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Study of polymeric coatings used in the clay ceramic industry: A short review

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Abstract

The clay ceramic industry is a notable sector in Brazil, generating an annual revenue of around USD 4.3 billion. This paper is a literature review about polymeric coatings used to cover clay ceramics. The components of the coatings, methods of application, parameters for substrate pretreatment, curing techniques, potential application failures, and quality standards were examined. Once the key characteristics were identified, the review focused on the advantages and disadvantages of the application methods used. These methods include electrostatic, triboelectric, high volume low pressure (HVLP), and airless guns. It was found that more viscous liquid inks ensure a greater layer thickness, resulting in increased abrasion resistance. On the other hand, solid inks are preferred due to their reusability, absence of volatile organic compounds (VOCs), and minimized loss resulting from overspray.

Keywords: Polymeric coatings; Clay ceramic industry; Application methods; Substrate treatment; Abrasion resistance.

1. INTRODUCTION:

The global coating industry reached a market value of USD 132 billion in 2020, with an average annual growth forecast of 4.2%. This growth trend is expected to continue, potentially reaching a market value of USD 183 billion by 2028. The increasing demand for surface finishes, enhancements, and tailored engineering solutions is driving this growth. The application of coatings spans across various industries, including manufacturing, aerospace, automotive, decorative, structural, furniture, electronics, medical, food, and marine sectors [1].

Ceramic products have a long history, dating back to the discovery of fire. The term “ceramic” refers to non-metallic inorganic materials used in various applications, such as flooring, crockery, fiber optics, and bone and dental implants. In the industry, ceramic processing is typically carried out through serial production methods [2]. Clay ceramics, specifically, are characterized by their reddish color and find extensive use in civil construction, including bricks, tiles, blocks, tubes, and light clay aggregates [3]. The Brazilian National Association of the Ceramic Industry (ANICER) represents companies involved in clay ceramic processing. According to outdated data from 2010, the sector generated approximately USD 3.8 billion in revenue [4].

Given the increasing demands for quality and higher processing volumes, there is an ongoing need to improve productivity in the clay ceramic industry. Coating certain surfaces of machinery and equipment becomes essential due to the highly abrasive nature of the medium. Continuous contact with ceramic powder, typically clays, leads to undesirable wear on the equipment and parts involved in the process [5].

Polymers serve as versatile materials for coatings in the industry, providing high-quality finishes, a range of colors, and good mechanical properties for various applications. Their molecular simplicity allows for diverse development approaches, enabling a wide variety of application methods [6].

The application methods for polymeric coatings are diverse and influenced by various factors, including the application rate, substrate types, physical state of the applied polymers, specific requirements, technological complexity, economic considerations, and other aspects. Therefore, the aim of this review was to analyze different types of polymeric coatings, their characteristics, factors influencing coating adhesion, substrate treatments, applicable standards, and application methods that ensure quality and productivity for the equipment used in the clay ceramic industry.

2. BIBLIOGRAPHIC REVIEW:

This section focuses on presenting the characteristics of polymeric coatings, factors that impact their performance, application methods, relevant standards, and the recommended methods for the clay ceramic industry.

2.1. Polymer coatings:

Polymers are large molecules characterized by factors such as size, chemical structure, and molecular interactions. The atoms are connected through repeated covalent bonds, forming a patterned chain. The degree of polymerization, which refers to the number of bonds within the same chain, determines the polymer's characteristics [7].

Polymeric coatings consist of molecular chains of a base polymer with specific properties, incorporated into a formulated mixture to fulfill specific requirements. When applied to a substrate, typically of metallic origin, they provide various characteristics such as protection against destructive factors, aesthetic improvement, thermal and electrical insulation, among others [8].

According to the Fortune Business Insights report (2022), polymeric surface coatings are classified into different groups based on their compositions and technologies. The most established coating groups in the market include:

- Acrylics and alkyds: Leading the global production, these coatings offer good appearance, durability, and cost-effectiveness.
- Urethanes: Known for their chemical resistance, attractive appearance, and excellent mechanical properties, including flexibility and abrasion resistance.
- Epoxies: Providing high mechanical strength, thermal protection, and superior corrosion resistance.
- Esters: Offering good overall properties.
- Fluorinated coatings: Recognized for their non-adhesive properties, low coefficient of friction, chemical inertness, durability, and considerable abrasion resistance.

