from forming inside the nozzle and clogging it. This requires impelling the suspension with sufficient force to keep agglomerates from forming in the nozzle feed, or if they do form, to make them deaggregate by the flow itself, without remaining in the piping and reaching the nozzle. Besides this, as stated, the considerations made in the relevant section on discing also hold for airbrushing.

3.1.2. Dry application

The use of granulars is perhaps the most important dry application for decorative purposes. Independently of the specific aesthetic effect, for an application point of view please see point 2.1.2 of this paper, as the same product and the same systems are involved.

Other alternative dry glaze application systems for decorative purposes use different methods, which vary widely depending on the targeted effect, however it would make this study too protracted to detail them here. It may simply be said that they use particulate materials, generally with a fine particle size, whose main requirement is good flowability so that there are no faults in application to impair the sought-after decorative effect. In other cases, materials with larger-size particles are applied to protect or raise the hardness or abrasion resistance of the tile surfaces.

Dry screen printing deserves special mention, used for special decorative effects in third firing, etc. In this case, particle size and flowability are even more critical to ensure correct application. Furthermore, particle shape also needs to be suitably regulated to favour solids passage through the screen openings, reducing on-screen retention to the greatest possible extent. Certain products have recently appeared in this sense, which act as fluidisers for dry powders and foster their flow in applications of this kind.

3.2 NEW SYSTEMS

It is possibly in the field of decoration where the greatest innovation in ink or suspension application methods has occurred. Perhaps the need to produce ever-more complicated and sophisticated effects has led to the search for systems based on different principles from traditional ones, often implemented in other industrial branches. Given their recent appearance in the ceramic sector, they are still undergoing optimisation and the most appropriate conditions that inks need to exhibit for correct application are still being studied.

Figure 21. Printing roll of a rotogravure decorating.machine.

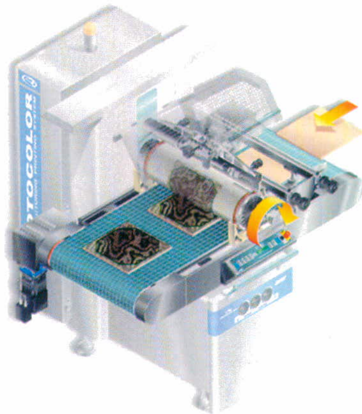


Figure 22. Rotogravure decorating machine.

- *Rotogravure*

This is a technique based on the same principle set out in point 2.2.1, using a roll (Figure 21) with a series of cavities made on the surface by a laser system, which together define the design to be transferred to the tile. The diameter and depth of these cavities are established when the cylinder is etched.

Figure 22 shows a rotogravure application machine. The ink is deposited at the top of the roll and spread over the surface with a squeegee, which also forces the ink into the cavities of the roll and wipes the rest of the surface clean. When the roll enters into contact with the tile, the ink is transferred from the cavities that hold the ink to the tile, owing to its greater adhesion to a porous surface such as a green or biscuited tile.

The importance of certain system variables has already been highlighted in the corresponding section, such as the type of cavity or squeegee adjustment. In the case of decoration, squeegee adjustment is critical to regulating the quantity of ink fed into the roll cavities and subsequently transferred to the tile. Thus, after adjustment to eliminate the surplus material, the greater or lesser proximity of the squeegee will raise or lower the amount of ink entering the cavities, and the same will occur on modifying the contact angle between the two elements. In practice, squeegee adjustment has been found to be decisive to achieving not just a decoration free of faults (smears, lack of sharpness, etc.), but also the adjustment of the deposited ink, which is ultimately what determines the colour of the decorated tile.

