EASY GUIDE TO PAINT TECHNOLOGY

INDORAMA VENTURES

Blucher

Coordinators

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EASY GUIDE TO PAINT TECHNOLOGY

A quick and practical handbook to formulating paints and emulsions

3rd edition

Easy Guide to Paint Technology: a quick and practical handbook to formulating paints and emulsions

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Introduction

At our core, we believe in the power of knowledge. But even more than that, we recognize the immense value in sharing it. With this purpose in mind, we created this handbook—a resource designed to ignite curiosity, provoke fresh perspectives, and inspire industry professionals to explore new paths.

Our goal is simple: to encourage questions, spark innovation, and foster transformative thinking within the paints and coatings industry. We hope that the insights gained from these inquiries will be generously shared, creating value for all stakeholders and driving positive change.

The inaugural edition of this handbook was published in 2017, exclusively in Portuguese, with a focus on the Brazilian market. Since then, it has become an integral part of the daily lives of countless professionals in the paint industry. Its practical guidance has helped them enhance their paint formulations and emulsions effectively.

Building on this success, we embarked on a new journey—a revised edition. This time, we've not only updated the content but also translated it into English. Our aim is to reach an even wider audience of readers, inspiring professionals worldwide to collaborate, share knowledge, and elevate the industry as a whole.

Our company has undergone a significant transition, a new era has begun. We are Indovinya, a business division of Indorama Ventures, a leading surfactant market company with global relevance in the chemical industry and the largest ethylene oxide producer in the Americas. Indovinya is the combination of tradition and the future. The term "INDO" refers to Indorama Ventures, reaffirming our commitment to maintaining the core values and growth mindset that have ensured the success of our parent company. Meanwhile, "Avinya," translated from the Sanskrit language as innovation, reflects our vision to evolve as a specialty chemicals, high-value-added sustainable solutions company and customer centricity across our diverse end markets. This change makes us even more robust and reaffirms our purpose of reimagining chemistry together to create a better world. We have expanded our sustainability initiatives and research, intending to bring increasingly efficient responses and solutions to the global coatings market.

Join us in this pursuit of excellence, where every idea shared contributes to a brighter, more innovative future for paints and coatings.

Enjoy the reading!

Alastair Port | Indovinya Executive President

Preface

The idea of this handbook arose from the need to offer, in a simple way, fundamental concepts of paint technology. Aimed at researchers, formulators, technicians, and all professionals in the areas of research and development and technical assistance of the paint industry, whether beginners or specialists. This manual is designed for permanent consultation, easily and quickly, on an office table or on the laboratory bench.

This book is not an exhaustive compendium of information. It reflects the knowledge of Indorama Ventures' team of researchers and technicians. It brings their experience in several fields presented in seven distinct parts, which assertively address information and tools for developing high-performance paints and emulsions.

One of the most critical points in the excellent performance of paints is the film formation process. The concepts are presented in Part 1, in which the main factors for solvent-based and water-based paints are discussed, and the influence of coalescing agents on the film formation temperature and its quality.

The film formation is a complex process, which can influence the properties of the final paint significantly, so, the correct choice of solvent composition is crucial to achieve good results with a paint formulation. Part 2 presents the methodologies that must be considered when choosing solvents, such as Hansen's solubility parameters, evaporation rate, dielectric constant, VOC (Volatile organic compound), among other factors. Control and analysis of the solvent composition are also presented in this part.

The formulation of water-based paints is only possible through the use of surfactants. In Part 3, the main concepts used for the correct choice of surfactants in pigment wetting and dispersion are analyzed in detail, including the influence of pigment volumetric concentrations (PVC and CPVC), and also the use of surfactants for emulsion polymerization, and its application in alkyd emulsions will be discussed. The Hydrophilic/Lipophilic Balance (HLB) determines several properties of surfactants, such as their affinity for pigments and resins. One of the main applications of surfactants is to promote wetting and stabilization of pigments during the dispersion process, which is one of the critical points of paint production. Surfactants are also essential in producing latex, the most common resin used in architectural water-based paints. This part also presents a practical view of the process and criteria for choosing surfactants.

A problematic paint composition can cause defects. Part 4 presents the main defects in water-based and solvent-based paints and strategies to avoid them. Two methodologies will be detailed to evaluate the problems of dirt pick-up and leaching, defects that have become increasingly common in architectural paints due to increasingly restrictive VOC regulations.

In an ever-changing world, environmental changes have become faster and more constant. In the paint industry, this is reflected in increasingly fierce competition, which brings the growing need for focus on innovation and ever-faster product development cycles. In this context, statistical development methodologies are essential tools that offer agility by increasing the robustness of developments. Part 5 discusses the Design of Experiments (DOE) methodology when applied to paint development. In the end, a practical example of application in the rheological adjustment of paint is demonstrated.

Always an important topic, safety should be a focus and part of the culture of any company. In Part 6, we intend to practically convey concepts and tips that can be applied to paint and latex development laboratories for safety improvements.

Finally, we dedicated Part 7 mainly to presenting the Life Cycle Analysis (LCA) methodology and its application in paint development. Sustainability is an essential issue today. Due to human action, we are increasingly limiting resources for future generations, and we urgently need to think about viable solutions to this problem. However, we see a lack of tools that really help an in-depth analysis of the impacts of flows, processes, and products on the environment. We are constantly inundated with a plethora of information with no verification or depth (greenwash). The LCA tool is increasingly popular in academia and industry and has much to offer to the product development process.

Thus, we hope this handbook can contribute to the day-to-day life of research and development laboratories. Only through knowledge we will be able to be increasingly innovative, creating sustainable and high-performance solutions, leading the paint sector to be increasingly relevant in the well-being and lives of everyone today and in the future.

Silmar Barrios | Marketing and R&D Director of Coatings and HPC
Fabrício Pereira | R&D Manager of Coatings

There is an old expression:

“Good Judgement comes from experience and experience comes from trying and learning what did and did not work”.

The key is to learn from other’s successes and learning experiences, and that is what we will try to convey in this book.

Paint formulation is a challenge where the interplay of the raw materials can be significant.

Raw materials are added with the purpose to address specific properties of the coating but can affect other properties both positively and negatively. The key to a successful paint formulation is maximizing the positive and minimizing the negative.

With 37 years of coatings formulation experience - 17 years with coatings companies and 20 years with raw material suppliers - I have witnessed firsthand the intricacies of the industry. This handbook aims to deliver, in a didactic and uncomplicated manner, a rich and comprehensive content on the formulation of paints and emulsions. We trust that this manual will further enrich the reader’s knowledge, aiding them in refining their formulations, correcting defects, enhancing performance, and exploring new avenues of research.

My years of experience underscore the necessity of knowledge exchange within the industry, always striving for technological advancement and a deep understanding of the end market, customer needs, and how to refine innovative solutions. The endeavor to disseminate knowledge not only fosters professional growth but also contributes significantly to the progression of the field, ensuring that the industry remains adaptive and responsive to evolving demands and challenges. Therefore, this manual serves not only as a guide but also as a testament to the ongoing commitment to excellence and continuous improvement within the realm of paint technology.

The paint industry is immensely complex, both due to the vast number of raw materials involved and the potential interactions between them during formulation. The application and drying stages also present extreme complexity, owing to the specificity of each end industry, the need for increased productivity, and efficiency in the process. Furthermore, there is the complexity of the requirement for high quality and performance of the environments protected by the coating, with enhanced durability, fewer layers, and reduced thickness. Last but certainly not least, we must continuously evolve regarding sustainability issues, striving to deliver solutions with minimal environmental and social impact.

This book is the result of the work of a many people and I would like to acknowledge Silmar Barrios for moving the driving force behind this project and the contributions of: Fabricio Pereira, Fabio Rosa, Bruno Dario, Rafael Salvato, Alann Bragatto, Jaqueline Barne, Raquel da Silva, Marina Passarelli, Amanda Costa, Robson Pagani, Juliane Santos, Larissa de Almeida, Henrique Liviero, Thiago Magri, Nina Dantas, Natalia e Paula, and Brandon da Silva.

So please learn from us and let us know how we can improve future editions.

Michael Praw | Technical Service and Development Manager
for Coatings and Performance Products

Part 1

Introduction to paint technology and film formation

1 Introduction to paints and film formation process

Rafael C. J. P. S. Salvato | Alann de Oliveira Piagentini Bragatto

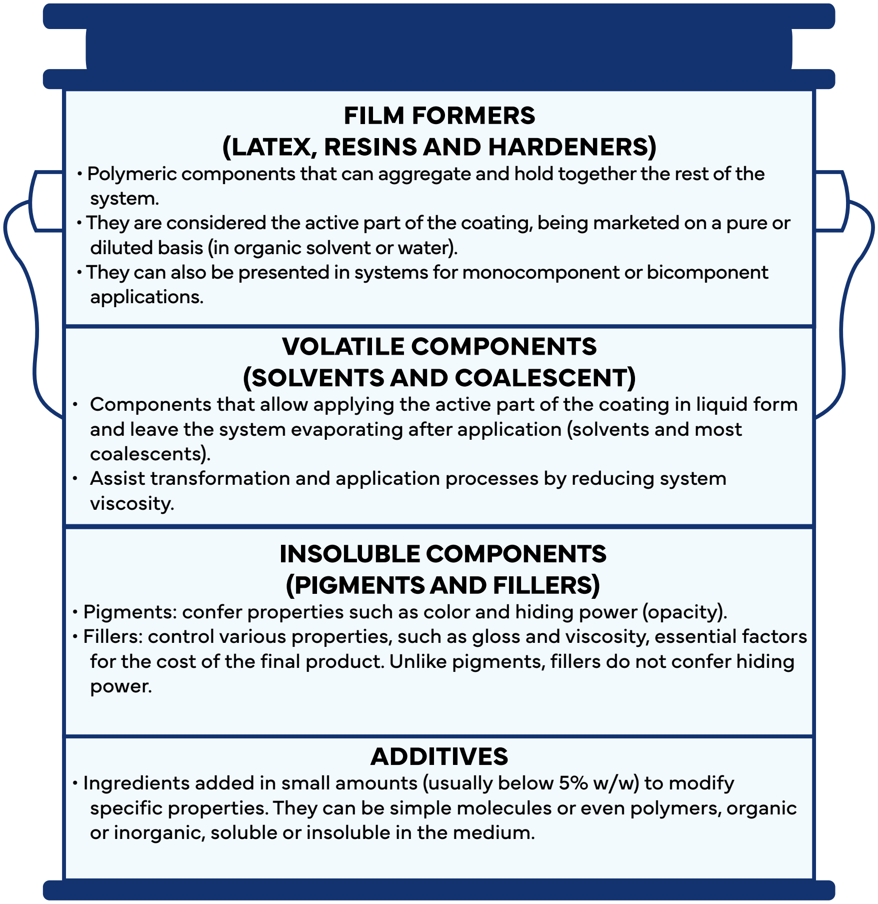
1.1 INTRODUCTION

We find paints everywhere around us, whether in the urban or rural environment. Due to the possibility of decorative or strictly functional uses, the paints need to meet diverse and broad-spectrum requirements.

Most paints are liquid, and its viscosity is adjusted to the method of application. An exception to this context is powder coatings, in which the powdered solid is liquefied in situ, that is, in application. Upon application, this liquid transforms into a solid film, which in fact generates the desired coating to protect a given substrate or beautify a surface. This transformation process is referred to, in the literature, as film formation and the physical and chemical changes that occur in it are critical for the final appearance and for the performance of the resulting coating (TRACTON, 2006; WICKS, 2007).

1.2 BASIC PAINT COMPONENTS

To generate a coating from paints that meets all the needs of the applications listed above, several materials are combined in different quantities and presentations. However, all these materials can be grouped into four main categories according to their role in the system, as illustrated in Figure 1.1.



FILM FORMERS
(LATEX, RESINS AND HARDENERS)

- Polymeric components that can aggregate and hold together the rest of the system.
- They are considered the active part of the coating, being marketed on a pure or diluted basis (in organic solvent or water).
- They can also be presented in systems for monocomponent or bicomponent applications.

VOLATILE COMPONENTS
(SOLVENTS AND COALESCENT)

- Components that allow applying the active part of the coating in liquid form and leave the system evaporating after application (solvents and most coalescents).
- Assist transformation and application processes by reducing system viscosity.

INSOLUBLE COMPONENTS
(PIGMENTS AND FILLERS)

- Pigments: confer properties such as color and hiding power (opacity).
- Fillers: control various properties, such as gloss and viscosity, essential factors for the cost of the final product. Unlike pigments, fillers do not confer hiding power.

ADDITIVES

- Ingredients added in small amounts (usually below 5% w/w) to modify specific properties. They can be simple molecules or even polymers, organic or inorganic, soluble or insoluble in the medium.

Figure 1.1: *Categories of materials that make up paint formulations and their main characteristics depending on their role in the coating forming system.*

As seen in Figure 1.1, the choice of nature and amount employed of each component consider the way the coating will be generated (application) and the desired/required final properties of the final coating (post-application).

1.3 FILM FORMATION BY SOLVENT EVAPORATION FROM THERMOPLASTIC SOLUTIONS

Films can be formed in several ways, the simplest being the dissolution of a polymer in a solvent (or mixtures of solvents) at a given concentration necessary to enable its application on a desired surface, allowing the solvent to evaporate until a solid and workable continuous film is obtained (TRACTON, 2006; WICKS, 2007).

In summary, this process has three main stages: application, fixation and drying (GARBELOTTO, 2007). In Figure 1.2, these stages are presented schematically.

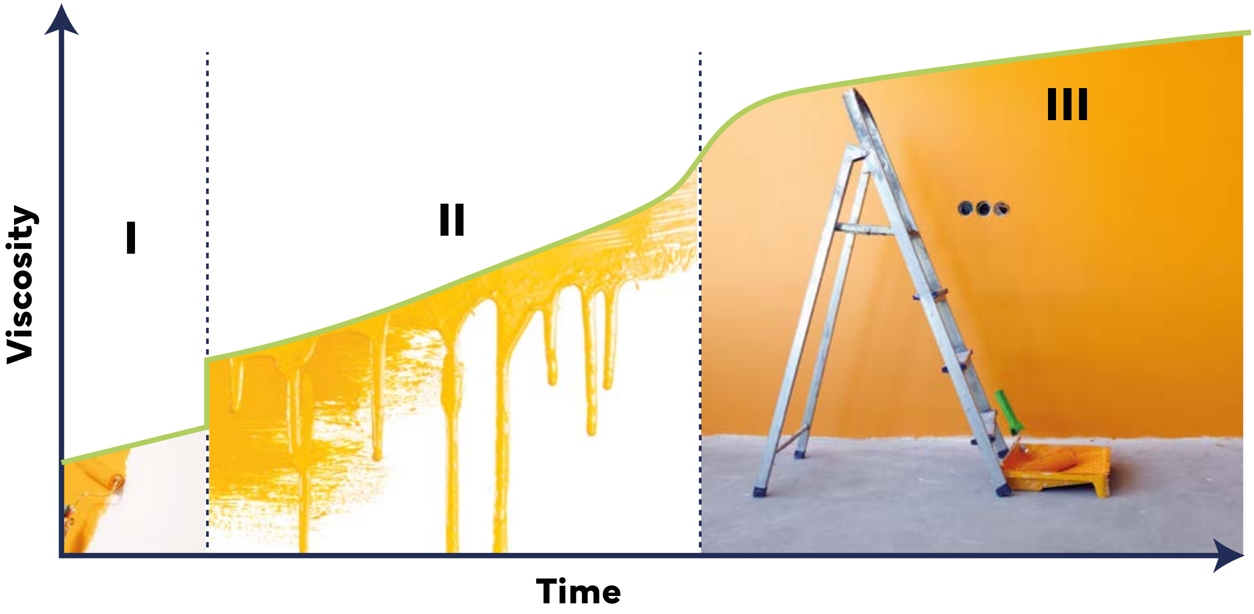


Figure 1.2: *Evolution of viscosity as a function of the stages of film formation by solvent evaporation.*

Source: adapted from Garbelotto (2007) and Tracton (2006).

As shown in Figure 1.2, shortly after application, there is rapid evaporation of the solvent from the surface, resulting in increased polymer concentration and subsequent evolution of viscosity. Then more solvent will be evaporated by diffusing the molecules through the layers of concentrated polymer. That way, the polymer concentration continues to increase, which results in the immobilization of the polymer chains, giving the film a "dry" appearance. Finally, a good part of the residual solvent slowly abandons the film by diffusion, and a single, homogeneous film is obtained, with characteristics of a high-viscosity liquid –or a dry solid one – to the touch.

In all stages described, the solvent employed in the system plays a fundamental role, and its correct choice is key to a quality coating formation. Given its importance, this topic will be covered in more detail in Chapter 2 of this handbook.

1.4 FILM FORMATION IN THERMOSETTING RESIN PRECURSOR SOLUTIONS

One of the main limitations of coatings obtained from thermoplastic in solutions lies in the need for high solvent contents (typically comprising 65% to 90% of the formulation weight) to achieve the viscosity required for application. This stems from the high molar weight of the thermoplastic polymers, thus causing difficulties in dissolving and spacing the polymer chains necessary to prevent them from interact strongly and to allow them flow freely. An alternative to this condition is to have as a starting point in the formulations solutions of partially reacted resins, which have reduced molar weight. During solvent evaporation, shortly after application, these resins also react chemically, forming cross-links and making the thermoset polymer. Such bonds, commonly called cross-links, also modify the final properties of the film, generally magnifying the mechanical and chemical strengths. The film formation process, in this case, also follows the three stages described in the previous section, with the only difference being that the viscosity increase is much more pronounced.

1.5 FILM FORMATION BY POLYMERIC PARTICLE COALESCENCE

In contrast to the film formation process from thermoplastic or thermosetting solutions, the dispersion of polymeric particles in water depends on a distinct mechanism, which involves the coalescence of these particles during water evaporation (TRACTON, 2006; WICKS, 2007).

Polymer dispersion in water is called latex (also latexes) and is usually obtained from the technique of polymerization of acrylic and/or vinyl monomers in emulsion (FAZENDA, 2009). The latex's monomeric composition determines the polymer's glass transition temperature (Tg). By definition, the Tg of a polymer is the temperature at which polymer chains have sufficient mobility to evolve from the glassy or brittle state to the amorphous or rubbery state (FAZENDA, 2009).