These coating groups are commonly categorized into three different technologies based on the production vehicle: water-based, solvent-based, or solid-based. They are further classified into two general application types: liquid or powder. The application configurations range from monolayer systems to models with two or three layers, involving terms such as primer (base coat), primer surfacer (intermediate layer), and topcoat (final layer).

Coatings, colloquially referred to as "paints", are complex products that encompass various components in addition to their base polymer. These components include binders, additives, pigments, extenders, and solvents. The general function of these components is to enhance the properties of the paints, whether in solid or liquid form [9,10].

While the essential characteristics of coatings are determined by the base polymer, they are influenced by the additional components. By incorporating these products, improvements can be achieved in areas such as color characterization, enhanced protective functions, film formation, and the generation of flexibility and resistance through plasticizers [11].

2.2. Factors that influence the coating adherence:

Polymeric coatings find applications in various sectors, ranging from the architectural field, such as painting real estate, to industrial sectors where they are tailored to meet specific engineering requirements in automotive, naval, and general industries. The properties to which coatings are exposed are influenced by both the environment and external forces. Therefore, the selection of coatings should be based on the intended purpose, considering factors such as surface wear and adhesion [9].

Surface wear refers to the gradual deterioration of materials over time, typically starting from the outermost layer. This process directly affects the lifespan of the object, and advanced stages of wear can render the component unusable [12]. Generally, material removal occurs due to mechanical actions resulting from contact and relative motion against solid, liquid, or gaseous agents. Surface wear can manifest in several ways, including adhesion, fatigue, chemical interference, mechanical-corrosive action, or abrasion.

Adhesion refers to the ability of one material to adhere to another even when subjected to stress. It is influenced by various physicochemical interactions between the materials, such as Van der Waals forces, mechanical anchorage, and substrate polarity, with the latter being particularly significant [13].

Surface roughness plays a crucial role in achieving good adhesion. It is determined by the geometric micro-irregularities present on the material's surface, resulting from the manufacturing process and specific properties of the compound. Surface roughness is typically quantified in terms of average roughness (R_a), which measures the height and width of these imperfections. The presence of surface irregularities contributes to the adhesion at the interface between the substrate and the applied polymer, as well as the coefficient of friction (COF) [14].

2.3. Substrate pretreatment:

Before painting, the surface of the substrate must be adapted, ensuring that the application conditions are satisfactory and that after completion, a good quality of finish is achieved (according to standards of regulatory bodies, or the company responsible for the process) [15].

The purpose of surface pretreatment is threefold: removal of impurities such as solid or liquid particles, enhancement of contact area through adhesion mechanisms, and improvement of surface hardness through the application of compressive stresses. Pretreatment processes can be categorized into physical or chemical mechanisms. Among these, one of the most commonly used methods is abrasive blasting, which involves the high-pressure spraying of solid components onto the surface [10].

Chemical treatments are specialized and cost-intensive processes employed for specific and unusual metal substrates. They offer similar benefits to physical treatments, such as increased surface roughness, improved adhesion, and enhanced coating durability. Notably, chemical treatments also play a crucial role in influencing corrosion resistance and delaying oxidation. Examples of chemical treatments include phosphating, chemical attacks using bases (e.g., sodium hydroxide) and acids (e.g., chromic, sulfuric, and hydrochloric acids) [16].

Roughness measurements underscore the significance of surface treatment in achieving the desired quality of a coating. Effective surface treatment improves the adhesion of the polymer to the substrate by facilitating microscopic interlocking of the material within the surface irregularities of the metal. This process significantly influences the lifespan of the product and the quality of its protective barrier [17].