With regard to the characteristics to be exhibited by the suspensions for rotogravure application, even though they have not been optimised, they can be defined in general lines. Their behaviour shall meet the needs set out on describing the glaze application system based on the same rotogravure technique. Thus, the inks shall have a low yield stress so that they can readily leave the roll cavities and a relatively low viscosity at working shear rates (1000 s^{-1}). This indicates a Newtonian type of behaviour in this working range as shown in Figure 23. The very scarce thixotropy of these types of inks can also be observed to avoid excessive rises of viscosity when at rest, which hinder cavity discharge. Figure 24 presents the particle-size distribution of this ink and Table 4 gives the values of the most representative parameters of the behaviour of this type of suspension.

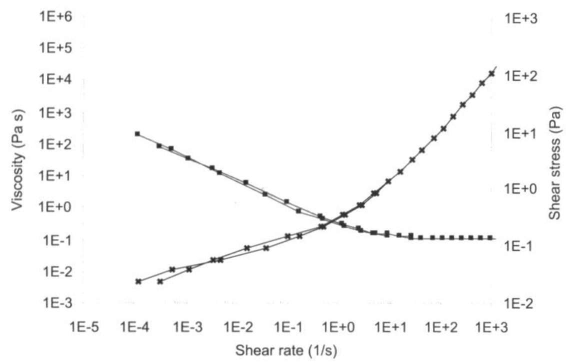


Figure 23. *Rheological behaviour of a rotogravure ink.*

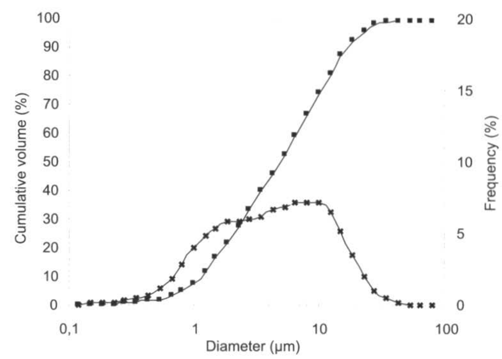


Figure 24. *Particle-size distribution of a rotogravure ink.*

Density (g/cm^3)	1.4-1.6
$\eta_{\gamma=0.1s^{-1}}$(cP)	1000-5000
$\eta_{\gamma=1000s^{-1}}$(cP)	≅100
D_{50}(µm)	5-6

Table 4. *Characteristic values of rotogravure inks.*

If these values are compared to those of a conventional screen printing ink, it can be observed that conventional ink viscosity is much higher and that it exhibits a more pseudoplastic character, with a higher yield stress as a result of application requirements. The fact of having to work at lower viscosities, with a low yield stress, makes it necessary to reduce rotogravure ink solids content, so that the solids dispersion in the vehicle does not excessively increase the pseudoplastic character of the suspension.

Ultimately, if they are carefully analysed, it can be observed that the characteristics of these types of inks are very similar to those used in bell glazing, although in this case, these properties are reached by working at high densities and deflocculating, whereas in the rotogravure suspensions, lower working densities are used without deflocculation with more viscous vehicles than water.

Before concluding this section, it is worth repeating that work is currently ongoing to achieve a deeper understanding of the particularities of this type of application, which will provide a greater knowledge of the properties that the suspensions need to exhibit to be appropriately adapted to this application.

- *Flexography*

Similarly to the technique described in the previous point, this is a system based on mass transfer by contact. However, the operating principle is just the opposite. In this case, the ink is not retained in the cavities of the cylinder, but in a profile. The system (Figure 25) consists of a smooth roll on which a polymer sheet is fixed (Figure 26), which presents a profiled area corresponding to the design to be reproduced.

Figure 25. Flexography decorating system.

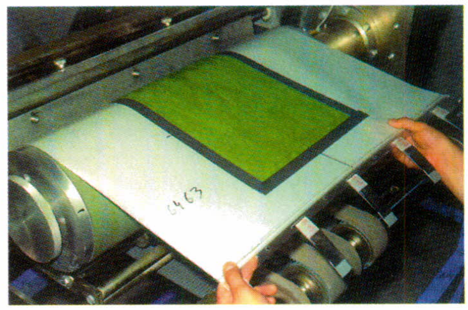


Figure 26. Polymer sheet etched with the design to be reproduced.