When pure latex or paint formulated with latex is applied on a substrate, after letting the water evaporate, a continuous and homogeneous film is formed if the temperature and humidity conditions are appropriate. In the literature, this process is known as film formation process (BRAGA, 2003; KEDDIE, 1997). Ironically, although a significant effort is made in the synthesis of latex to keep the particles stable, during film formation, these same particles must overcome mutual repulsion to form a continuous film. Dispersants, wetting agents and emulsifiers influence the film formation process and can affect the characteristics of the final film and its adhesion, plasticity, gloss, water resistance and permeability properties (STEWARD; HEARNA; WILKINSON, 2000).

Several models describe the latex film formation and the forces involved in each stage (STEWARD; HEARNA; WILKINSON, 2000; TRACTON, 2006; WANG; WINNIK, 1990; WICKS, 2007). Latex film formation based on these models can be divided into three stages, as shown in Figure 1.3:

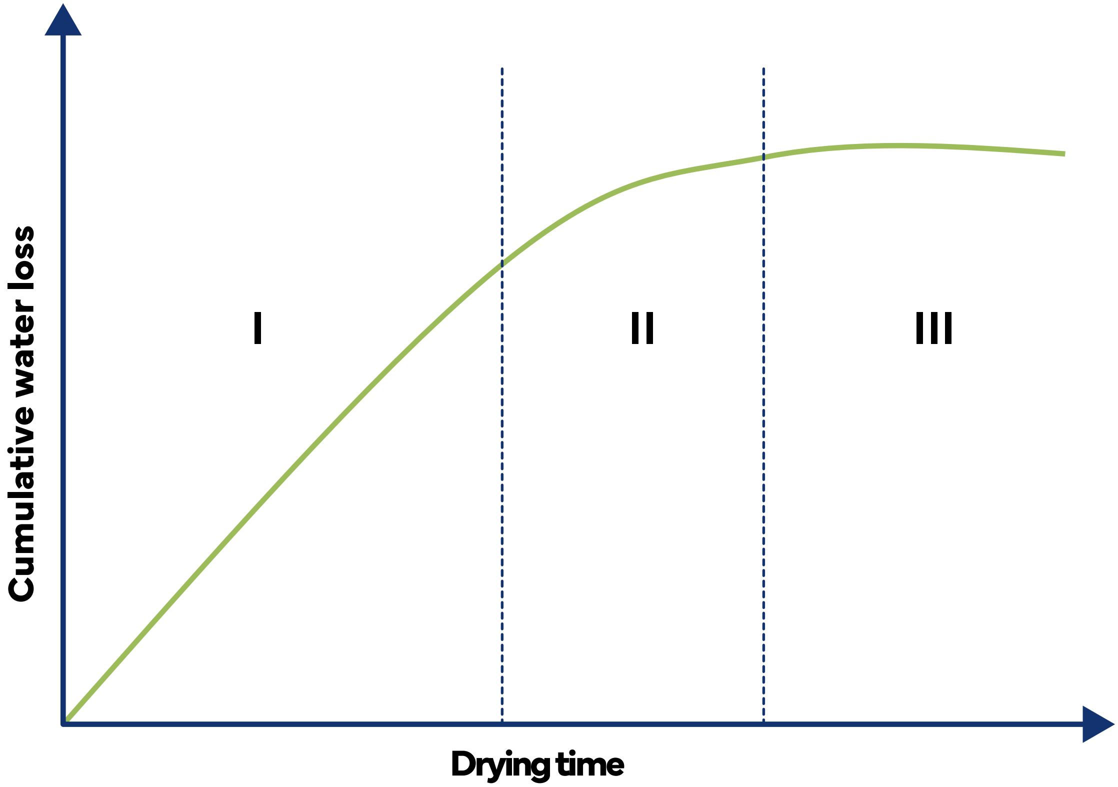


Figure 1.3: *Schematic form of water loss throughout the latex film formation stages.*

Source: adapted from Wicks (2007).

In addition to the evaporation of the solvent (in this case, water), there is an essential evolution in the approximation and contact of polymeric particles to enable proper film formation. A schematic view of the three stages of the polymeric particles' morphological evolution into film can be seen in Figure 1.4.

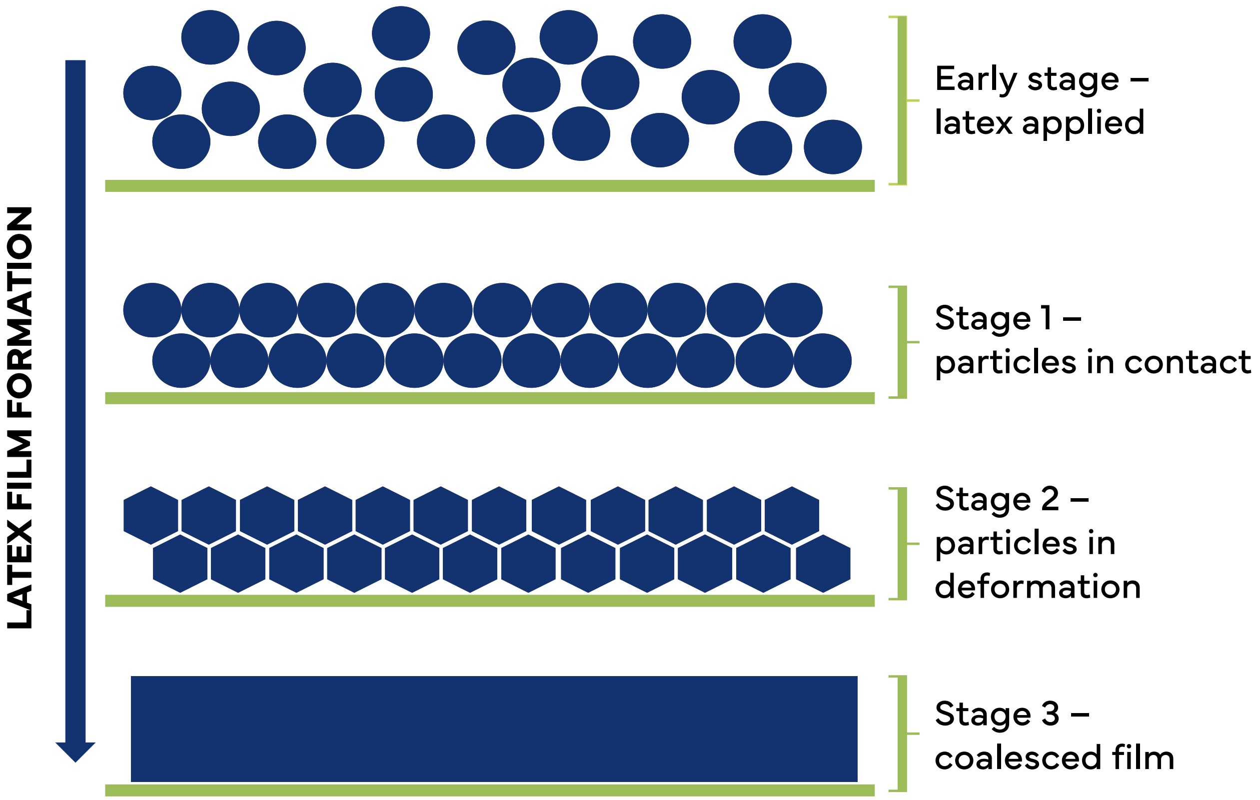


Figure 1.4: *Evolution of the morphology of polymeric particles during drying and latex film formation.*

Source: adapted from Tracton (2006).

- **Stage 1:** the water present in the dispersion of the polymeric particles evaporates at a high and constant rate, promoting the concentration of polymer particles and the packaging of polymeric particles (SHEETZ, 1965). Stage 1 is the longest of all and lasts until the polymeric fraction reaches 60% to 70%.
- **Stage 2:** there is irreversible contact of the particles, evaporation of the residual water and deformation of the particles, favoring film formation without holes and transparency. At this stage, the packaged and deformed particles can be organized in the film into

various geometric spatial arrangements, such as simple cubic, face-centered cubic, simple hexagonal, face-centered hexagonal, body-centered cubic, rhombic dodecahedron and trapezo-rhombohedra (KEDDIE, 1997; STEWARD; HEARNA; WILKINSON, 2000). In Stage 2, the rate of evaporation of water remains constant, but it is much lower than the rate of evaporation of water in Stage 1. According to the graph of accumulated water loss as a function of time, shown in Figure 1.3, water evaporates preferentially in Stages 1 and 2. By the end of Stage 2, the film is already continuous, but it's still brittle.

- **Stage 3:** if the temperature of the medium is higher than the Tg of the polymer, the interdiffusion of the polymer chains occurs in the contact regions between the particles, resulting in their coalescence, which promotes the formation of a continuous and homogeneous film. Coalescence is followed by an entanglement of the chains from neighboring particles, which causes an increase in the mechanical strength of the film (WANG; WINNIK, 1990). During coalescence, the polymer must have a certain mobility to allow the deformation of the particles and, at a later stage, the entanglement of the chains for the irreversible formation of the film. If the interpenetration does not occur satisfactorily, the film will look cracked, powdery, with low mechanical stability.

1.6 INFLUENCE OF TEMPERATURE ON LATEX FILM FORMATION

The ability of a polymeric structure to form films is a phenomenon associated with several factors, the main one being temperature (HOY, 1973; TOUSSAINT, 1997). Each monomeric composition gives to the polymeric structures, present in the latex, a characteristic temperature below which film formation does not occur, since mobility is insufficient to permit the coalescence of the particles. In other words, this specific temperature is the Tg mentioned above (intrinsic property of the polymer chain) and must be situated below the room temperature of the application. However, although the determination of Tg is widespread, it is done by sophisticated and expensive techniques, such as DSC (***Differential Scanning Calorimetry***), according to a methodology internationally standardized by ASTM E1356 (ASTM, 2023). Additionally, several real situations indirectly interfere with film formation, such as the presence of residual monomers, surfactants and the presence of solvents/coalescent. A more practical and realistic alternative is determining the Minimum Film Formation Temperature (MFFT), the temperature in which the latex is converted into a continuous and transparent film.

The MFFT is also determined through an internationally standardized methodology (ASTM D2354), which consists of applying the latex with a 75 µm extender on a copper surface with a temperature gradient between the ends, one cold and the other hot, and monitoring in which position a film occurs free of major imperfections, without being turbid and sticky (ASTM, 2018). The operating range is between -5 °C to 90 °C; however, temperatures below 0 °C in practice are difficult to determine due to water freezing (PILZ, 2004). Figure 1.5 displays MFFT equipment and a visually perceptible comparison of the effect of adding agents that promote coalescence in this test.

(A)

(B)

Figure 1.5: *Equipment for determining MFFT (A) and example of latex film formation with and without adding agents that promote coalescence (B).*

MFFT is widely used and, unlike Tg, is influenced by several factors, corresponding not only to the polymer's property, but its entire formulation. Thus, MFFT is usually lower than Tg due to the plasticizing effect of surfactants and other residual components of the polymerization process (PILZ, 2004). In some cases, the water can confer a plasticizing effect, especially when highly hydrophilic monomers, such as vinyl acetate, are used in the latex polymer composition (WICKS, 2007). A comparison of these two measures can be seen in Table 1.1.

	Vinyl acrylic resin	VEOVA vinyl resin	Pure acrylic resin	Acrylic styrene resin	Styrene butadiene resin
Tg (°C)	6.5	23.7	34.7	20.5	-2
MFFT (°C)	~ 0	15	26	16	~ 0

Table 1.1: *Comparison of Tg and MFFT measurements with standardized methods for different market resins.*
Source: adapted from Pilz (2004).

1.7 COALESCING AGENTS OR COALESCENTS

In many situations, aqueous systems are applied in adverse conditions, considering both temperature and humidity. Even in these cases, it is necessary that they can form a film homogeneously. In addition, the system used in the coating must guarantee typical properties linked to the performance of these materials, such as scrub resistance, hardness, chemical resistance and dirt pick-up. Sometimes these properties may not be achieved by employing a resin consisting of monomers that confer low Tg. At the same time, the use of monomers that impart polymers of higher Tg than ambient temperatures generally require conditions of high application temperatures. Thus, it is necessary to use agents to assist in this film formation process, especially in the final stage of particle coalescence. In practice, coalescent is a solvent that plasticizes the polymer phase present in paint, enamel and adhesive formulations; decreasing their Tg and favoring the deformation of particles in Stage 2 and the interdiffusion of polymer chains in Stage 3.

The coalescent must have solubility parameters compatible with the polymer phase to be plasticized. It cannot destabilize the polymer particles, pigments and fillers present in the paint formulations. The ability to reduce the Tg of the film-forming polymer by the action of the coalescing agent, called plasticizing power, is related to its ability to interact with the polymer chains and increase the free volume between them (KEDDIE, 1997; STEWARD; HEARNA; WILKINSON, 2000). This increase in free volume between the chains increases the mobility of the polymer chains. It favors the polymer particles' deformation, the polymer chains' interdiffusion and the formation of a continuous and homogeneous film. Another critical issue is the elimination of the film coalescent: the coalescent must be volatile enough to be eliminated, at least partially, during the drying of the films, preferably after the evaporation of water. Otherwise, the unwanted effect of permanent plasticization of the film may occur.

The effect of the coalescing agent on the interdiffusion of polymer chains has been extensively investigated in the literature (SHEETZ, 1965; WANG; WINNIK, 1990). Coalescing agents, such as glycolic solvents, can increase the speed of polymer chains interdiffusion in films of aged latexes under the same temperature and humidity conditions.

Some models predict the decrease in MFFT as a function of coalescing concentration (TOUSSAINT et al., 1997). These models suggest that the greater the partition of the coalescent in the polymer phase, and the lower the Tg of the polymer are, the greater its efficiency will decrease the MFFT.

The main characteristics to be considered in selecting a coalescing agent are presented in Figure 1.6.

Resistance to hydrolysis	• To allow use in low and high pH systems.
Solubility in water	• Low to avoid migration when applied to hydrophilic substrates and mitigate hydrophilicity contribution to the film, but not too low to avoid problems during incorporation process and incompatibility in the film.
Freezing point	• Low, preferably less than 10 °C, to enable uncomplicated factory handling.
Color	• As low possible to mitigate interference with paint coloring.
Odor	• As low possible to enable employment in interior paints.
Coalescence efficiency	• Polymer affinity, but not high, to avoid segregation in the formulation. • Compatible solubility parameters for residing at the polymer-water interface.
Evaporation rate	• Lower than water. • Not too low to avoid high permanence, making the film sticky.
Boiling point	• Medium-high temperature range. • Suitable to classify, from low to almost zero, the content of Volatile Organic Compounds (VOC) in the coalescent, depending on the regulations of the region of use.

Figure 1.6: *Main characteristics to be considered in selecting a coalescing agent.*
Source: adapted from Pilz (2004).

The type and amount of coalescing agent to be used must be chosen according to the desired property adjustment in the system and the primary inputs that compose it. Several materials can be used as a coalescent, and Table 1.2 presents the classes and examples of the most representative materials used in the market.

Classes	Examples
Hydrocarbons	• White Spirit
Simple glycols	• Ethylene glycol • Propylene glycol
Glycolic ethers	• Ethylene glycol ethyl ether • Ethylene glycol phenyl ether/Diethylene glycol phenyl ether • Propylene glycol phenyl ether • Monoethylene glycol propyl ether • Diethylene glycol propyl ether • Monoethylene glycol n-butyl ether • Dipropylene glycol n-butyl ether • Ethylene glycol 2-Ethylhexyl ether
Esters	• Methyl fatty esters • 2,2,4-trimethyl 1,3-pentanediol monoisobutyrate • Monoethylene glycol ethyl ether acetate

Table 1.2: *Classes and examples of coalescent used in the market.*
Source: adapted from Pilz (2004); Raja et al. (2010; 2012); Wang et al. (2016); Indorama Ventures (2023).

Figure 1.7 allows graphical visualization of the quantitative effect of a coalescing agent such as diethylene glycol phenyl ether on a styrene-acrylic latex.

Typically, amounts of about 2 to 8 phr (mass amount of coalescing for every 100 parts of pure resin) are employed in paint formulations, but with a great tendency to use the smallest possible amounts to mitigate not only costs, but the contribution to the total content of volatile organic compounds in the final formulation.

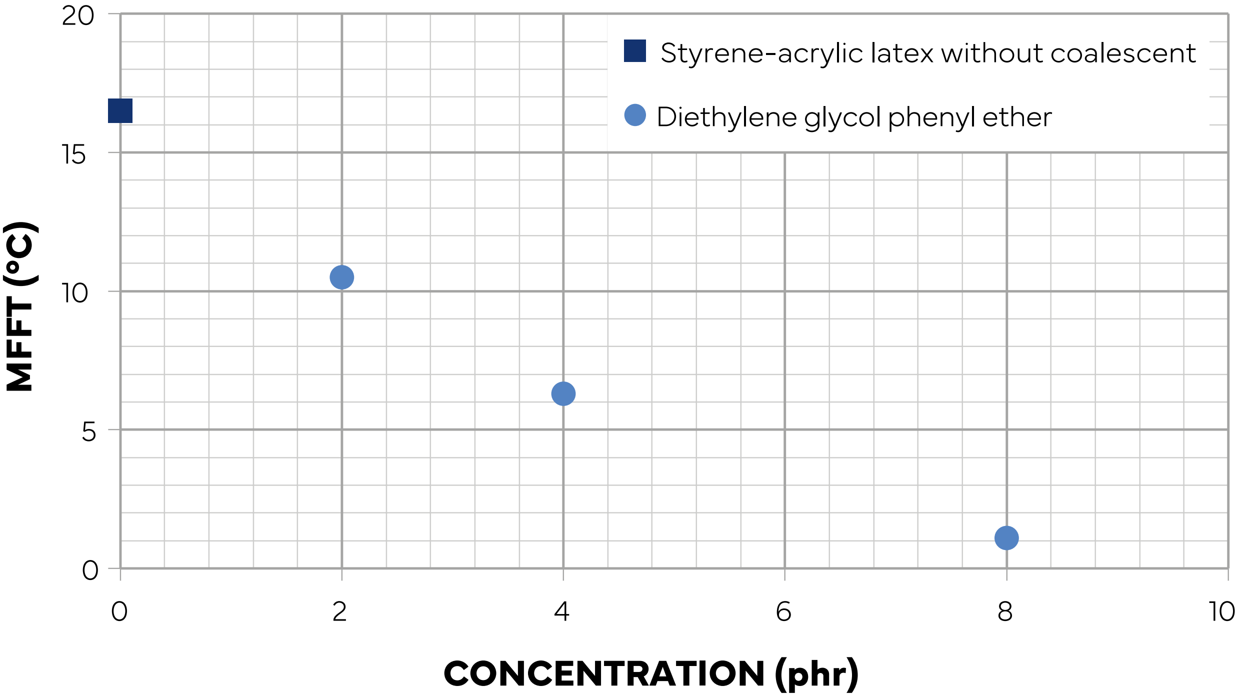


Figure 1.7: *Effect of amount of coalescing agent on MFFT response.*

1.8 CONCLUSION

It can be evidenced that the film formation process is one of the most important within paint technology. It is latent that its understanding is fundamental to obtain the desired coating, either for aesthetic purposes or to protect the substrate to ensure the expected quality and performance. It can also be concluded that this process suffers different influences and depends strongly on the composition of the paint, its form and application conditions. In the specific case of water-based systems, the film formation process is somewhat more complex and requires agents promoting polymeric particles' coalescence. These coalescing agents may belong to several chemical families and be obtained by different routes, but what defines them is, above all, the ability to promote a good and homogeneous film formation from latex.