A study conducted by a Polish team from Wrocław University of Science and Technology [18] investigated the adhesion of coatings on aluminum parts with different surface treatments and roughness values (R_a and R_z). The study employed polyurethane (Biresin U1305, Sika) and epoxy (Epidian 652 + hardening agent IDA) resin-based coatings, with the inclusion of four types of fibers (glass, carbon, aramid, and hybrid). Surface treatments included degreasing or sandblasting under controlled conditions of temperature, humidity, angle, and time. The study found that surfaces treated only with acetone (A) exhibited the lowest roughness, followed by surfaces that were sandblasted using corundum grains and subsequently cleaned with acetone (F80), and abrasive blasting using steel grits (GH40). The pull-off test, conducted according to the PN-EN ISO 4624:2016 standard, involved measuring the force required to detach the coating using a hydraulic pump-operated measuring device. The results showed that increased roughness resulting from abrasive blasting improved the adhesion of the coatings to the substrate. The highest pull-off resistance was observed in non-reinforced coatings or those reinforced with carbon fiber after sandblasting with corundum grain

F80. However, the authors also noted that excessive roughness could negatively affect the adhesion of coatings by reducing the penetration of the polymer matrix into the substrate material. Very high roughness levels can prevent the polymer from penetrating the microporosities of the part, leading to the formation of air bubbles. This can adversely affect the coating's rate of application and impair its fixation to the substrate.

2.4. Polymer coatings application methods:

There are various methods for applying coatings, but for the industrial segment analyzed in this review, the focus is on methods that offer criteria such as cost-effectiveness, large-scale application, consistent coating on complex geometries, low complexity, and good repeatability. The main application methods for liquid paints include conventional spray guns, high volume low pressure (HVLP) guns, low volume low pressure (LVLP) guns, airless guns, and dip coating. For solid paints, electrostatic painting and fluidized bed coating are common methods [19].

Conventional painting involves the indirect application of paint onto the substrate. The paint is pressurized and released in the form of a spray, forming a film on the surface. This method is widely used due to its simplicity and ease of automation. The liquid paint is stored in a reservoir connected to an application gun, which is inserted into a pressurized system typically ranging from 20 to 60 psi [20]. The gun system can be classified into three types: gravity feed, suction feed, and closed system feed (Fig.1(a)).

Airless guns utilize a hydraulic pump to pressurize the paint flow, resulting in high-energy spraying. The paint is atomized by passing through a small diameter hole. The pressure can reach an average of 7500 psi, allowing for easier application of more viscous coatings [21]. This method enables a high application rate, capable of spraying up to 2 liters of paint per minute, making it suitable for coating large areas that are difficult to manipulate (Fig.1(b)). Airless spraying also offers higher material utilization in comparison to pneumatic processes [9].

Figure 1. (a) conventional pistol, adapted from [9]; (b) airless pistol [22]

HVLP (high volume low pressure) guns operate similarly to conventional spray systems but spray a larger volume of paint at reduced pressures (around 10 psi). This creates a continuous spray pattern that is less aggressive compared to conventional systems. As a result, HVLP guns provide better control and higher efficiency by reducing the amount of paint wasted through overspray. HVLP systems are suitable for use with more viscous paints, while the LVLP (low volume low pressure) system operates inversely. The LVLP system is recommended for lower pressures, offering improved application control with reduced paint volume, specifically for paints with lower viscosities and lower concentrations of solid particles [23].

In dip coating, the object to be coated is immersed into a coating bath (Fig.2), taking advantage of the viscous properties of the liquid to adhere to the surface of the part. The part and the coating are often heated to enhance the adhesion conditions of the paint [10]. Although dip coating is a simple method, it lacks precise control over parameters. Impurities can enter the paint reservoir as it is exposed to the environment, and controlling runoff after application is challenging due to gravity. The thickness of the coating layer may not be uniform. It's difficult to control the quality of the coating parts with cavities due to the retention of the liquid in concave areas [9].