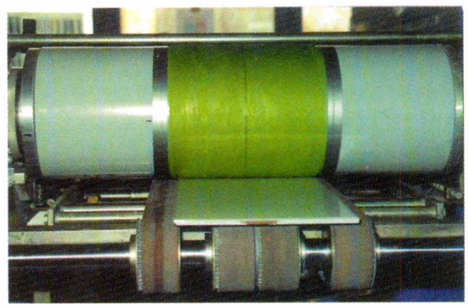


Figure 27. Tile printing by flexography.

After arranging the sheet on the roll, it is brought into contact with a suspension-proportioning roll, so that the surface profile becomes impregnated with the suspension. When the roll, owing to its own rotation, subsequently enters into contact with the tile (Figure 27), it transfers the ink it bears onto the tile, producing the print.

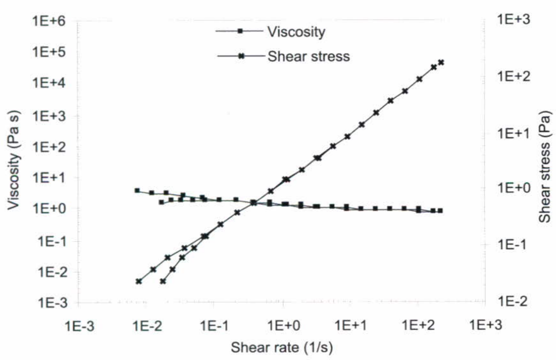


Figure 28. Rheological behaviour of a flexographic ink.

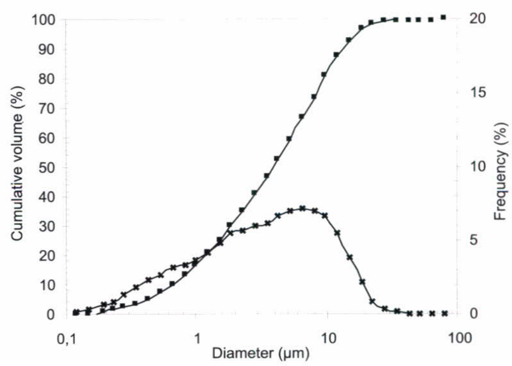


Figure 29. Particle-size distribution of a flexographic ink.

Density (g/cm^3)	1.5
$\eta_{\gamma=0.1s^{-1}}$ (cP)	≅5000
$\eta_{\gamma=100s^{-1}}$ (cP)	≅1000
D_{50}(µm)	3.5-4.5

Table 5. Characteristic flexographic ink values.

Facilities based on this technique are currently starting to be installed and put into operation, so that they are still going through an optimisation stage, just like those based on rotogravure. It should be remembered however, that a system appeared on the market some years ago, whose operating principle was also flexography, although the roll itself was etched in that case, not a polymer sheet, and the system achieved no significant implementation in the ceramic sector.

Figure 28 presents the rheological behaviour of a suspension used in this type of machines and Figure 29 gives its particle-size distribution. Table 5 sets out the values of the most significant parameters of this type of suspension.

It can be observed that the behaviour of these suspensions is slightly pseudoplastic with relatively similar viscosity values at different shear rates. Their yield stress is quite small and they hardly exhibit any thixotropy. These characteristics are similar to those of rotogravure inks, as they ultimately have to meet analogous requirements: relatively high viscosity at low shear rates, so that the ink does not leave the polymer relief before entering into contact with the tile, or slide down the proportioning roll.

It is however still early to be able to accurately define the most suitable conditions for flexographic inks, owing to their current minor degree of implementation. As the system becomes more widespread, more experience will become available to determine optimum running conditions.

- *Ink jet printing*

Unlike the foregoing two methods, whose implementation is in a more or less advanced stage, there is another method, which is at present just a future possibility, whose feasibility has yet to be adequately analysed. The procedure has been used in other fields for years, as in graphic printing, where it is quite widespread. Some trials have been run in the ceramic sector, not just with ceramic tiles, and development is still in a very early stage.