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Part 2

Solvents: basic concepts, selection criteria and composition analysis

2 Solvents in paints: basic concepts and selection criteria for various applications

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2.1. INTRODUCTION

The use of coatings and their dilution solvents for surface painting is intended for two main functions: protection, thus increasing the material's durability and decoration. Solvents, due to their excellent properties and versatility of use, have an essential function in coating formulations since the inception of the paint industry.

There are several criteria for choosing a solvent for paint and varnish formulations. The proper choice of solvent depends on the desired characteristics of the final coating in the application and the process used. The final characteristics are usually linked to the solvents' physicochemical properties and chemical nature.

2.2 HANSEN SOLUBILITY PARAMETERS

Paints form films on a substrate from organic polymers (resins) after solvent evaporation by drying or coalescing. The solvent system plays a key role in controlling the solubility of the resins and the drying speed, which will consequently have a strong influence on the final properties of the coating.

The knowledge of the resin solubility behavior is essential from a technological point of view, as different film morphologies have been obtained changing the solvent and polymeric systems.

The solubility of a polymer and other solid materials of paint in a given solvent is understood by semi-empirical models, such as Hansen solubility parameters (HSP), developed by scientist Charles Hansen.

It is particularly useful for aiding in the best choices of solvents or solvent mixtures in a formulation from a solubility point of view.

The HSP is related to the quantification of the intermolecular forces of a compound. The model demonstrates that the closer the intermolecular forces between different compounds are, the greater their affinity. Thus, properly combining these properties is critical to ensure good solubility and compatibility of the solvent with the resins present in the paint formulation. The intermolecular forces of compounds are expressed in units of energy as $(\text{joules/cm}^3)^{1/2}$, which is equivalent to $\text{MPa}^{1/2}$, or in $(\text{cal/cm}^3)^{1/2}$, and those considered in the PSH model are as follows:

- London forces (δD) = dispersive forces - attractions or repulsion between molecules by dipole effects.
- Polar forces (δP) = displacement of electrons according to the nature of the atoms and their distribution in the molecule.
- Hydrogen bonds (δH) = formation of hydrogen bonds.

Dr. Charles Medom Hansen, born in 1938 in Louisville, KY, worked for his PhD at the Technical University of Denmark. In 1967, his thesis provided the basis for what came to be called Hansen Solubility Parameters.

2.2.1 London forces (δD)

The London forces, also known as Van der Waals forces, come from interactions of the motions of electrons among the atoms of a substance. They are equivalent to the sum of all attractive or repulsive forces of a substance and are not correlated with covalent bonds between molecules.

2.2.2 Polar forces (δP)

When two atoms of different electronegativities bond by covalence, the sharing of the bonding electrons is done unevenly, with the most electronegative atom receiving a more significant portion of the total electron density of the bond. This gives rise to dipoles in the molecule, as schematized in Figure 2.1 (methanol molecule).

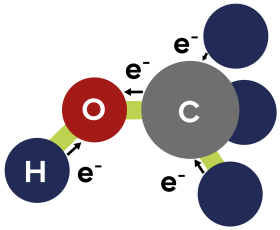


Figure 2.1: *Intrinsic polarity covalent bonds.*
Source: *adapted from Ponzetto; Kuniyoshi; Rosa (2002).*

2.2.3 Hydrogen bonds (δH)

This intermolecular force occurs in molecules that have a bonded hydrogen atom in their composition, by covalence, to another atom that is strongly electronegative, such as oxygen, nitrogen, or fluorine. When this occurs, the hydrogen atom becomes an electron receptor. It can act as a bridge between two oxygen atoms (electron donor), and bonds can occur by covalence or electrostatic forces.

Butylglycol is an example of a solvent that presents this intermolecular force effectively, as shown in Figure 2.2.

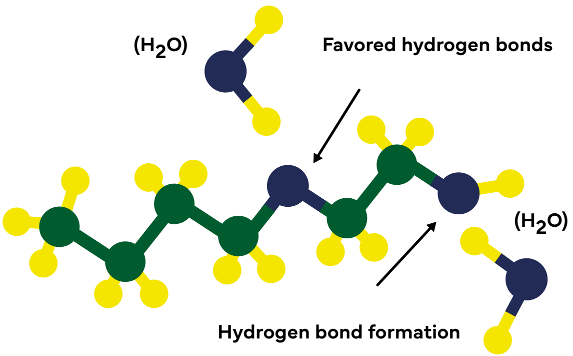


Figure 2.2: *Basic representation of hydrogen bonds.*
Source: *adapted from Ponzetto; Kuniyoshi; Rosa (2002).*

Hydrogen bonds influence several properties of compounds, such as boiling point, evaporation behavior, and water solubility, among others.

2.3 HANSEN THREE-DIMENSIONAL SYSTEM

The HSP can be considered such as a point in space starting from the vector of each of the three intermolecular forces. This point is determined by Equation (1), Hansen three-dimensional system:

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \qquad (1)$$

That way, Hansen three-dimensional system allows the graphical visualization of the point of solubility of a given solvent in space, as shown in the graph in Figure 2.3. This facilitates the comparison of different types of solvents and assists in predicting the best solubilization conditions for obtaining formulations.

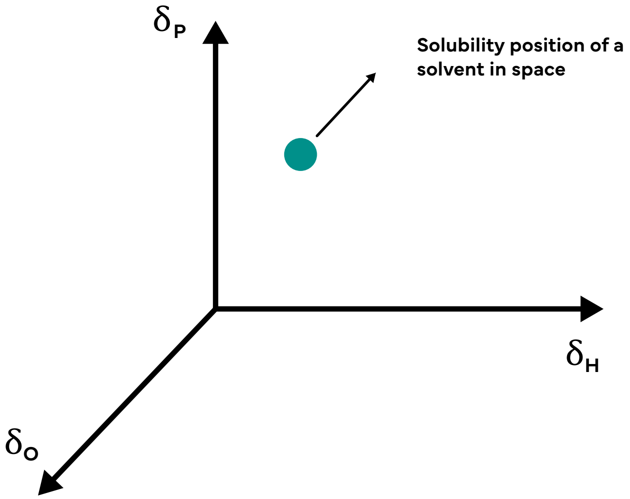


Figure 2.3: *Position of solubility of a solvent in space.*
Source: *adapted from HSP ([201-]).*

The Hansen model also makes it possible to obtain HSP from solvent mixtures. The calculation is valid if we consider the weighted average of the volumetric fraction of each solvent in a given mixture.

Table 2.1 demonstrates an example of calculating the HSP of a solvent mixture.

Solvents	δD	δP	δH	Volumetric %
X-solvent	15	7	2	50
Y-solvent	17	9	6	50
Mixture	16	8	4	100

Table 2.1: *Calculation of Hansen solubility parameters for a solvent mixture.*
Source: *adapted from HSP ([201-]).*

Combining different solvents allows one to achieve the desired solubility properties that could not be obtained with a single solvent.

2.4 RADIUS OF INTERACTION

It is possible to verify whether a particular solvent or a mixture of solvents can solubilize a resin. For this verification, the determination of the radius of the interaction of the solvent with the resin was equated. Equation (2) allows verifying the distance in the space between the HSP of the solvent concerning the HSP of the resin:

$$D(s - p) = [4(\delta Ds - \delta Dp)^2 + (\delta Ps - \delta Pp)^2 + (\delta Hs - \delta Hp)^2]^{1/2} \qquad (2)$$

W herein:
D(s - p) = distance between solvent and center of resin solubility
δXs = Hansen parameters of solvent
δXp = Hansen parameters of polymer

For a solvent to solubilize a resin, it must have HSP close to the HSP of the resin, and there is a distance limit between these values for solubilization to occur. This limit is related to the radius of solubility or interaction of the resin, which differs from polymer to polymer.

In such a way, the interaction radius provides a solubility volume for each resin which can be observed in a three-dimensional system.

That is, solvents whose HSP is located below the interaction radius of a given resin will be within the solubility volume and will be considered true solvents.

Figure 2.4 shows the volume of solubility of a resin and the position of different solvents concerning this resin, so that it can be observed which is inside or outside the solubility radius.

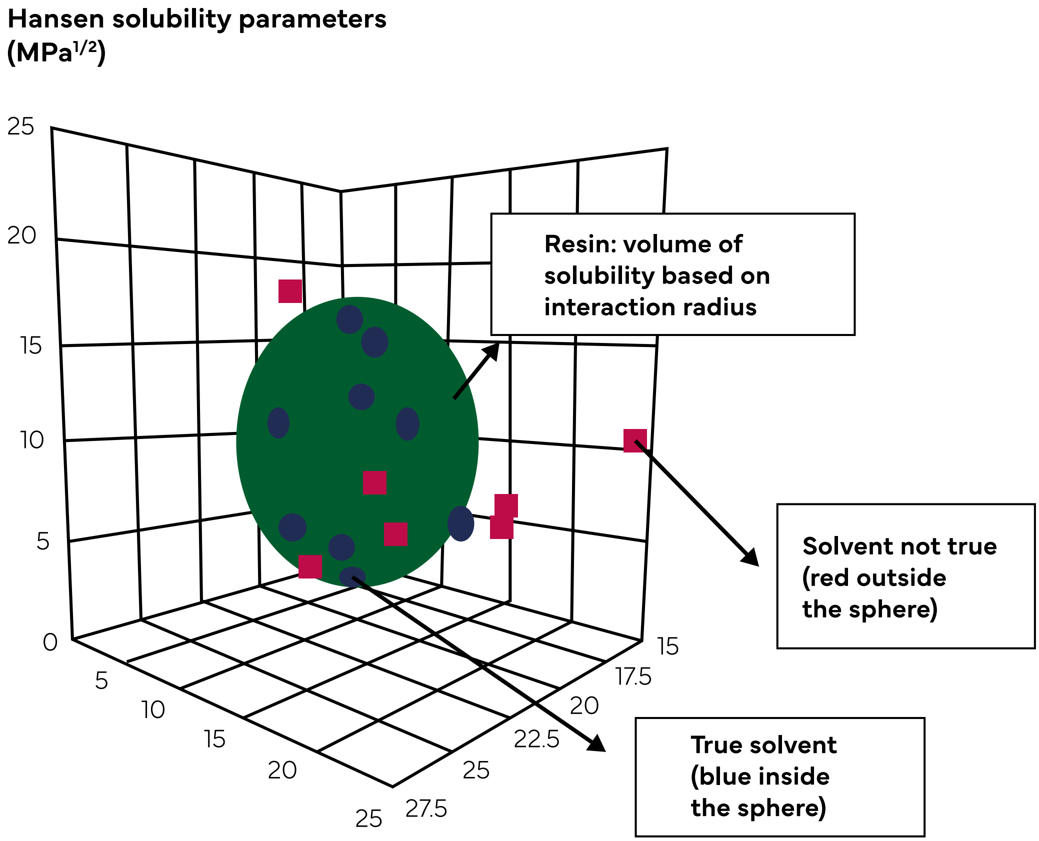


Figure 2.4: *Schematic containing a three-dimensional spherical diagram of Hansen solubility parameters for resin/solvent system.*

Source: *adapted from HSP ([201-]).*

Table 2.2 presents examples of the solubility radius of different types of resins compared to the solubility radius of different solvents.

Polymer	**$\delta MPa^{1/2}$**			
	δD	**δP**	**δH**	**R**
Cellulose acetate	18.6	12.7	11.0	7.6
Epoxy	20.4	12.0	11.5	12.7
Isoprene-elastomer	16.6	1.4	-0.8	9.6
Nitrocellulose ½ sec	15.4	14.7	8.8	11.5
Polyamide	17.4	-1.9	14.9	9.6
Poly(isobutylene)	14.5	2.5	4.7	12.7
Poly(ethyl methacrylate)	17.6	9.7	4.0	10.6
Poly(methyl methacrylate)	18.6	10.5	7.5	8.6
Polystyrene	21.3	5.8	4.3	12.7
Poly(vinyl acetate)	20.9	11.3	9.6	13.7
Poly(vinyl butyral)	18.6	4.4	13.0	10.6
Poly(vinyl chloride)	18.2	7.5	8.3	3.5
Polyester	21.5	14.9	12.3	16.8

Table 2.2: *Hansen solubility parameters and radius of interaction of resins.*
Source: *HSP ([201-]).*

2.5 PRACTICAL DETERMINATION OF HANSEN SOLUBILITY PARAMETERS

The HSP of a resin and its radius of interaction with solvents can be obtained by laboratory experimental values or by software simulations with data by the contribution of molecular groups. The HSP of a resin in the laboratory is determined by resin/solvent solubility experiments, which will provide information about the solubility or non-solubility of the resin in the solvent.

Experimental data are processed in specific software based on the HSP of each solvent used to obtain the HSP and the radius of the interaction of the resin.

2.5.1 Experimental procedure

1. Define the polymer to be studied.
2. Use thirty solvents for polymer solubilization. The ratio of solvents is in Table 2.3.

Identification	Solvents of the method
1	2-etil hexanol
2	Sec-butyl acetate
3	Ethyl acetate
4	Ethyl glycol acetate
5	Acetone
6	Acetonitrile
7	Water
8	Furfuryl alcohol
9	Cyclohexane
10	Cyclohexanone
11	Diacetone alcohol
12	DIBK
13	Dimethyl sulfoxide (DMSO)
14	N,N–dimethylformamide (DMF)
15	Ethanol
16	Ethanolamine (MEA)

Identification	Solvents of the method
17	Ethylbenzene
18	Ethylene glycol (MEG)
19	Ethyl glycol
20	Hexylene glycol
21	Isophorone
22	Isopropanol
23	Ethyl lactate
24	m-Cresol
25	MIBK
26	n-Butylamine
27	n-Hexane
28	Nitrobenzene
29	n-Methyl pyrrolidone
30	Tetrahydronaphthalene

Table 2.3: *Solvents for Hansen solubility parameter - HSP.*

3. Add 0.5 g of polymer and 4.5 mL of pure solvent in a test tube. Perform this operation for the thirty solvents in different tubes.

Notes:

- The polymer must be weighed on an analytical balance, with an accuracy of 0.01 g.
- The solvent should be added to the test tube through an appropriate syringe that resists solvent attack.
- There can be no solvent loss by evaporation, so the tubes must be well sealed.

4. Place the tubes on a tube stirrer, rotary-table type (see Figure 2.5), at 3-5 revolutions per minute (RPM), remaining agitated for 24 hours.

Figure 2.5: *Rotary table tube stirrer used in Hansen solubility parameter survey tests.*

Source: *EPA (2016).*

5. Then remove the tubes from the stirrer and let them rest for another six days, totaling one week of testing. The entire procedure is conducted at room temperature (23 °C to 25 °C).

6. After this rest time, collect the results through visual evaluation, as outlined in Figure 2.6.

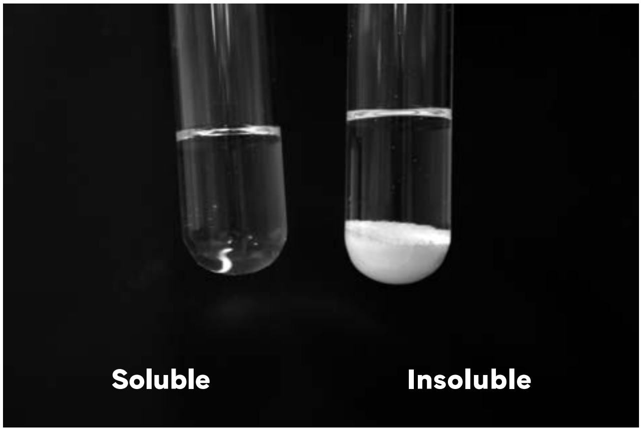


Figure 2.6: *Visual evaluation for solvent-reference affinity classification in Hansen solubility parameter survey tests.*

7. For each solvent evaluated, classify the results obtained as soluble or insoluble.

8. Insert this data into the specific software (e.g., HSPiP - Hansen Solubility Parameters in Practice) to determine polymer solubility parameters.

2.6 EVAPORATION BEHAVIOR

Evaporation behavior is essential in developing a balanced formulation adapted to the conditions of application and formation of the paint film.

The heat exchange of the solvent with the environment causes evaporation of the solvent. However, the solvents have different evaporation behaviors when combined in resin/solvent systems. According to the illustrative scheme shown in Figure 2.7, the solvent composition must be balanced to avoid incompatibility with the resin and obtain adequate control of evaporation, thus ensuring the quality of the paint during and after its application.