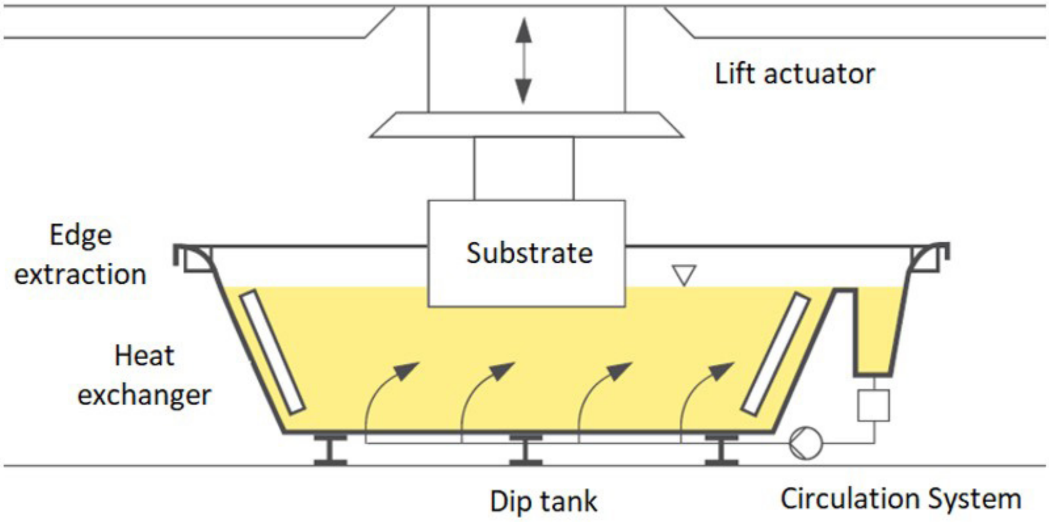

Figure 2. Dip coating method. Adapted from [9]

Electrostatic painting involves the use of powder paints that are fluidized by pressurized air within a closed environment. The flow of powder particles is transported by an injector to the spray gun. The coating particles are electrostatically charged and directed towards the object. The object is grounded and carries a reverse charge compared to the paint. As a result, the paint particles are attracted to the grounded object before being deposited due to the electrical attraction [24].

There are two main methods to electrically charge powder particles. The first method utilizes ionization (corona charge), which can be achieved through internal or external charging. Electrostatic painting is known for its ease of handling and has great potential for application in continuous production lines (Fig.3(a)). The second method charges the particles through friction, known as kinetic or tribological charging. Fluidized bed coating is an analogous system to dip coating but is specifically used for powder coatings due to the physical effect of fluidization. In this method, a reservoir contains solid paint particles and pressurized airflow is injected into the lower part of the system. The air permeates a porous apparatus and flows against the surface of the object (Fig. 3(b)). As the pressurized air moves through the system, it carries the powder particles along, making them behave like a fluid [25].

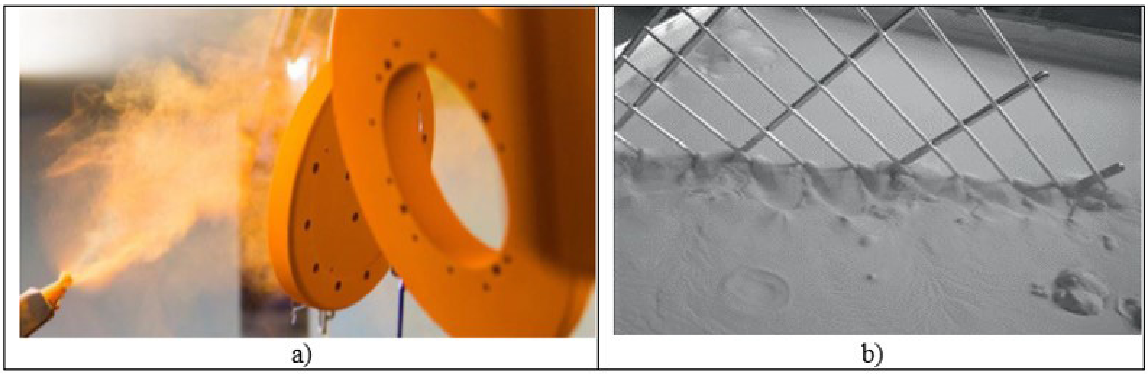

Figure 3. (a) electrostatic [20]; (b) fluidized bed coating [24]