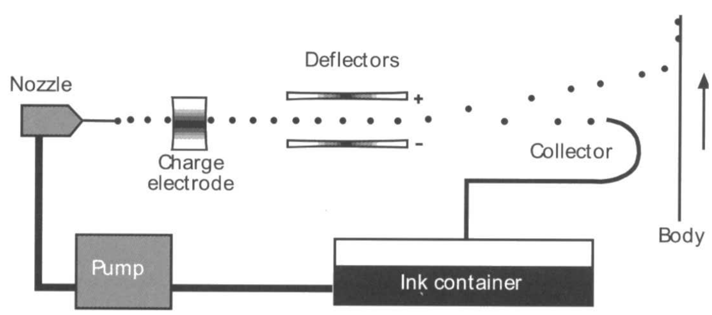


Figure 30. *Schematic illustration of the jet ink printing procedure.*

Figure 30 presents a schematic illustration of the ink jet printing method. Ink is forced through a nozzle, which sprays it in a jet of droplets that must reach the substrate and produce a design on the substrate. In this case, unlike other procedures, the droplets must be deflected so that they impact the substrate at different points to create the desired design. This action can be combined with the movement of the substrate, yielding more complex decorations.

An electric system is used to deflect these drops selectively. First, when the jet breaks up into droplets, these are subjected to the action of certain electrodes that charge them electrically by induction, the charge that each drop acquires varying according to the voltage applied to the electrodes when the drops form. The drops then pass between deflecting plates that generate an electric field in this area and therefore deflect the drops to a greater or lesser extent, depending on their charge. Thus, varying the charge by means of a charge electrode regulating system, the deflection of the drops on being subjected to an electric field can be controlled. Moreover, if some drops are not to reach the body, they are left without a charge, so that their movement is not altered by the electric field. They are then collected and recycled by a recovery system. The definitive design is thus achieved by acting upon this charge - charge-less system.

Independently of the process variables, there are two critical points with regard to the ink to be applied: its particle size and electrical susceptibility. To achieve the latter, as occurs with the electrostatic application, additives need to be incorporated into the ink base composition to make it sensitive to electrical induction. These additives need to be carefully chosen so as not to produce any type of fault during subsequent heat treatment of the decorated tile.

With regard to particle size, this must be adjusted to the nozzle that sprays the suspension. Although nozzles are used in other fields with a very small diameter for this technique, nozzle diameters are now starting to be made of up to 100 μm, which could allow using materials with similar particle sizes to those currently being employed in the ceramic sector.

Despite all this, the development of an ink jet application for decorating ceramic products is still in a very early stage, even though it opens up a series of possibilities that might allow achieving results that are otherwise unattainable with other decorating techniques.

4. FINAL NOTE AND ACKNOWLEDGEMENTS

Without being exhaustive, it has been attempted in this paper to provide an overview of the most common application methods for glazes and decorating inks, as well as of the methods that are currently in the process of being implemented or that might become a future alternative to conventional systems. This has been done from the point of view of the materials used in each application system, whether suspensions or dry products, in order to modestly contribute to systematising knowledge and information that is often scattered, and which summed up and ordered can be useful and interesting for all who, in one way or another, are engaged in areas relating to the manufacture of ceramic products, and hence in Ceramic Technology.

Finally, I should like to thank the technicians from various companies, who kindly spared me some of their time to provide information on some of the subjects dealt with, for their help in preparing this paper. I should furthermore like to express my gratitude to the following companies: ESTUDIO CERÁMICO, S.L., CERAMICA SALONI, S.A., TAULELL, S.A., KERABEN, S.A., FRITTA, S.L., TALLERES FORO, S.A., LAMBERTI ADITIVOS CERÁMICOS, S.A., and SYSTEM ESPAÑA S.A., as well as to ALICER, for their co-operation.

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