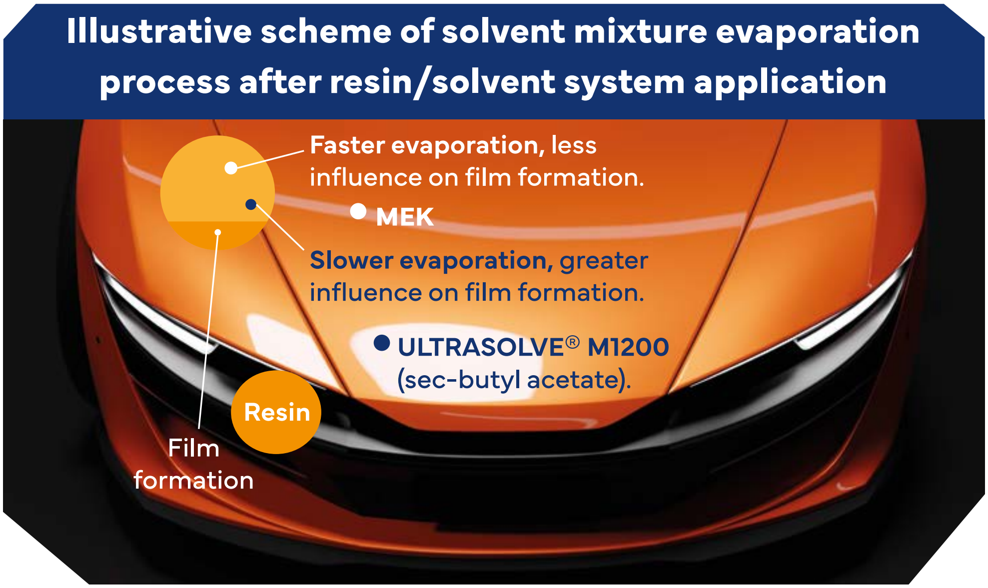


Figure 2.7: *Evaporation of solvents after application of resin/solvent system.*

The Evaporation Rate (ER) measures a solvent's evaporation behavior. It comprises the ratio between the time required for the evaporation of 90% of the mass of n-Butyl acetate and the time required for the evaporation of 90% of the mass of the solvent analyzed under the standard test conditions. ER = 100 is adopted for n-Butyl acetate as the universal standard. The mathematical expression describing the evaporation rate according to the previous description is presented in Equation (3).

$$\text{Evaporation rate} = \frac{t_{90\%\ \text{standard}} \times 100}{t_{90\%\ \text{sample}}} \qquad (3)$$

Note: The evaporation rate data of the solvents can be verified in Table 2.14.

The determination of solvent and solvent mixture evaporation rates is commonly evaluated by an evaporometer (see Figure 2.8) in the laboratory and from modeling of physical properties and molecular interaction between solvents.

Figure 2.8: *Equipment called evaporometer, used for determining solvent evaporation rates.*

The graphical evaluation helps to visualize the differences in evaporation behavior.

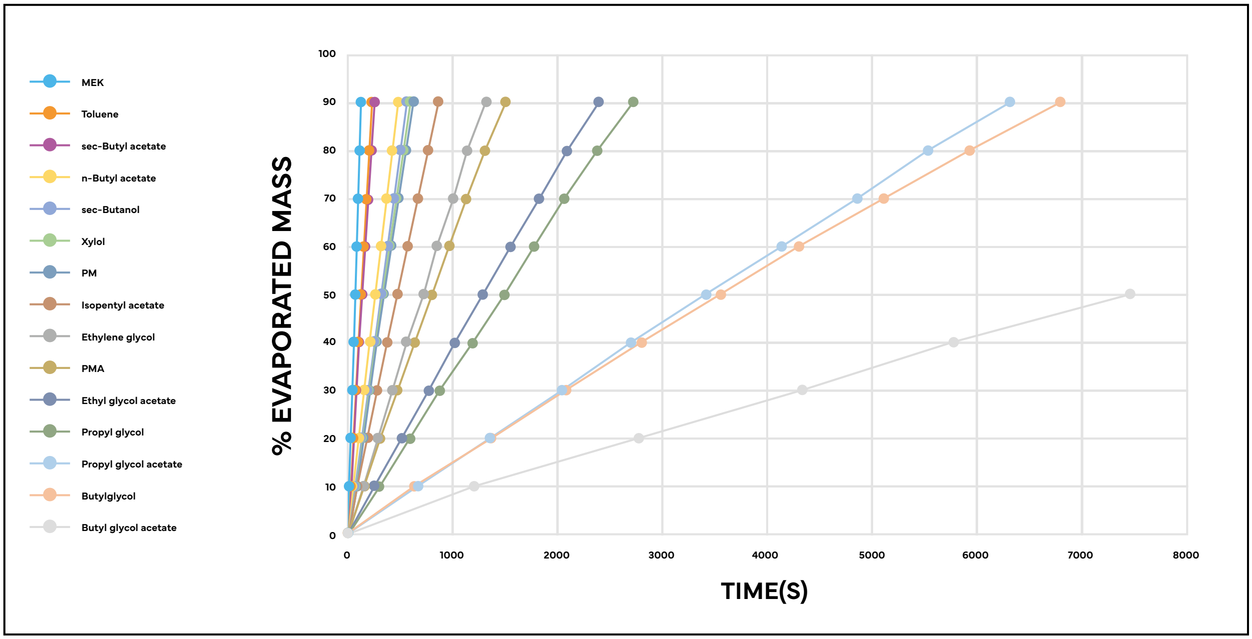


Figure 2.9: *Solvent evaporation curve, according to ASTM D3539 method.*

Solvents can be classified as light, medium and heavy in correlation with their evaporation rate although this classification is a function of temperature or boiling point.

- Light solvents: solvents that have a boiling point < 100 °C.
- Medium solvents: solvents with a boiling point between 100 °C and 150 °C.
- Heavy solvents: solvents that have a boiling point > 150 °C.

2.7 BLUSHING RESISTANCE

Blushing corresponds to the staining that may appear on the paint film during drying. This effect is caused by water absorption from the environment when solvent evaporation occurs, with consequent resin precipitation or hydrolysis precipitation.

This effect can be eliminated with proper solvent balancing. By using a mixture of products with high, medium, and low evaporation speeds, compatible with the resin, the system undergoes adequate evaporation to the quality required for the dry film. Figure 2.10 shows some results of the resistance of some solvents to blushing.

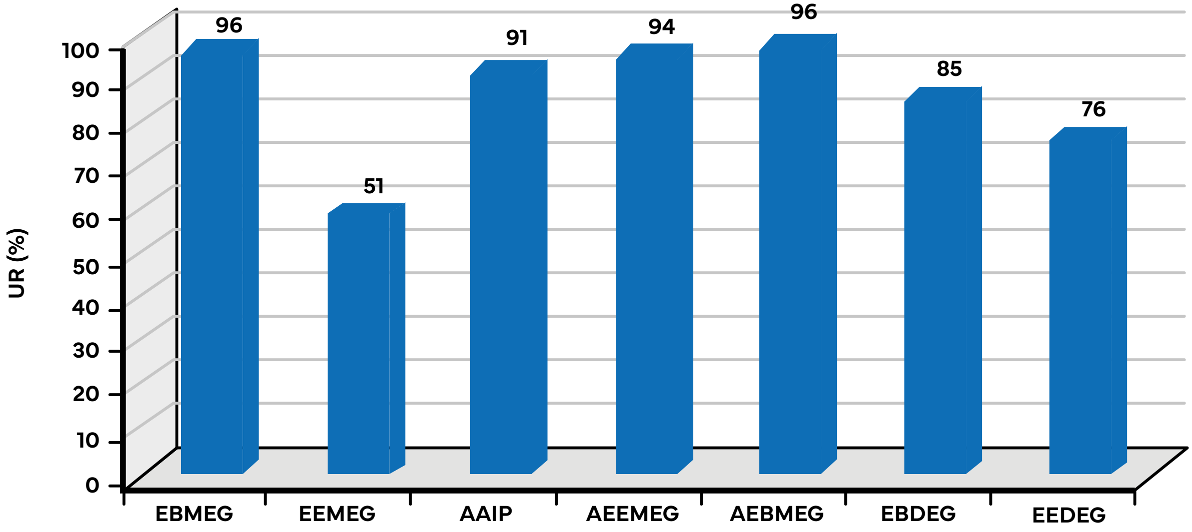


Figure 2.10: *Blushing resistance, 25 °C, % RH (relative humidity).*

Caption: EBMEG = butylglycol; EEMEG = ethylglycol; AAIP = isopentyl acetate; AEEMEG = ethylglycol acetate; AEBMEG = Butylglycol Acetate; EBDEG = butyldiglycol; EEDEG = ethyldiglycol.

2.8 COUPLING POWER

Coupling power measures a product's ability to turn miscible a mixture of immiscible organic products with water, as illustrated in Figure 2.11.

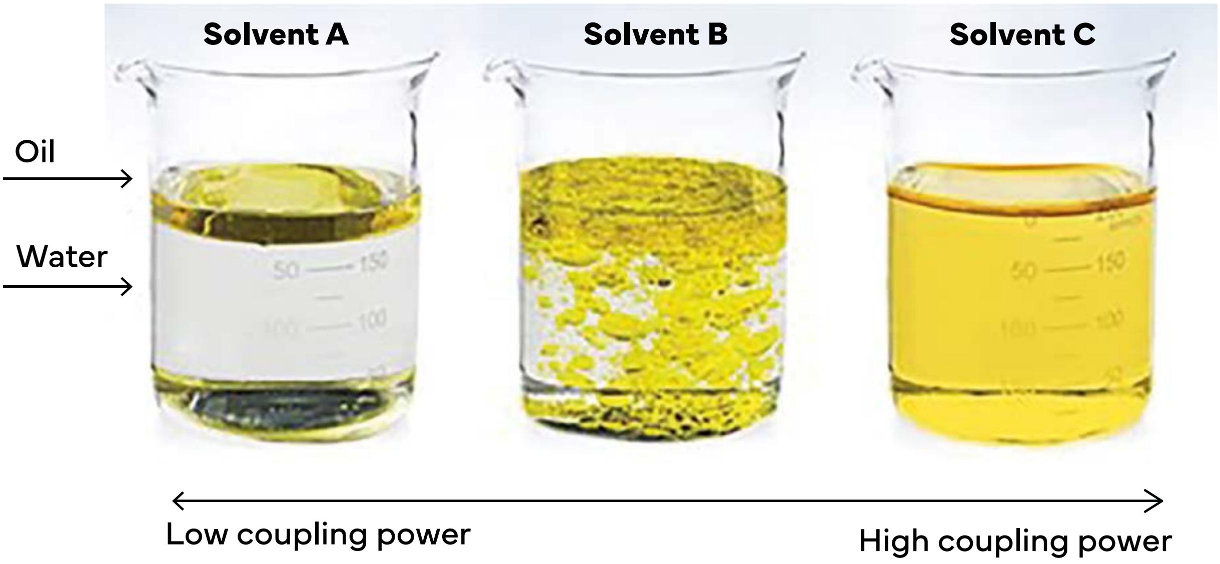
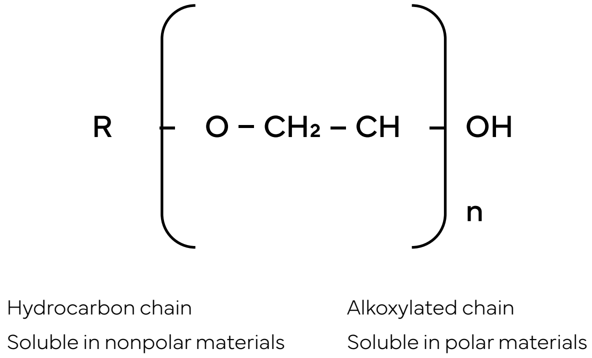


Figure 2.11: *Miscibility of products - water/oil/ solvent mixtures.*

The smaller the amount of solvent required to homogenize the system, the greater is the coupling power. For water-soluble systems, that is, water-dilutable paints, the most used solvents are those that present high polarity, especially glycol ethers, thus conferring sufficient solubility in water to obtain high stability of organic materials in the aqueous phase.

Glycol ethers, because they contain in their molecular structure a hydrocarbon chain and an alkoxylated chain, have unique solvency characteristics for a wide variety of applications in addition to favoring miscibility and coalescence in water-soluble systems, as illustrated in the figure below:



$$R - \left[O - CH_2 - CH \right]_n - OH$$

Figure 2.12: *General structure of ethylene oxide derived glycol ethers.*

2.9 ELECTRICAL RESISTANCE/CONDUCTIVITY

Electrical conductivity is a property inversely proportional to electrical resistance or resistivity. This property is particularly important in electrodeposition application systems, where the final coating result depends on the electrical conductivity of the systems.

In addition, the control of the electrical conductivity of paint is critical in the electrostatic painting process, in which the diluted paint is provided before painting. An electrical load is necessary for the paint to have adequate levels of electrical conductivity, to obtain a more significant transfer of paint to the surface and, at the same time, sufficient electrical resistivity to avoid short circuits in the automated painting system. It avoids risks of accidents such as fire or explosion. All ingredients in a paint affect its electrical resistance, but solvents are widely used to adjust it. Polar solvents have high electrical conductivity, while nonpolar solvents have low electrical conductivity. The electrical conductivity can be evaluated by the constant dielectric through measurement in the laboratory using the conductivity meter, as shown in Figure 2.13.

Figure 2.13: *Conductivity meter equipment: electrical conductivity and resistivity measurement.*

2.10 VOLATILE ORGANIC COMPOUND (VOC)

A commonly used term in the industry is VOC (Volatile Organic Compound). They are emitted from various sources, such as automobile exhaust, industrial processes, consumer products, paints, and coatings, among others. The coatings industry contributes a small portion of VOC emissions; however, in applications, the solvents account for the majority of VOC emissions.

Ozone is formed when the VOC reacts with nitrogen oxide from the atmosphere under the influence of sunlight and heat. Some of them react faster than others, and some produce more ozone per emitted volume than others. Ozone formed in the lower atmosphere causes pollution in the air we breathe, which can cause damage to the human respiratory system.

According to the Environmental Protection Agency (EPA), the term VOC refers to any carbon compound, excluding carbon monoxide, carbon dioxide, carbonic acid, metal carbides or carbonates, and ammonium carbonate, which participates in photochemical reactions in the atmosphere (USA, 1986). Solvents not included in the EPA definition are called "exempt compounds." This category of compounds is established and modified by legislation. According to the EPA, organic compounds "have been determined to have negligent photochemical reactivity." These "exempt compounds" are beneficial when performing solvent functions without increasing the VOC content in the formulations.

One of the ways to evaluate VOC and its impact on the environment is by the photochemical reactivity of each VOC. The photochemical reactivity is based on the ozone formation potential of a given VOC under specific atmospheric conditions and nitrogen oxide concentrations and can be represented by Equation (4):

$$\text{VOC} + \text{NO(x)} + O_2 + \text{Light} \rightarrow O_{3\,\text{(main pollutant)}} + HNO_3 + \text{organic compounds} \tag{4}$$

It is possible to evaluate the maximum potential photochemical reactivity of each VOC. Through this evaluation, the Maximum Incremental Reactivity (MIR) is obtained. The MIR is expressed in grams of ozone formed per gram of VOC (5):

$$\text{MIR}\,(\text{g O}_3 \div \text{g VOC}) = \max \left(\frac{\text{mass O}_3}{\text{mass VOC}} \right) \qquad (5)$$

VOCS have different photochemical reactivities, producing more or less ozone. The graph in Figure 2.14 compares the MIR of some solvents.

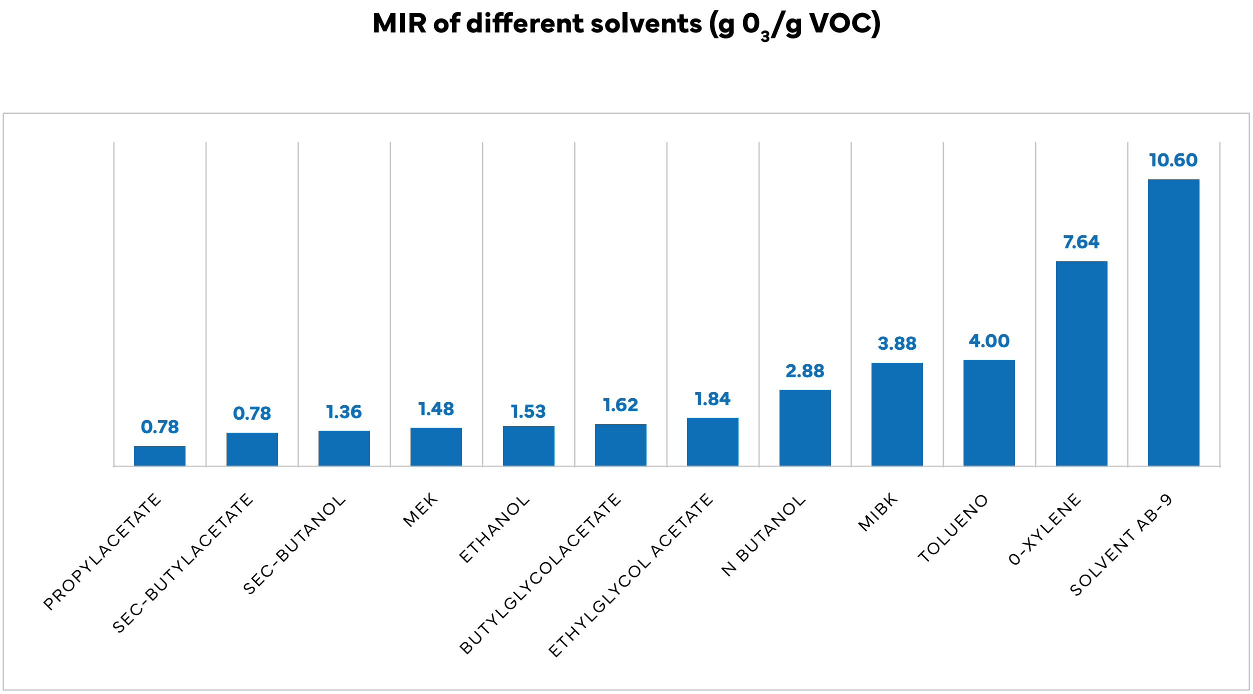


Figure 2.14: *MIR of different solvents.*
Source: *CARB (2023).*

The choice of solvents with the lowest MIR value possible will help obtain a paint with the lowest potential for pollutant (ozone) formation after application. The MIR values of other solvents can be found on the California Air Resources Board (CARB) website: https://ww2.arb.ca.gov/sites/default/files/2020-12/cp_reg_mir-tables.pdf

2.11 HAZARDOUS AIR POLLUTANTS (HAP)

Some solvents are regulated as Hazardous Air Pollutants (HAP). The EPA resolution dealing with the matter includes a list of 191 chemical compounds and categories of highly toxic compounds.