Objects with convex geometries are typically coated using spray guns with internal loading or triboelectric charging mechanisms. Internal loading guns apply a lower voltage to the electrode, resulting in less distortion of the field lines caused by the Faraday Cage effect. In triboelectric guns, the charging of the coating material is achieved through friction with an internal material (usually a polymeric compound) within the gun. The fixation of powder paint to the substrate in these methods is primarily facilitated by the flow of compressed air, with the Faraday effect being less significant. As a result, the electric field generated in the system is almost negligible [24].

The essential stages in the transformation of liquid or powder paint into a physically resistant coating involve changes in the chemical composition of the paint. The film formation occurs during the curing process, which typically involves raising the substrate temperature to above 200 °C. The paint applied to the object must reach a temperature that allows for the alteration of molecular structures and interconnections within its polymer chains. This process includes the evaporation of solvents present in the mixture (in the case of liquid paint), which subsequently harden the deposited film [26]. Efficient equipment capable of providing thermal energy is required to raise the temperature of the substrate and the paint system. According to [10], the most common types of furnaces used for curing coatings are convection, infrared heating, and induction heating.

2.5. Quality standards:

To ensure the quality of coatings, regardless of the substrate or paint used, it is essential to adhere to certain standards to prolong the lifespan of the materials, equipment, and application [9]. Several factors contribute to the quality assurance process, including:

- Workforce qualification: Operators must possess knowledge about the proper handling of equipment and materials, as well as the parameters to be followed during the painting cycle.
- Substrate preparation: Proper procedures for preparing the substrate before applying the coating are crucial to achieve optimal adhesion and durability.
- Equipment calibration and maintenance: Regular maintenance and calibration of equipment ensure consistent and accurate application of the coating.
- Painting and curing procedures: Following established procedures for applying the coating and the curing process helps achieve the desired coating properties.
- Inspection and testing: Samples should be inspected according to regulatory standards, which include criteria such as mechanical strength, adhesion strength, fault monitoring, and layer thickness.
- Proper handling of non-reusable materials: Correct disposal methods should be followed in accordance with environmental regulations set by relevant agencies.

Standards for polymer coatings are established by regulatory bodies in each country. In Brazil, the Brazilian Association of Technical Standards (ABNT) provides national standards that define the requirements and guidelines for polymer coatings (Tab.1).

Table 1. Main Brazilian standards

Standard	Scope
ABNT NBR 7348	Industrial painting. Preparation of steel surface with abrasive blasting or hydro jetting
ABNT NBR 10443	Paints and varnishes. Determination of the thickness of dry film on rough surfaces. Test method
ABNT NBR 11003	Paints. Determination of adhesion
ABNT NBR 14951	Painting systems on metal surfaces. Defects and corrections
ABNT NBR 15156	Industrial Painting. Terminology
ABNT NBR 15158	Cleaning of steel surfaces by chemicals products
ABNT NBR 15185	Surface inspection for industrial painting
ABNT NBR 15239	Steel surface treatment with hand and mechanical tools
ABNT NBR 15442	Industrial Painting. Inspection of receipt of closed containers
ABNT NBR 15488	Industrial painting. Metallic surface for application of paints. Determination of the roughness profile
ABNT NBR 15877	Industrial painting. Traction adhesion test
ABNT NBR 16172	Anticorrosive coatings. Determination of discontinuities in anticorrosive coatings applied on metal substrates
ABNT NBR 16267	Determination of particle size of abrasives for blasting

In the application of the paints, there must be observed some parameters to obtain a coating with quality, since the process of pre-treatment, extending to the properties of the paint, the conditions of application and curing. The most common types of defects (Fig 4) are: air trapping (bubbles), pinholes, craters, "fish eyes", cracks, extreme roughness, wrinkles and runoff [9,10,26].

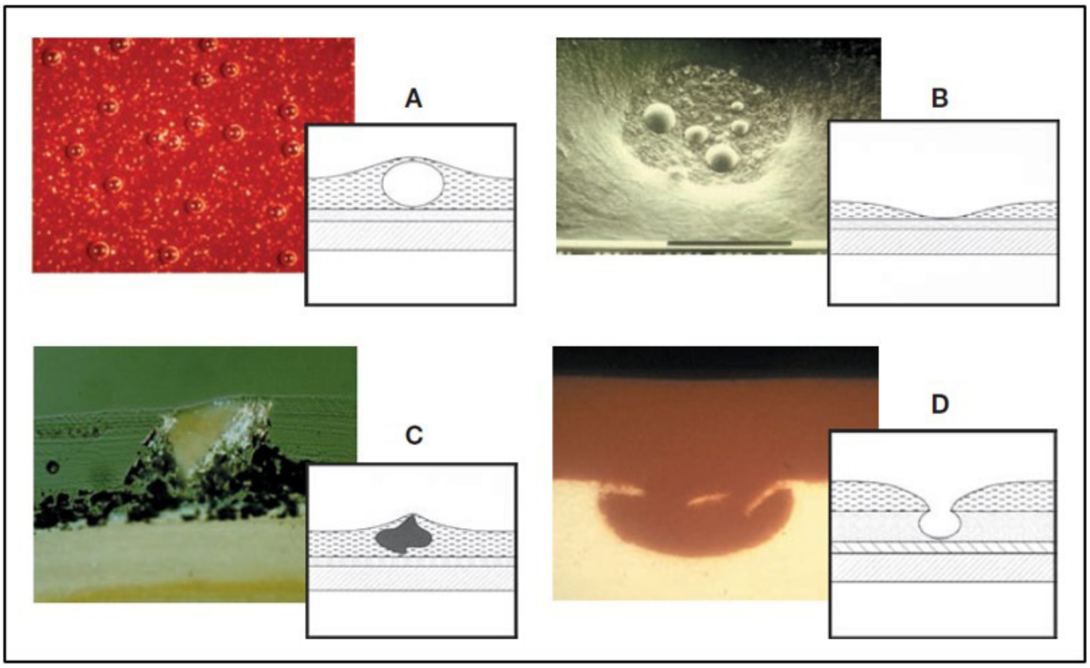

Figure 4. Common defects: (a) bubbles; (b) craters; (c) impurities; (d) pinholes [9]

Errors in the process harm the final quality. Part of the solution to this problem is to identify it correctly. The causes of defects in production lines are usually associated with human errors during application, paint formulation errors, impurities found in the painting environment, previous cleaning of the substrate done incorrectly and nonconformities in the curing process [9].

3. DISCUSSION:

3.1 Most relevant methods for the clay ceramic industry:

In the clay ceramic industry, the use of polymeric coatings serves several purposes, with the main objective being to prolong the lifespan of equipment and machinery involved in various processes, including conveyors, presses, molds, feeder cars, and more. Continuous contact abrasion and intermittent temperature cycles are the most significant environmental factors that can cause damage. In equipment responsible for compressing ceramic powder, such as stamping and feeding presses, it is essential to minimize adhesion between the parts and the raw material. This ensures smooth powder flow between the equipment and facilitates the manufacturing process [27,28].

The most damaging environmental factors are continuous contact abrasion and intermittent temperature cycles. In parts/components used for the pressing of ceramic powder (both in the stamping and in the feeding of the press), it is desirable that there is a low adhesion of the parts with the raw material, ensuring fluidity of powder flow between the equipment. To achieve this, it is necessary to apply suitable surface treatments with polymeric coatings that address the specific requirements of the industry. Economic factors also play a role in determining the choice of coating method [29, 30].

Among the application methods mentioned earlier, the most advantageous options for the clay ceramic industry are liquid pulverization using HVLP guns, airless liquid spraying, and triboelectric electrostatic solid spraying. These methods offer benefits such as efficient and controlled application, ensuring proper coating coverage and quality while minimizing waste and overspray [31].