Some of the listed compounds are widely recognized for their dangerousness, and others are generally considered to be of low toxicity. As with VOCS, the EPA limits the amount that can be emitted, but does not propose to ban the emitted. HAP products can be found on the EPA website: https://www.epa.gov/haps/initial-list-hazardous-air-pollutants-modifications.

2.12 APPLICATIONS AND EXAMPLES OF FORMULATIONS

The solvents fulfill fundamental functions in preparing, stabilizing, and applying paints and varnishes. They are present in the formulations of the most diverse segments: original automotive, car refinish, can coatings, wood, industrial maintenance, inks, coil coatings, among others.

Some examples of applications and formulations will be presented below.

2.12.1 Original automotive paint

Solvents can be used in all stages of original automotive painting and its complements, providing excellent performance in the application.

2.12.1.1 Surface primer

Automotive surface primer technology typically utilizes epoxy, alkyd, or polyester resins, modified or unmodified, and requires active solvents to ensure good and defect-free application.

Solvent-based *surface primer* example

Components	% mass
Modified urethane polyester resin	30.00
Melamine/formaldehyde resin	9.00
Blocked isocyanate	6.00
Leveling agent	2.00
Pigment (titanium dioxide)	12.00
Mineral filler (synthetic barium sulphate)	18.00
Dispersant agent	0.15
Rheological modifier	0.80
Propylglycol acetate	3.50
sec-Butanol	5.00
Butylglycol acetate	7.50
Xylol	7.05
Total	**100.00**

Table 2.4: *Solvent-based surface primer formulation – original automotive.*

2.12.1.2 Base coat

Base coats can be composed of polyester or acrylic resins cross-linked with melamine resin to favor the application of the varnish before total drying, ensuring greater durability and a better appearance for metallic colors.

Example of solvent-based base coat formulation

Components	% mass
Hydroxylated saturated polyester resin	4.0
Melamine resin	1.5
CAB resin (cellulose acetate butyrate)	2.5

Aluminum pigment	2.2
5% Polyethylene wax solution	29.0
Sec-butyl acetate	36.0
Xylol	24.8
Total	**100.0**

Table 2.5: *Solvent-based base coat formulation – original automotive.*

Example of dilution thinner for solvent-based base coat

Components	% mass
Sec-butyl acetate	40.0
sec-Butanol	10.0
Xylen	50.0
Total	**100.0**

Table 2.6: *Thinner formulation for solvent-based base coat – original automotive.*

Example of water-based base coat formulation

Organic solvents with coupling function are used in most resins to facilitate miscibility with water. As organic solvents have a much lower surface tension than water, they facilitate the adhesion and wetting of the system.

Components	% mass
Acrylic dispersion	47.8
Polyester resin	9.3
Aluminum pigment	3.6
Crosslinking agent	4.5
Butyl glycol	7.3

Water	25.5
Neutralizing agent (Amine - DMEA)	2.0
Total	**100.0**

Table 2.7: *Water-based base coat formulation – original automotive.*

2.12.2 Automotive Enamels

High-temperature drying paints, from 130 ºC to 140 ºC, used for monolayer systems that replace the double-layer system of base coat and clear coat.

Automotive enamel formulation example

Components	% mass
Hydroxylated saturated polyester resin	28.0
Pigment (titanium dioxide)	22.4
Crosslinking agent	17.6
Dispersant agent	1.8
Rheological agent	21.0
Leveling agent	0.6
Catalyst (neutralized dodecyl benzene sulfonic acid amine - DDBSA)	0.5
Butylglycol acetate	3.6
Xylene	4.5
Total	**100.0**

Table 2.8: ***Enamel Formulation – original automotive.***

2.12.3 Car Refinish

The need to repair and repaint vehicles brings a great challenge to the automotive repainting market, which is to provide products that reproduce the color and the finishing of the original paint. The primary final products are primers (top coating), paints, thinners, and complements, such as grading pastes and polishing waxes.

2.12.4 Varnishes

Products based on acrylic resins and isocyanates used to give a better appearance and resistance to the final finishing. Table 2.9 exemplifies a safer formulation with 70% VOC reduction.

Varnish formulation example

Raw material	(1) Conventional 2K PU varnish	(2) VOC reduction 2K PU varnish
Polyester Resin	31.4	31.4
Propylglycol acetate	0.0	4.0
Sec-butyl acetate	0.0	23.0
Isopentyl acetate	0.0	15.4
C5-C12 aliphatic solvent	0.0	9.5
MIBK (methylisobutyl ketone)	10.0	0.0
PMA (methyl propylene glycol acetate)	25.0	0.0
Xylol	16.9	0.0
Leveling agent	0.1	0.1
Catalyst	0.1	0.1
UV absorber (ultraviolet)	1.0	1.0
Aliphatic isocyanate	15.5	15.5
Total	**100.0**	**100.0**
MIR g O_3/g VOC	2.0	0.6

Table 2.9: *2K PU varnish formulations – car refinish.*

2.12.5 Base coats

2.12.5.1 Polyester base

Polyester resin-based products can be modified with CAB (cellulose acetate butyrate) and other polymers. The application must be followed by polyurethane varnish to confer properties such as gloss, chemical resistance, and ultraviolet resistance to the final finishing.

Polyester finishing base formulation example

Components	% massa
CAB 381-20	2.0
CAB 531-1	1.5
Polyester Resin	5.5
Pigment	3.5
Polyethylene Wax	1.0
Sec-butyl acetate	67.0
Xylene	19.5
Total	**100.0**

Table 2.10: *Suggestive formulation – car refinish polyester base coat.*

2.12.6 Thinners

Diluents for finishing bases and primers require adequate balance to offer good solvency power and evaporation balance during the application process. Table 2.11 provides an example formulation with VOC reduction and aromatic compound-free products.

Example of polyester thinner formulation

Componentes	Conventional Thinner 1 (market tandard)	Alternative Thinner 2 with VOC reduction
Propylglycol acetate	0.0	9.0
Sec-butyl acetate	30.0	56.0
Isopentyl acetate	0.0	35.0
PMA (methyl propylene glycol acetate)	18.0	0.0
Xylol	52.0	0.0
Total	**100.0**	**100.0**
MIR g O_3/g VOC	4.6	1.1

Table 2.11: ***Automotive polyester thinner formulations*** *– car refinish.*

In the graph in Figure 2.15, it is possible to observe the evaporation behavior of the thinners.

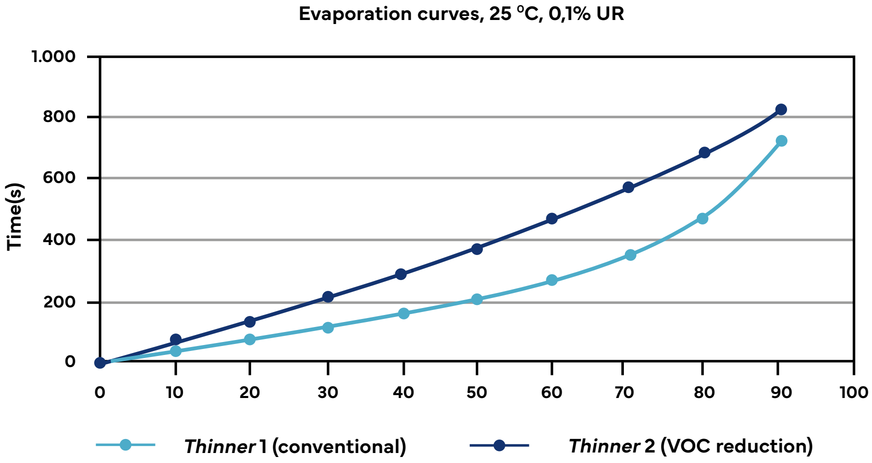


Figure 2.15: *Evaporation behavior of automotive polyester thinners 1 and 2, according to ASTM D3539 method.*

2.12.7 Wood paints and varnishes

The products intended for painting wood surfaces serve a wide range of products of the furniture industry, such as furniture, floors, carpets, and partitions. The main technologies involved comprise water-based systems, UV curing and solvents (polyurethanes, nitrocellulosics, alkyd, phenolics, melamines). The solvents are used in all stages of painting the wood and its complements, providing excellent performance in the application and influencing several properties of the paint or varnish, such as adhesion, chemical resistance, flexibility and hardness, in addition to assisting in the application process by different systems, such as spray, roller and immersion. The following are the most used in wood coatings formulations: ketones, acetates, alcohols, glycol ethers, and aromatic and aliphatic hydrocarbons.

Example of solvent-based varnish and sealer formulation

Components	Varnish (m/m%)	Sealer (m/m%)
CAB	16.7	20.3
Maleic resin	16.7	12.4
Alkyd resin (60% of solids)	2.7	4.7
Plasticizer	1.2	1.8
Additives	1.9	1.1
Xylene	8.9	20.4
Toluene	35.7	20.4
sec-Butanol	8.6	14.6
MEK	7.6	4.3
Total	**100.0**	**100.0**

Table 2.12: ***Varnish formulation and solvent-based sealer - woods.***

Example of formulation of nitrocellulosic and polyurethane thinners

Components	Nitrocellulosic thinner (% m/m)	Polyurethane thinner (% m/m)
MEK	10.0	15.0
Propylglycol	10.0	-
Propylglycol acetate	0.0	5.0
Isopentyl acetate	12.0	15.0
Ethanol	20.0	-
Toluene	22.0	30.0
Xylene	26.0	35.0
Total	**100.0**	**100.0**

Table 2.13: *Formulation of nitrocellulosic and polyurethane thinners - woods.*

2.12.8 Printing inks

Printing inks are intended for application on various surfaces, such as paper, plastic films, rubber, metal, and plastic, among others. One of the significant challenges of this segment is the variety of formulations required to meet the requirements of the different substrates and printing machines.

Ink, solvents, substrate, and printing machines work together to achieve the desired printing results. Ink is the most flexible adjustment component and the key factor in the final quality of a print job. Printing inks are classified according to several characteristics, such as:

- printing process;
- final application;
- curing method;
- physical form (liquid or pasty).

The most common classification is made according to the printing process; the most frequent being offset, rotogravure, flexography, typography, screen printing, and digital printing.

2.12.8.1 Flexography and rotogravure

The solvents employed in the manufacture of flexographic and rotographic printing, widely used for printing flexible packaging, comprise mixtures of n-Propyl acetate, sec-Butyl acetate, ethyl acetate, isopropanol, glycolic ether of mono propylene glycol and mono ethylene glycol, ethanol, sec-Butanol, iso-propanol, n-Propanol, among others.

2.12.8.2 Application with high performance

The solvents have the disadvantage of presenting large differences in evaporation rates, causing unbalance of the formulation and emission to the atmosphere of high-volatility solvents during the application process, specifically during the handling and recirculation of the ink in the printing machine.

Handling the printing ink by flexography and rotogravure occurs before the printing step, and the manipulation of the ink occurs to adjust the viscosity, an important property for good printing quality. Viscosity adjustment is performed with dilution thinners.

In flexographic or rotogravure printing, the ink is transferred from its storage container, through pumping to the printing cylinders, which will transfer the exact amount of ink to the substrate to be printed. Excess ink returns to the storage container through pumping. In this way, an ink recirculation cycle is established between the "ink cartridge" and the printing cylinders. In this recirculation cycle, solvents are lost by evaporation of the paint and its dilution. Thus, there is a need to replace dilution thinners in the inks that are handled and recirculated in the printing process to maintain the appropriate viscosity for the application and quality of the final printing.

The use of medium evaporation solvents, such as n-Propyl Acetate and sec-Butyl acetate, ensures less loss of solvents in the handling and recirculation of the ink in the printing machine. In addition, it is possible to reduce retarding solvents, which are very heavy, in the formulation of diluents or thinners, which reduces the risks of solvent retention in flexible plastic films after printing the ink.

2.12.8.3 *Flexographic* thinners

It is possible to obtain diluents formulations for flexographic paints with advantages such as decreased use of retardant solvents and higher yield in application.

Example of flexographic thinner formulations

Components	Thinner reference A (% m/m)	Alternative Thinner B (% m/m)	Alternative Thinner C (% m/m)
Sec-butyl acetate / n-Propyl acetate	0.0	20.0	20.0
sec-Butanol	0.0	18.0	20.0
Ethyl acetate	15.0	0.0	0.0
Monopropylene glycol propyl ether (PM)	15.0	4.0	0.0
Propylglycol	0.0	0.0	2.0
Isopropanol	15.0	0.0	0.0
Anhydrous ethanol	55.0	58.0	58.0
Total	**100.0**	**100.0**	**100.0**

Table 2.14: *Flexographic thinner formulations.*

Application simulations carried out in the laboratory allow for quantifying the losses of solvents by evaporation and the stability of the ink in the printing machine during the industrial process of flexible plastic film printing.

The test samples are generated by diluting a standard paint with the dilution thinners to obtain a viscosity of 20 seconds in a Zahn 2-cup viscometer at a temperature of 25 °C. The samples are subjected to stirring (Cowles disc, at 700 rpm) for 5 hours in an open vessel, causing the evaporation of the solvents.

Subsequently, the amounts of solvents lost by evaporation are determined, and the characteristics of the paint after application are analyzed as follows:

Figure 2.16: *Study of solvent emission/ replacement in the laboratory*

- drying time to touch in s, at 25 °C;
- color and color difference by instrumental measure (ABNT, 2004);
- brightness (ABNT, 2012b).

Gains over solvent replacement due to evaporation during stirring range from 5% to 30% compared to the examples presented. Figure 2.17 shows a simulation of ink handling in machine application.

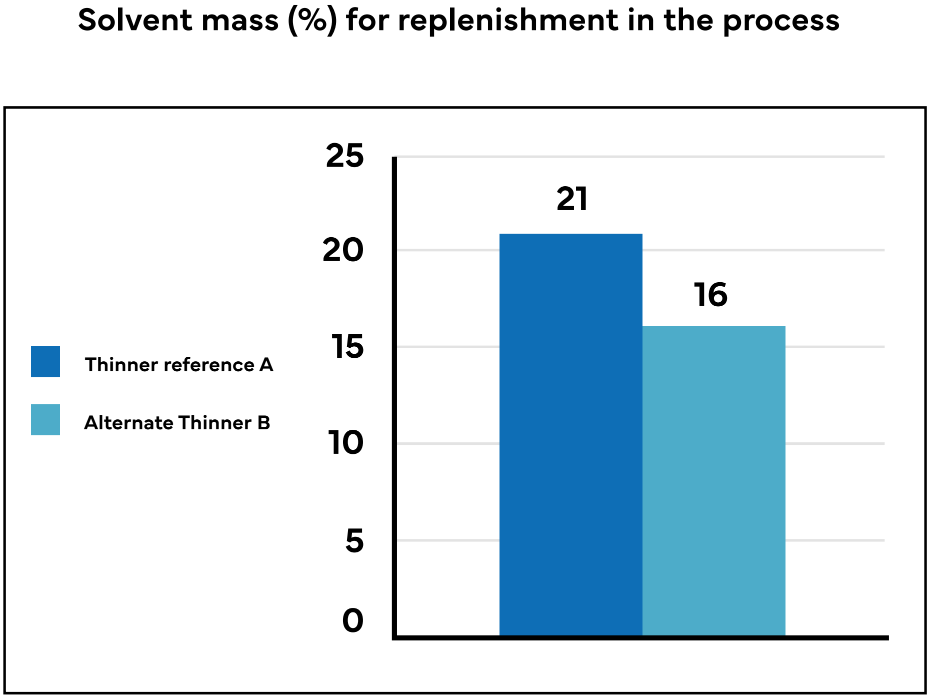


Figure 2.17: *Solvent losses by evaporation during the application after 5 hours of stirring (% m/m).*

Solvent retention is a key requirement for flexible packaging printed with inks and can be determined in the laboratory. Figure 2.18 shows an example of an analysis of solvent retention in polyethylene film with the application of paint diluted with thinners A and B.

Testing conditions:

- Evaluation of PE film with nitrocellulose/polyurethane paint;
- Application of paint with 40 μm extender;
- Drying with hot air.

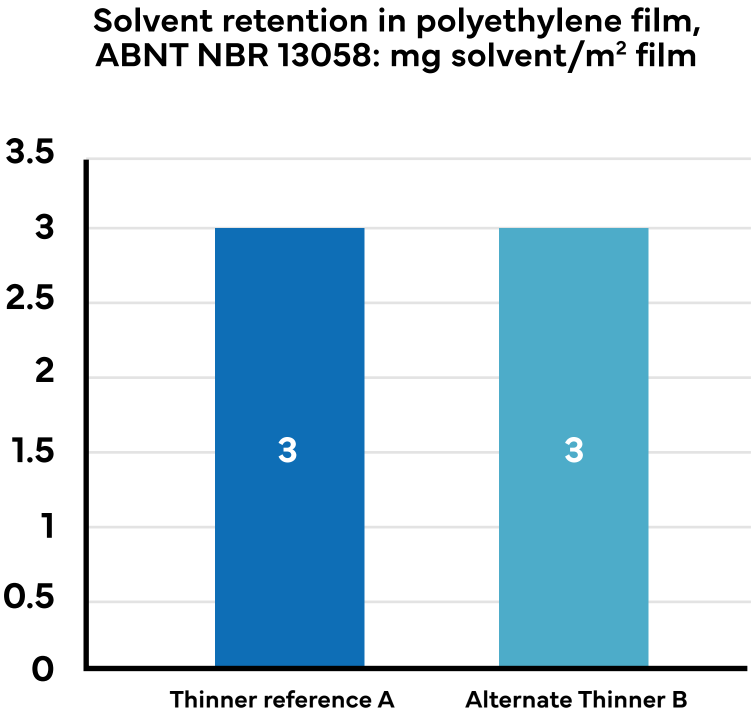


Figure 2.18: *Solvent retention in polyethylene film (mg solvent/m² film), according to ABNT NBR 13058.*

The solvent retention results are similar after applying the nitrocellulose/polyurethane paint diluted with thinner A and B.