In the ceramic sector, the coatings applied to equipment require increased thickness compared to other industries, aiming for enhanced durability and corrosion resistance. Typically, these coatings consist of multiple layers, including a primer and topcoat, which contribute to the overall effectiveness of the coating. The higher layer thickness is often a result of the larger volume of additives, binders, plasticizers, and other compounds used in the composition [28,30].

HVLP and electrostatic gun applications are well-suited to meet the requirements in the ceramic sector. These methods enable the application of a uniform and thicker coating layer. They are technically straightforward and can be integrated into continuous, automated production lines. HVLP and electrostatic guns are commonly used when the paint volume per piece is lower, allowing for easy application on complex geometries and concave cavities [32].

Tab.2 provides a summary of the main advantages and disadvantages of different coating methods.

Table 2. Advantages and disadvantages of different coating methods

a) HVLP gun [36]	**Advantages**	**Disadvantages**
	More viscous paints can be used; Best suited for fine finishes; Simpler and more conventional equipment; Fine-tuning of spray parameters.	In manual applications, there is a greater possibility of errors; Issuance of VOCs; Overspray; Low application speed; Coarse atomization.
b) Airless gun [36]	**Advantages**	**Disadvantages**
	Easy handling; Small spray mist; High area coverage, with high speed; Effective for more viscous paints.	Requires higher investment; Shorter equipment lifespan; Low control of application parameters; Issuance of VOCs; Overspray.
c) Electrostatic gun [36]	**Advantages**	**Disadvantages**
	No release of VOCs; Minimal overspray, which can be reused; High transfer efficiency; Deposition of thick layers; Manual operation with reduced errors.	High investment, for equipment and safety; Application environment must be strictly controlled; Faraday cage effect; Low control in finishes and minute situations.

For applications with high paint volumes, such as in large machinery and assembled equipment, the airless process is often preferred. This method provides greater flexibility for workers, allowing them to apply paint over larger distances and at higher speeds, ensuring even coverage across all areas. Additionally, if room-temperature drying paints are used, large parts may not need to be placed in curing furnaces for coating drying [33].

Liquid paint applications, compared to solid paint, may present disadvantages such as overspray in non-automated applications and gravity-related issues like paint runoff when building up a thick film. These drawbacks can be overcome by using solid paints, which offer the possibility of recycling excess powder from overspray [34].

To aid in the selection of coatings and application methods, manufacturing companies often provide technical manuals that describe the essential aspects of each coating line and model. These manuals specify paint properties such as coverage ratio, viscosity, volatile organic compound (VOC) content, coefficient of friction, and resistance. They also recommend application methods, layer thickness, curing time, curing temperature, pre-treatment requirements, and other relevant aspects.

4. CONCLUSIONS:

The aim of this review was to analyze the various types of polymeric coatings and their characteristics, factors that influence their performance, substrate treatments, applicable standards, and suitable application methods to ensure quality and productivity for the equipment used in the clay ceramic industry. The key aspects considered were:

The application environment must adhere to strict quality standards to ensure a highly repeatable process and minimize potential defects. The pre-treatment parameters of the substrate play a crucial role in establishing favorable adhesion conditions for the coating, leading to enhanced durability and wear resistance.

The selection of paint directly influences the application method, and it is important to consider the technical manuals provided by the manufacturers. The curing process is determined by the manufacturer based on the chemical composition of the paint. However, the method used to raise the temperature does not alter the properties of the polymer coating.

The choice between liquid or solid paints is a critical aspect of the process as it determines the selection of equipment. The two methods differ in terms of efficiency, particularly in terms of the reusability cycle of solid coatings and the non-recoverable overspray associated with liquid paints.

The safety and sustainability of solid coatings are important considerations. Solid coatings do not release harmful or flammable gases, such as volatile organic compounds (VOCs), into the atmosphere. Additionally, their interaction with electric fields and currents, as well as the presence of suspended particles, needs greater safety measures and investment.

In the equipment of the clay ceramic industry, it is crucial for the polymeric coating to exhibit excellent resistance to abrasion. The most efficient application methods for achieving this are: solid paint spraying using a triboelectric electrostatic gun, liquid paint spraying using HVLP guns, and airless pistols.

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