Solvents	CAS Number	Density (20/20 °C)	Boiling point at 760 mmHg (°C)	Evaporation rate (n-Butyl Ac = 100)
Ketones				
Acetone	67-64-1	0.792	56.1	560
Diacetone alcohol	123-42-2	0.939	169.2	12
Methyl ethyl ketone	78-93-3	0.806	79.6	390
Alcohols				
n-Butanol	71-36-3	0.811	117.7	46
Ethanol	64-17-5	0.791	78.3	165
Isopentanol	123-51-3	0.812	131.4	20
Isobutanol	78-83-1	0.803	107.8	62
Isopropanol	67-63-0	0.786	82.4	150
n-Propanol	71-23-8	0.805	97.2	89
sec-Butanol	78-92-2	0.808	99.5	89.7
Esters				
n-Butyl acetate	123-86-4	0.883	126.1	100
Butyl glycol acetate	112-07-2	0.942	191.6	3.7
Ethyl acetate	141-78-6	0.901	77.2	400
Ethyl glycol acetate	111-15-9	0.974	156.3	19
Isopentyl acetate	123-92-2	0.875	142.0	53
n-Propyl acetate	109-60-4	0.889	101.6	209
Propylglycol acetate	20706-25-6	0.94	173.6	8
Sec-butyl acetate	105-46-4	0.875	112.0	195

	Hansen solubility parameters $(J/cm^3)^{1/2}$			Viscosity (sol. 10% nitrocellulose 0,5 s, 25 °C) (cP)	Solubility at 20 °C (% weight)		Flashpoint (closed vessel) (°C)
	δD	δP	δH		Solvent in water	Water in solvent	
	15.5	10.4	7.0	12	100	100	-17
	15.8	8.2	10.8	295	100	100	45.0
	16.0	9.0	5.1	20	27.00	12.50	-5
	16.0	5.7	15.8	Insoluble	7.90	20.10	35.0
	15.8	8.8	19.4	Insoluble	100	100	12.78
	15.8	5.2	13.3	Insoluble	1.70	9.50	42.7
	15.1	5.7	15.9	Insoluble	9.50	16.90	28
	15.8	6.1	16.4	Insoluble	100	100	12.0
	16.0	6.8	17.4	Insoluble	100	100	15.0
	15.8	5.7	14.5	Insoluble	60.00	22.50	23.9
	15.8	3.7	6.3	49	0.70	1.60	22.2
	15.3	7.5	6.8	188	1.50	1.70	74
	15.8	5.3	7.2	36	8.70	3.30	-3
	15.9	4.7	10.6	130	23.80	6.50	52
	15.3	3.7	6.9	65	0.20	0.90	34
	15.3	4.3	7.6	38	2.30	2.60	14
	16.0	5.0	6.2	158	5.0	–	66.3
	15.1	3.7	6.3	63	2.00	2.60	17

Solvents	CAS Number	Density (20/20 °C)	Boiling point at 760 mmHg (°C)	Evaporation rate (Ac. de n-Butila = 100)
Glycolic esters				
Butylglycol	111-76-2	0.902	171.2	7
Butyldiglycol	112-34-5	0.956	230.6	< 1
Propylene glycol methyl ether	107-98-2	0.923	120.1	71
Ethyldiglycol	111-90-0	0.990	202.7	< 1
Ethyl glycol	110-80-5	0.931	135.1	35
Propylglycol	2807-30-9	0.913	151.1	20
Propyldiglycol	6881-94-3	0.969	215.0	< 1
Glycols				
Ethylene glycol	107-21-1	1.115	197.6	< 1
Diethylene glycol	111-46-6	1.118	245.8	< 0.1
Hexylene glycol	107-41-5	0.922	197.1	< 1
Hydrocarbons				
Toluene	108-88-3	0.870	110.5	200
Xylene	1330-20-7	0.869	140.0	77
Aromatic naphtha C-9	64742-95-6	0.867	165.9	27
Mineral spirits	64475-85-0	0.774	148.0	28

Table 2.15: *Table with main solvents and their characteristics.*

	Hansen solubility parameters $(J/cm^3)^{1/2}$			Viscosity (sol. 10% nitrocellulose 0,5 s, 25 °C) (cP)	Solubility at 20 °C (% weight)		Flashpoint (closed vessel) (°C)
	δD	δP	δH		Solvent in water	Water in solvent	
	16,0	5.1	12.3	220	100	100	65.5
	16.0	7.0	10.6	510	100	100	105
	15.6	6.3	11.6	187	100	100	32
	16.1	9.2	12.2	376	100	100	91
	15.9	7.2	14.0	143	100	100	43
	16.1	8.7	13.5	181	100	100	57.2
	16,0	7.2	11.3	443	100	100	93
	17.0	11.0	26.0	–	100	100	116
	16.6	12.0	19.0	–	100	100	124
	16.7	6.8	15.0	–	100	100	93
	18.0	1.4	2.0	Insoluble	0.06	0.05	4.4
	17.6	1.0	3.1	Insoluble	0.04	0.05	31
	17.6	0.8	2.0	Insoluble	0.02	–	40
	16.18	0.19	0.26	Insoluble	–	–	> 38

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3 Analysis of solvent composition in paints and determination of water content

Raquel da Silva

3.1 INTRODUCTION

The paints consist of a heterogeneous mixture of resins, pigments, fillers, additives, and solvents, which enter into formulations that can contemplate more than twenty different items. Because it is a complex matrix, composition evaluation becomes a major challenge. In this chapter, we will describe two essential analysis procedures for paint technology: determination of the water content and determination of the solvent composition present in the paint.

3.2 BASIC CONCEPTS

The Karl Fischer (KF) method is applied to determine free water or hydration in many organic and inorganic compounds, solid or liquid, using Karl Fischer reagent titration. This technique applies to samples with water contents between 0.05% and 100% (for contents between 10 ppm and 3%, the use of the coulometer is indicated).

Figure 3.1: *Karl Fischer titrator.*

The water present reduces iodine to colorless hydriodic acid. The endpoint, determined electrometrically, is the appearance of iodine-free of brown coloration. The presence of free iodine in the solution will cause a change in resistance due to the depolarization effect of the electrode, which will then detect the endpoint.

The headspace technique is quite precise and is used to analyze volatiles after the balance between the liquid/solid phase and the vapor phase. The gas phase that forms above the sample, called headspace, is the phase injected into a gas chromatograph, thus avoiding contamination of the equipment with non-volatile substances normally present in more complex matrices.

Figure 3.2: *Combipal system.*

3.3 DETERMINATION OF WATER CONTENT

3.3.1 Summary of the method

The sample is dissolved in an appropriate solvent, and then the water present in the solvent and the mixture with the sample is titrated with Karl Fischer reagent, using methanol as a diluent. Next, the water present in the sample is calculated considering the initial content present in the solvent used.

3.3.2 Interferences

The presence of ketones in the paint samples interferes with the determination of water by this method due to condensation and/or oxidation-reduction reactions with the Karl Fischer reagent. Such interference can be eliminated or reduced by replacing the solvent (methanol) with pyridine or glycolic ether (methyl glycol or ethyl glycol). The Karl Fischer solution must contain this glycolic ether as a solvent in the latter case.

3.3.3 Reagents

- Distilled water
- Methanol P.A.
- Pyridine P.A.
- Karl Fischer reagent
- Ethyl glycol (minimum purity 99%)
- Methylglycol (minimum purity 99%)
- Methyl ethyl ketone (MEK) for cleaning
- Anhydrous ethanol

Karl Fischer, a German chemist, published in 1935 the method for determining traces of water in samples. This method is now called "Karl Fischer titration". Fischer did not experience the dissemination of the methodology, as there was no instrumentation in his time. The first automatic equipment emerged in the 1960s.

The Karl Fischer reagent is a solution containing iodine, sulfur dioxide and imidazole. This solution can be obtained commercially from Sigma Aldrich and Merck suppliers.

3.3.4 Material

- Automatic titrator type DL 55 or Karl Fischer complete apparatus;
- Analytical scale;
- Glass syringe;
- 50-mL beaker;
- Small plastic cup;
- 20-mL glass bottle with rubber cap and aluminum seal.

3.3.5 Procedures

1. Sample preparation: Homogenize the paint sample and weigh 1 g in a 20-mL vial, add 10 mL of anhydrous ethanol and homogenize the mixture.

2. Place the solvent (methanol, ethyl glycol or methyl glycol) in the cup to cover the electrode terminals and neutralize.

3. Weigh 1 g to 2 g of the solution with the sample and insert it into the equipment cup.

Note: the sample is weighed by difference and introduced into the equipment cup through suitable containers (syringes, beakers, plastic cups, droppers, etc.).

4. Titrate with KF reagent until the appliance indicates the endpoint.

5. Determine water also in the solvent ethanol used to dissolve the sample.

Note: Clean the used vials, cup, electrode and tips of the equipment using a suitable solvent (MEK) and segregate the material used for exclusive use in paint analysis.

6. Calculate the water content in the solvent (ethanol) and in the mixture with the sample using Equation (1):

$$\text{Water content, \%p} = \frac{V \times F \times 100}{M \times 1.000} \qquad (1)$$

Wherein:

V = volume of reagent KF spent on titration, in mL

F = reagent factor KF

M = sample mass, in g

7. Calculate the water content in the paint sample using Equation (2):

$$\text{Water content, \%p} = \frac{((T2 \times M3)-(T1 \times M1))}{M2} \qquad (2)$$

Wherein:
T1 = water content in solvent (ethanol)
T2 = water content in solution with ethanol and sample (mixture)
M1 = mass of solvent used in solution with ethanol and sample (mixture)
M2 = mass of paint sample in solution with ethanol and sample (mixture)
M3 = mass of solution with ethanol and sample (mixture)

3.4 DETERMINATION OF SOLVENT CONTENT

3.4.1 Summary of the method

The sample is solubilized in a suitable solvent and heated in a sealed vial until liquid-vapor equilibrium is reached. The vapor phase is injected into a gas chromatograph equipped with a high-phase resolution capillary column suitable for analysis. After separating the components, the generated chromatogram is evaluated, and the volatile components are identified by GC/MS and quantified by GC by the standard addition technique.

3.4.2 Interferences

Any compounds incompatible with the chromatographic column or solvents eluting at the same retention time as the components of interest cause interference.

3.4.3 Reagents

- Triethylene glycol with a minimum purity of 98%;
- Liquid solvents such as alcohols, ketones, ethers, esters, and hydrocarbons, of known chromatographic purity, for use as analytical standards.

3.4.4 Material

- Agilent 6890 gas chromatograph, or similar, with an injector for the capillary column, flame ionization detector and data processing station;
- Capillary column type CP-Sil 5 CB or DB-1 with dimensions of 50 m x 0.032 cm x 1.2 µm or similar;
- Headspace system CombiPal CTC type or similar;
- 20-mL glass bottle suitable for headspace, with Teflon cap and metal seal;
- Analytical balance accurate to 0.1 mg;
- 2.5-mL gastight syringe;
- Agilent 5973 mass spectrometer or similar.

3.4.5 Procedures

3.4.5.1 Analytical conditions

Chromatograph analysis conditions

- Column type: CP-Sil 5 CB or DB-1
- Split ratio: 1:10
- Linear speed: 45 cm/s
- Injector temperature: 250 °C
- Detector temperature and GC/MS interface: 280°C

Furnace

- Initial temperature: 40 °C

- Initial time: 3 min
- Heating speed 1: 3 °C/min
- Intermediate temperature 1: 80 °C
- Intermediate time 1: 0 min
- Heating speed 2: 50 °C/min
- Final temperature: 270 °C
- End time: 5 min
- Injection volume: 500 µL

Note: These conditions can be changed to achieve the best possible chromatographic separation for the evaluated ink type.

Analysis conditions of Combipal headspace system

- Incubation temperature: 80 °C
- Incubation time: 3,600 s
- Syringe temperature: 85 °C
- Agitator speed: 300 rpm
- Syringe filling speed: 500 s
- Removal of bubbles from the syringe (fill strokes): 2
- Waiting time for injection (pull up): 0
- Injector: GC inj 2
- Injection speed: 1,000 s
- Wait time for injection (pre-delay): 0
- Wait time after injection (post-delay): 0
- Syringe cleaning time: 180 s
- GC run time: 30 min

Mass spectrometer conditions

- Filament: 70 eV
- Interface temperature: 300 °C
- Mode: Scan
- Mass range: 20 Da to 300 Da
- Library: NIST 2005

3.4.5.2 Identification by GC/MS

1. In a headspace vial, weigh approximately 0.02 g of sample (1 drop). Cover, seal and take the bottle to the headspace system for analysis.

2. Inject into the HS/GC/MS system and evaluate the chromatogram obtained by identifying each chromatographic peak by comparison in the NIST library.

3. Quantify by area percentage all peaks found, normalizing with the solids content.

3.4.5.3 Quantification by GC

1. Preparation of the synthetic standard mixture for quantification by GC: prepare a mixture with concentrations close to that expected in the sample obtained in GC/MS analysis, using TEG to replace the "solids" present in the sample. Homogenize and store in a refrigerator (use for a maximum of 15 days).

2. Sample preparation: in 2 vials of headspace, weigh around 8 g of TEG and approximately 0.1 g of the sample (note the mass as "m1" for vial 1 and "m2" for vial 2). In vial 1 (without addition), add 0.1 g of TEG, and in vial 2 (with addition), add 0.1 g of the standard synthetic mixture (note as "m3"). Seal each vial and homogenize, being careful not to contaminate the caps. Place the vials in the HS/GC system for analysis and obtain the chromatograms by integrating their areas properly using the data process station.

3. Perform the analysis in duplicate.

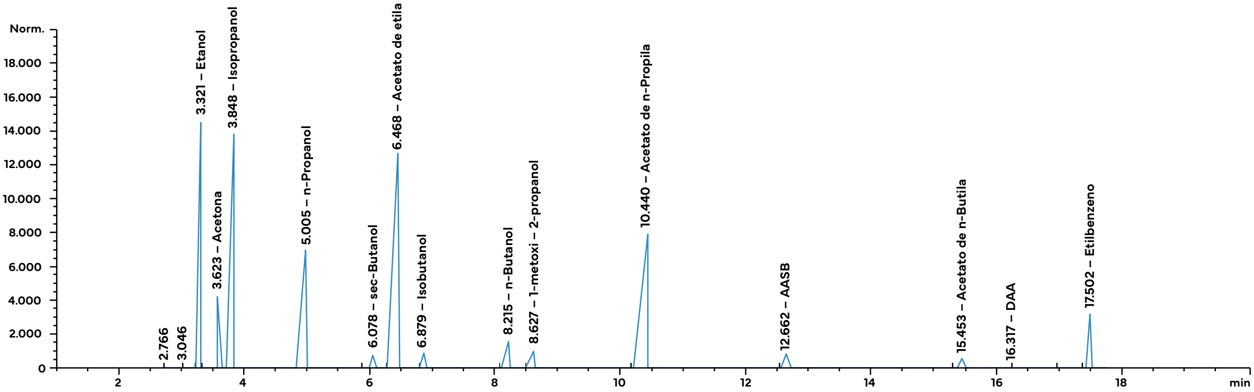

Figure 3.3: *Chromatogram - a mixture of solvents.*

3.4.6 RESULTS

Quantify each solvent present with Equation (3):

$$\% \text{ Solvent } 1 = A1 \times \left(\frac{B}{A2 - A1} \right) \times \frac{100}{MA} \qquad (3)$$

Wherein:
A1 = area of solvent 1 in chromatogram without the addition of standard
A2 = area of solvent 1 in chromatogram with the addition of standard
B = individual mass of solvent 1 added in vial 2
MA = mass of the sample

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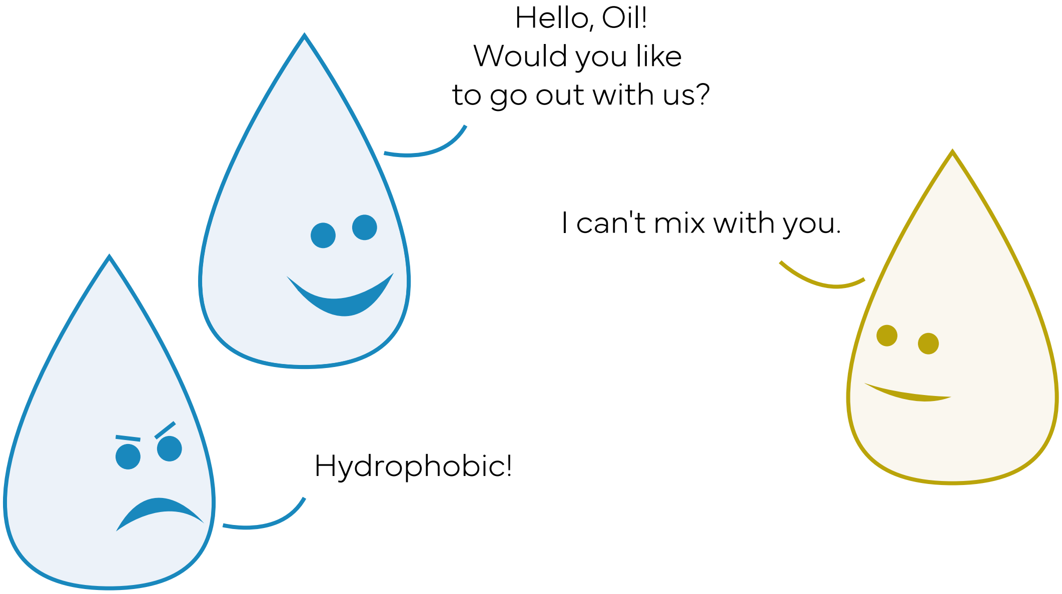
Part 3

Surfactants and their main applications in paints

4 Surfactants: main characteristics and their applications in paints

Bruno Dário



Source: adapted from Funforrest (2013).

4.1 SURFACTANTS

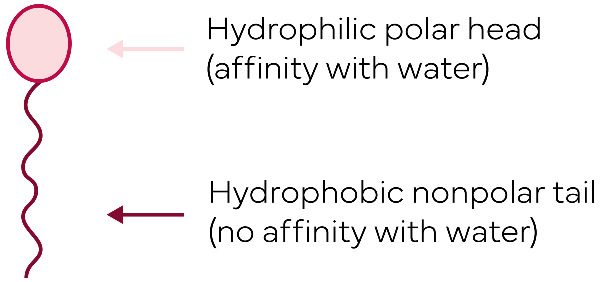


Figure 4.1: *Example of the surfactant molecule.*

Source: adapted from Farn (2006).

Surfactants are amphiphilic molecules composed of polar and nonpolar ends. The polar end, also called the hydrophilic end, has an affinity for water through hydrogen bonds, electrostatic forces (charged surfactants), or London dispersion forces. The nonpolar end, also known as the hydrophobic end, has no affinity for water. (HOLMBERG; JÖNSSON; KRONBERG, 2002). Surfactants have several applications in the most varied industries, such as food, cosmetics, pharmaceuticals, agrochemicals, and paints, and it is the combination of two parts with different polarities in the same molecule that gives these products many of the characteristics we know.

4.2 HLB CONCEPT

HLB is the acronym for hydrophilic-lipophilic balance of a surfactant. That is, it measures whether this molecule has more affinity for water or for oil. In general, it is a number that relates, in the molecule, the amount of hydrophilic groups to lipophilic ones. HLB is not a physicochemical property of the molecule, but rather an empirical scale. However, it is such a useful system that it often becomes one of the first features evaluated in selecting a surfactant for a given application. The HLB scale was determined so that the higher the HLB of a surfactant, the greater its affinity for water (Farn, 2006).

4.3 HLB CALCULATION FOR MOLECULES

There are several ways to calculate HLB for some molecules. Here is how it can be done for the main types of surfactants (GADHAVE, 2014):

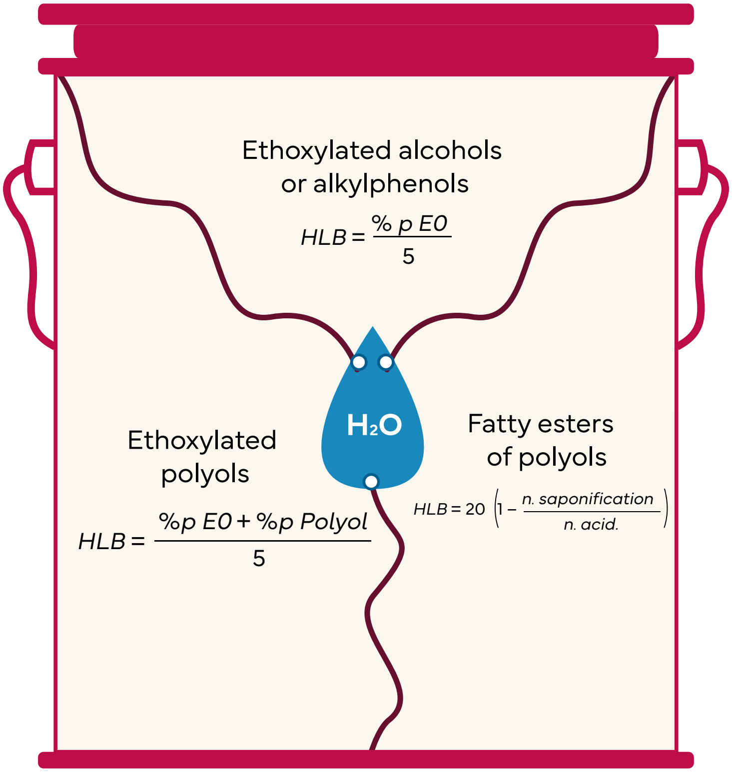


Figure 4.2: *Calculation of HLB for some molecules.*

Source: adapted from Gadhave (2014).

4.4 HLB CALCULATION FOR SURFACTANT MIXTURE

In most systems, a mixture of surfactants is more efficient for emulsification than a single surfactant. By mixing surfactants, we can adjust the ratio between them to achieve an optimized HLB value for the oil or resin to be emulsified. In addition, the fine-tuning of the mixture allows us to optimize the emulsion's properties, which is impossible when using a single emulsifier. Such mixtures are usually made between surfactants with different affinities, that is, one with greater hydrophilic character and the other with greater lipophilic character.

In addition to the HLB number, another important factor in choosing the surfactant is the chemical family to which it belongs. Two surfactants with the same HLB may perform differently in the same environment and that occurs because the intermolecular interactions between the surfactant, the compound to be emulsified, and the water are going to be different. Even though they have the same HLB, two surfactants can have completely different molecular weights, critical micellar concentration (CMC), surface tension reduction in the CMC, and adsorption tendency. For this reason, HLB is a great indicator to assist in choosing a surfactant and the proportion between two surfactants to be mixed. However, reliable results will only be obtained with application tests.

For mixing two surfactants to emulsify an oil or resin with HLB value being X, it is recommended to use the following formula:

$$\%A = \frac{100(X - HLB_{(B)})}{HLB_{(A)} - HLB_{(B)}}$$

$$\%B = 100 - \%A$$

Although simple, calculating the proportion of surfactants can be time-consuming if it is necessary to evaluate several surfactants. Therefore, a more straightforward way to determine the proportion of surfactants is through the following graph, the HLB abacus. With the abacus, we can simply place, on the left side, the surfactant with the lowest HLB, and, on the right side, the one with the highest HLB. When drawing a line connecting the two surfactants, we have the full range of HLB possible with that mixture. Checking the point where we have the desired HLB, the projection of this point on the horizontal axis determines the proportion between the surfactants.

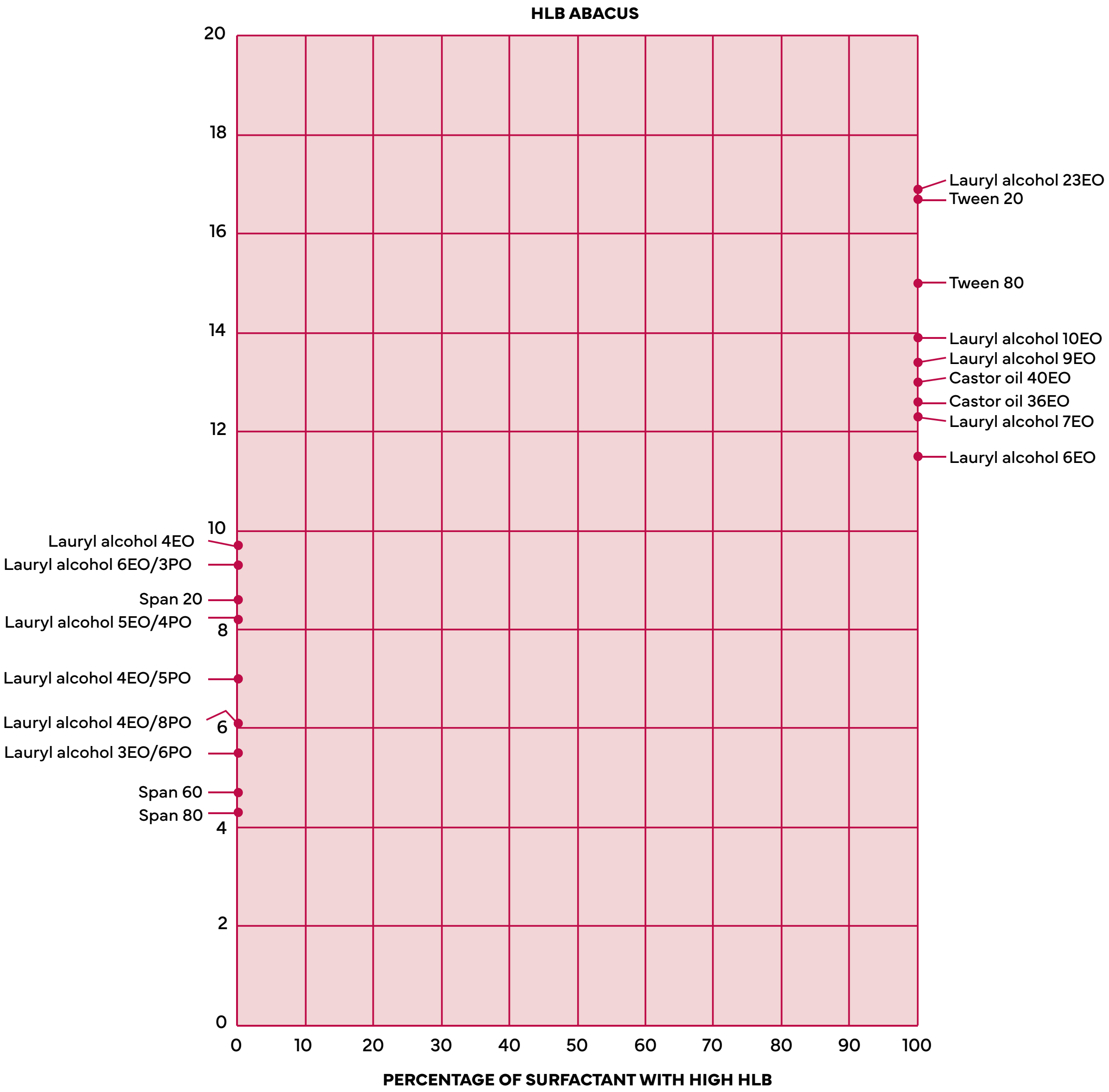


Figure 4.3: *HLB abacus.*

Source: ICI AMERICAS INC. (1984).

4.5 PAINTS - THE ROLE OF HLB

In emulsified systems, it is recommended to use a surfactant or a mixture of surfactants that has the same HLB as the emulsified compound (ICI, 1984). The choice of surfactant must be made according to the type of emulsion we want to prepare. Therefore, to prepare an oil-in-water emulsion, for example, we must choose a surfactant with higher HLB, between 8 and 14, that is, a more hydrophilic surfactant so that it will be able to emulsify the oil in a more water-rich system. For each type of application, we can determine an HLB range that will be most suitable for the system.

In water-based paints, we have very complex systems that contain several components, which, under normal conditions, would not form a homogeneous mixture. For this reason, several surfactants are used. They are responsible for stabilizing the resin and pigments and for assisting in the application, mainly by reducing the surface tension of the paint to better spread the paint and wet the substrate, ensuring better coverage of the area to be coated. In fact, even before preparing the final paint, we have another vital step that only occurs due to the presence of surfactants: emulsion polymerization (see chapter 7).

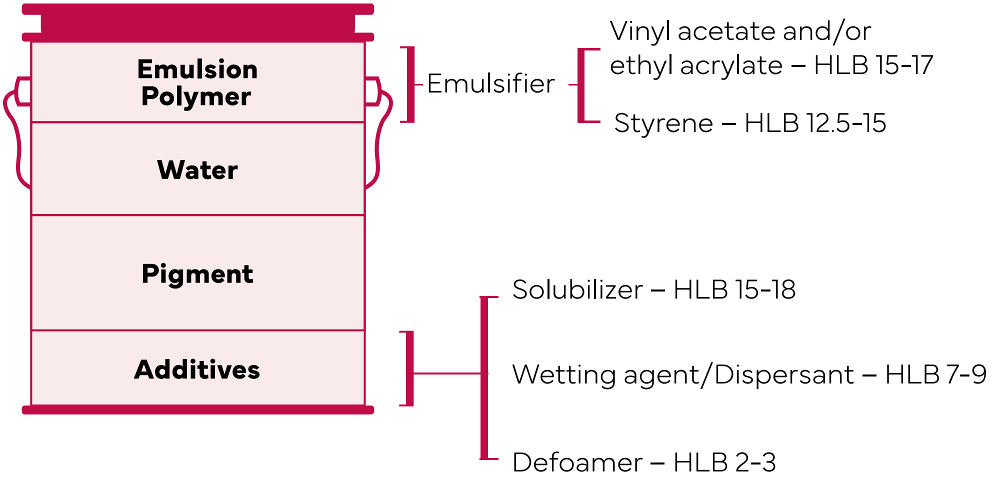


Figure 4.4: *HLB for the main surfactants used in paints.*

Source: Warson; Finch (2001).

As mentioned, surfactants also act as wetting agents and dispersants of pigments and fillers. In this case, surfactants with high HLB, from 18 to 20, are suggested for very hydrophilic pigments, such as carbonates and sulfates. For some organic pigments, such as blue phthalocyanine, molecules with HLB around 14 can be used. Other pigments, such as toluidine or even carbon black, can be dispersed with HLB surfactants between 10 and 13 (WARSON, 2001). However, it is always important to consider that pigments can undergo several types of surface treatments, which impact the choice of the best surfactant system since the surface on which the surfactant will adsorb has been modified. Adsorption of surfactants on solid surfaces can modify their hydrophobicity, surface potential, and other properties that govern interfacial processes such as dispersion, flocculation, and wetting. Adsorption is a process governed by a series of forces. Generally, it is the cumulative result of covalent bonding forces, electrostatic attraction, hydrogen bonds, Van der Waals forces, and associative or repulsive interactions between adsorbate (surfactant) molecules and solvation (DÁRIO, 2021). Thus, although HLB is a good driver in the choice of the additive, other factors must be considered.

4.6 CONCLUSION

Surfactants are essential components for the formulation of paints. They are used during the polymerization process to generate emulsion polymers, and also, in the final paint, during the dispersion process of pigments and fillers. In both processes, they act as stabilizers of the system (more details will be demonstrated in the other chapters of this handbook). In addition, surfactants can be used as additives at the end of the entire process to adjust specific properties, such as long-term stability and wetting of substrates. One of the main characteristics of a surfactant is its HLB (Hydrophilic-Lipophilic Balance) value, which guides the choice of the best surfactant for emulsification processes and has great influence on the final performance of the coating. The use of HLB is highly recommended as a starting point in the choice of surfactants. Still, a more detailed understanding of these molecules' structure and physicochemical properties is essential for proper use.

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5 Application of surfactants as wetting and dispersing agents for pigments in water-based paints

Marina Chieregati Passarelli | Alann de Oliveira Piagentini Bragatto

5.1 PIGMENTS – IMPORTANCE AND MAIN CHARACTERISTICS

Pigments are composed of small solid particles, ranging between nanometers and micrometers, which are insoluble in the medium and used mainly in paints and coatings to give their coloration and coverage (FAZENDA, 2009).

There are two main types of pigments: organic ones, which are synthetic; and inorganic ones, which have a natural origin, such as minerals. The characteristics of the pigment differ according to the type (FAZENDA, 2009). In general, these characteristics can be related as follows:

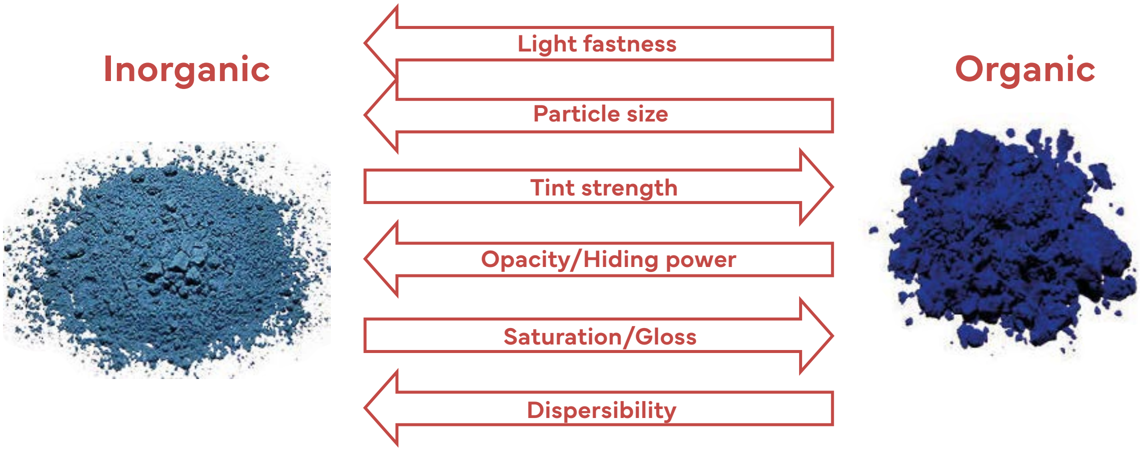


Figure 5.1: *Pigment properties as a function of type (inorganic and organic).*

Typically, inorganic pigments are manufactured by a calcination process of a precipitate, while organic pigments are synthesized via crystallization and filtration. As a consequence, they are provided in the form of aggregates (primary particles joined by chemical bonding) and agglomerates (primary particles joined by physical bonding) (WINKLER, 2012).

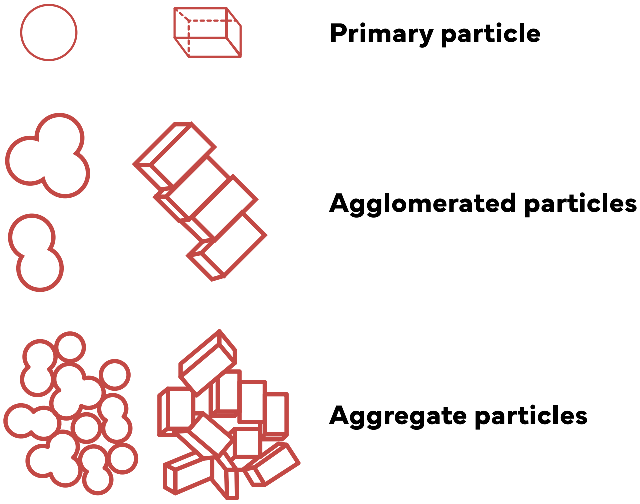


Figure 5.2: *Example of simple, agglomerated, and aggregated particles.*

Source: adapted from Particle Sciences Drug Development Services (2009).

The color of pigments occurs by the absorption and scattering of light on their surface. For this reason, the size of the pigment particles, in addition to the concentration, will directly interfere with the color produced, which is why the pigment dispersion step is one of the most demanding in the paint manufacturing process. It requires energy and the contribution of wetting and dispersing agents to occur more effectively (WINKLER, 2012; ZENO, 2007).

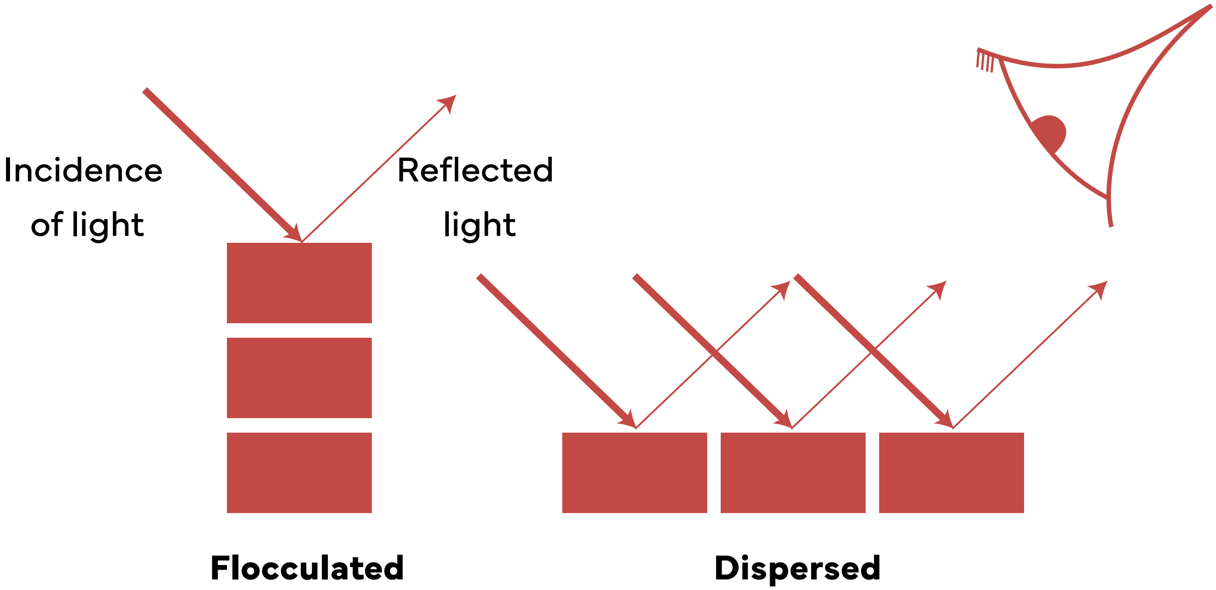


Figure 5.3: *Difference in the amount of reflected light comparing flocculated and dispersed systems. In the first case, light cannot reach all pigment surfaces because they are clustered together. In the second case, the pigments are separated, and the light can reach all surfaces, increasing the degree of reflection and color perception.*

5.2 DISPERSION PROCESS – MAIN STEPS

The breakdown of pigments aggregates and agglomerates is obtained during the dispersion process, which can be divided into three main steps (HEILEN, 2009):

I - Wetting of the solid surface of the pigment by water.

II - Physical separation of pigment agglomerates during the milling process.

III - Stabilization of the smaller particles generated, avoiding the reagglomeration process.

The dispersion process is dynamic, and all steps occur, on average, simultaneously. During this process, products that act in Steps I, II and III, called wetting and dispersing agents, are used. Each has a specific role in a certain stage and will act differently (HEILEN, 2009; ZENO, 2007). Wetting agents are molecules of nonionic surfactant that have lower molecular weight, while dispersants are more complex and have larger molecules (with polymeric characteristics) (SHAW, 2013; TADROS, 2011). Depending on the case, they have charges that will assist in stabilizing the particles.

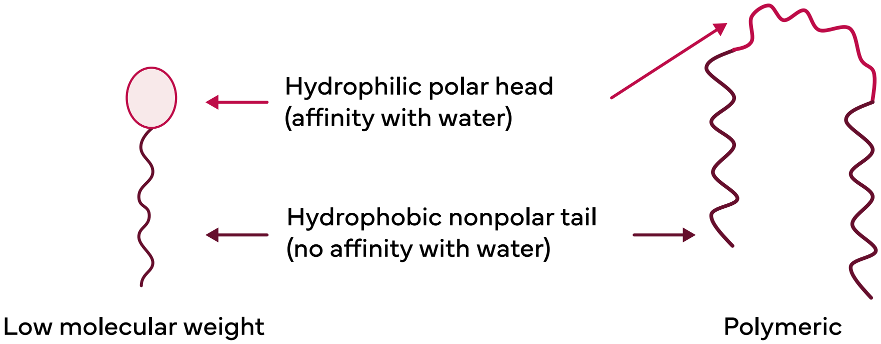


Figure 5.4: *Examples of conventional, low molecular weight (left), and polymeric, high molecular weight (right) surfactants.*

The choice of a suitable surfactant or surfactant system for the pigment dispersion should consider its ability to reduce surface tension during Step I to facilitate the wetting of the pigment by water. Then, the ability of its affinic group to adsorb onto the pigment surface rapidly during step II to prevent the re-agglomeration of the generated smaller particles .Finally, its ability to keep the system stable for long periods of time, which will depend on the effectiveness of the stabilization mechanism and the ability to remain adsorbed on the pigment particles over time.

For didactic purposes, below, we will present each step of this process separately.

5.2.1 Wetting

The wetting of pigments in water-based systems is a challenging phenomenon, mainly due to the high surface tension of water, compared to other media. This high surface energy generates a large energy difference between the pigment/water interface, hindering the wettability of aggregates and particle agglomerates in their incorporation into the grinding paste (HEILEN, 2009). Here it is clear the importance of using any additive that is capable of reducing the surface tension of water, allowing it to penetrate the pores of pigments. This additive is the wetting agent.

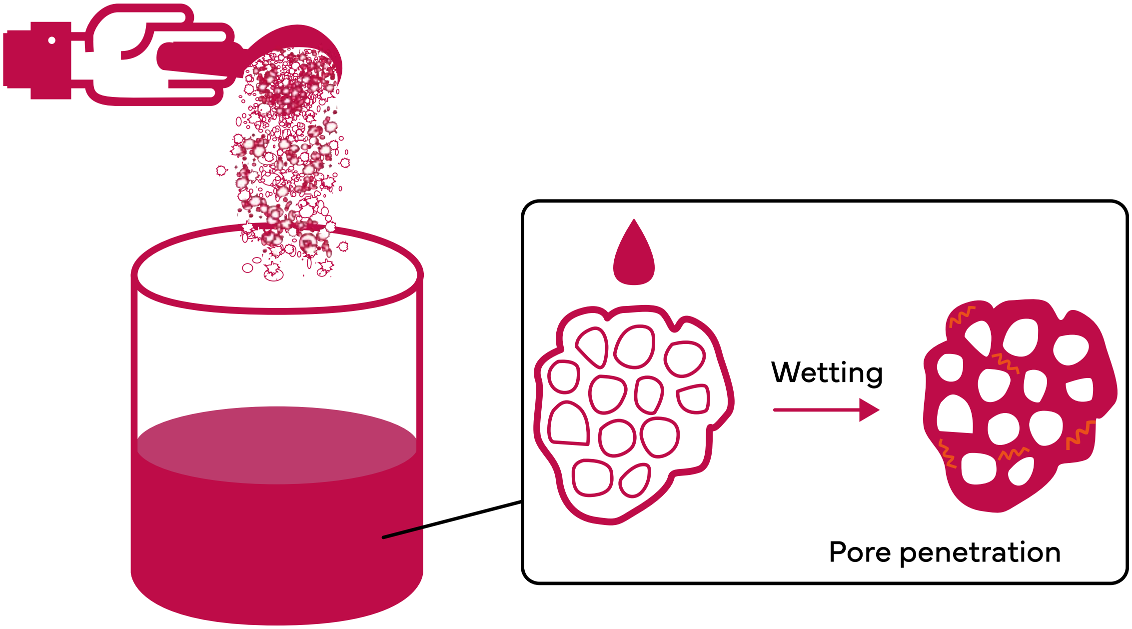


Figure 5.5: *Process of wetting of pigments by the medium, a phenomenon favored by the presence of wetting agents.*

The wetting agent adsorbs on the surface of the particles, reducing interfacial energy and favoring the penetration of water into the pores and interstices of aggregates and agglomerates, leading to a reduction in the viscosity of the grinding paste (HEILEN, 2009).

At this time, there is no decrease in the size of the particles, but a reduction in the interaction between them, causing a reduction in the viscosity of the medium. This behavior allows a greater load of pigments and fillers in the grinding paste (HEILEN, 2009; ZENO, 2007).

So, there are two essential points that a wetting agent needs to comply:

a) Reduction of surface tension of water.

b) Reduction of the viscosity of the grinding paste.

These aspects must be considered to determine a type of wetting agent and its optimal dosage (ZENO, 2007). The item (a) can be studied through various physicochemical equipment that makes interfacial tension readings directly or indirectly on various surfaces. However, it is not always possible to perform this type of reading during the development of a formulation. To make this determination more practical, item (b) can be a great performance driver.

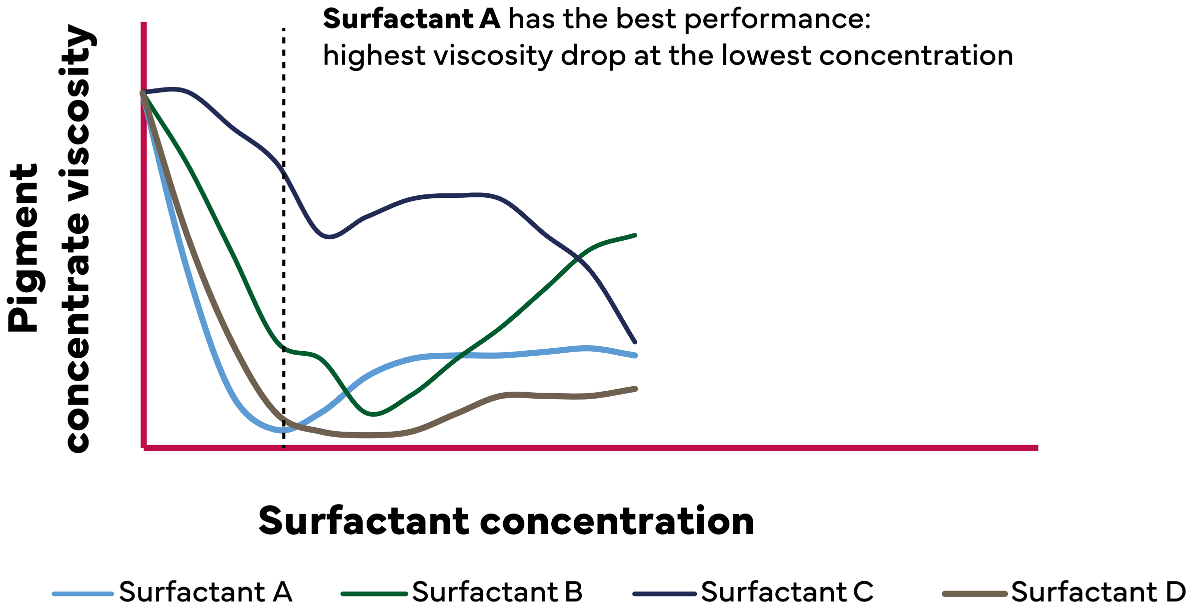


Figure 5.6: *Example of a viscosity study in a pigment concentrate to determine wetting dosage.*

Thus, it is necessary to verify which product can reduce the viscosity of the pigment or filler concentrate more efficiently, that is, reducing to the lowest value at the lowest concentration and obtaining a more optimized concentration to minimize possible defects in the final paint. Figure 5.6 presents an example in which surfactant A has the best performance, while surfactant C has the worst for having the lowest viscosity reduction of the system. Conducting this viscosity study is also critical to avoid problems related to the under and overdosage of additives. More details will be provided in the item related to stabilization.

5.2.2 Milling

The breakdown of agglomerates and aggregates into smaller particles occurs mechanically during grinding (HEILEN, 2009; WINKLER, 2012; ZENO, 2007). In the course of this process, the system's viscosity tends to increase due to the formation of new high-energy surfaces, which tend to stick together and flocculate. With the presence of wetting agents in the medium, this process is facilitated considerably because the additives also adsorb on the newly formed surfaces, minimizing the interaction between the particles and ensuring a constant viscosity of the paste throughout the process (ZENO, 2007)

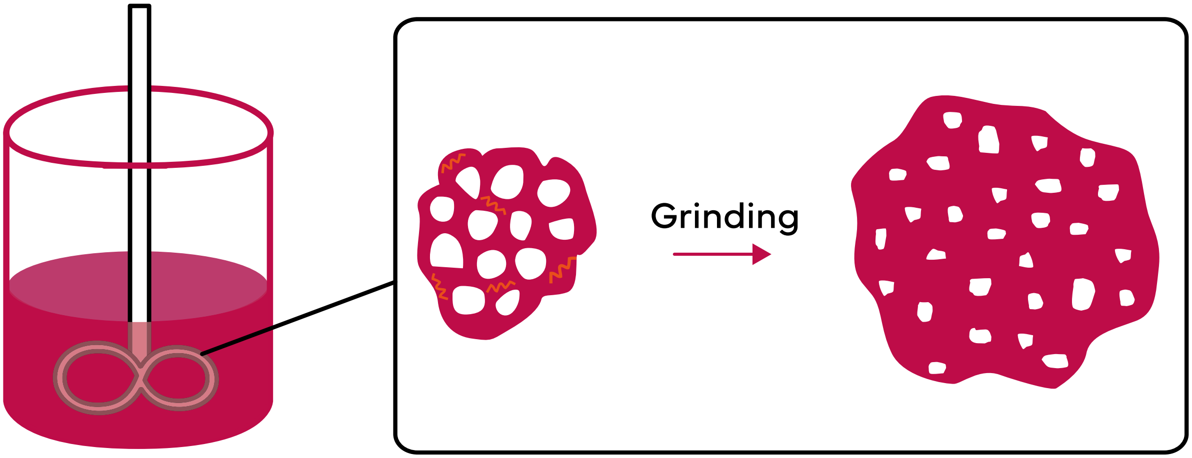


Figure 5.7: *Grinding process: breakdown of pigment particles.*

An optimum dispersion process makes obtaining a paint with better properties possible. The choice of an efficient wetting agent for your system can influence several attributes, such as:

- pigment and filler content;
- tint strength;
- hiding power;
- viscosity;
- final performance properties, such as scrub resistance and adhesion.

The most common pigment wetting agents are nonionic surfactants with low molecular weight, and HLB ranging between 7 and 20. Traditionally, nonylphenol ethoxylates (NPE) are very efficient as wetting agents of mineral pigments such as titanium dioxide.

However, some concerns regarding these types of products have reduced their use, and replacement studies of NPE show a new trend of alkylphenol ethoxylate (APE) free wetting agents (TADROS, 2011).

5.2.3 Stabilization

As already mentioned, the fillers and pigments are broken down into smaller particles, which tend to flocculate due to the high surface energy formed.

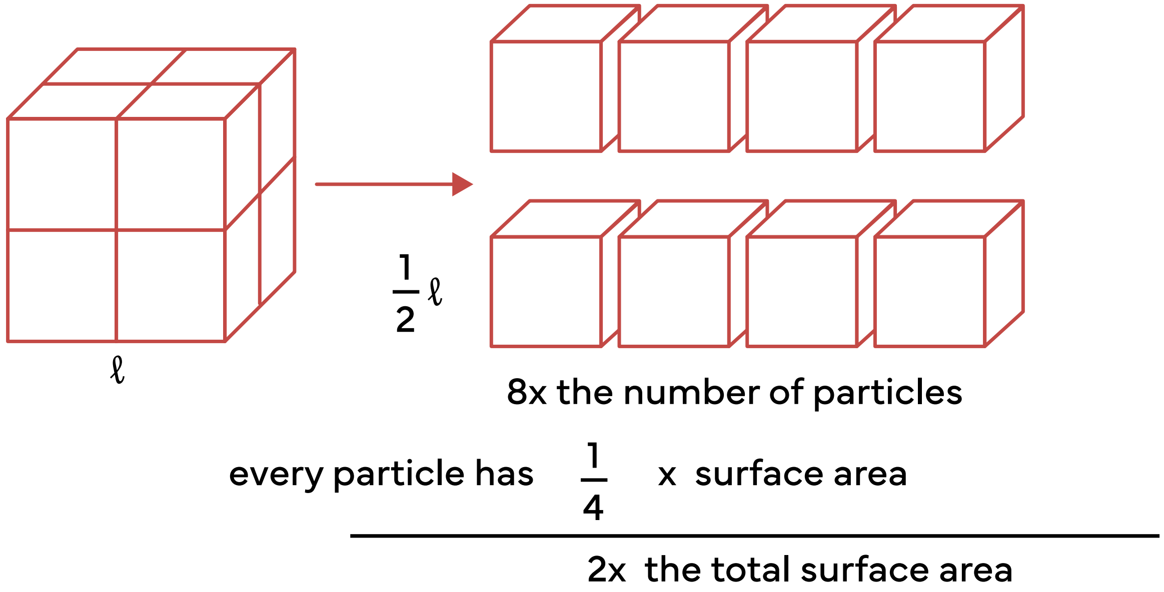


Figure 5.8: *Increase in surface area by reducing particle size.*

For flocculation not to occur, it is necessary to use additives that can adsorb on the surface of these particles and promote a barrier that prevents the particles from getting close to each other (WINKLER, 2012). These additives are known as dispersing agents. Dispersion mechanisms can occur in three ways (HEILEN, 2009; SHAW, 2013):

- Electrostatic stabilization: generated by molecules that can dissociate.
- Steric stabilization: generated by high molecular weight particles, such as polymeric ones.
- Electrosteric stabilization: generated by a mixture of the two mentioned mechanisms.

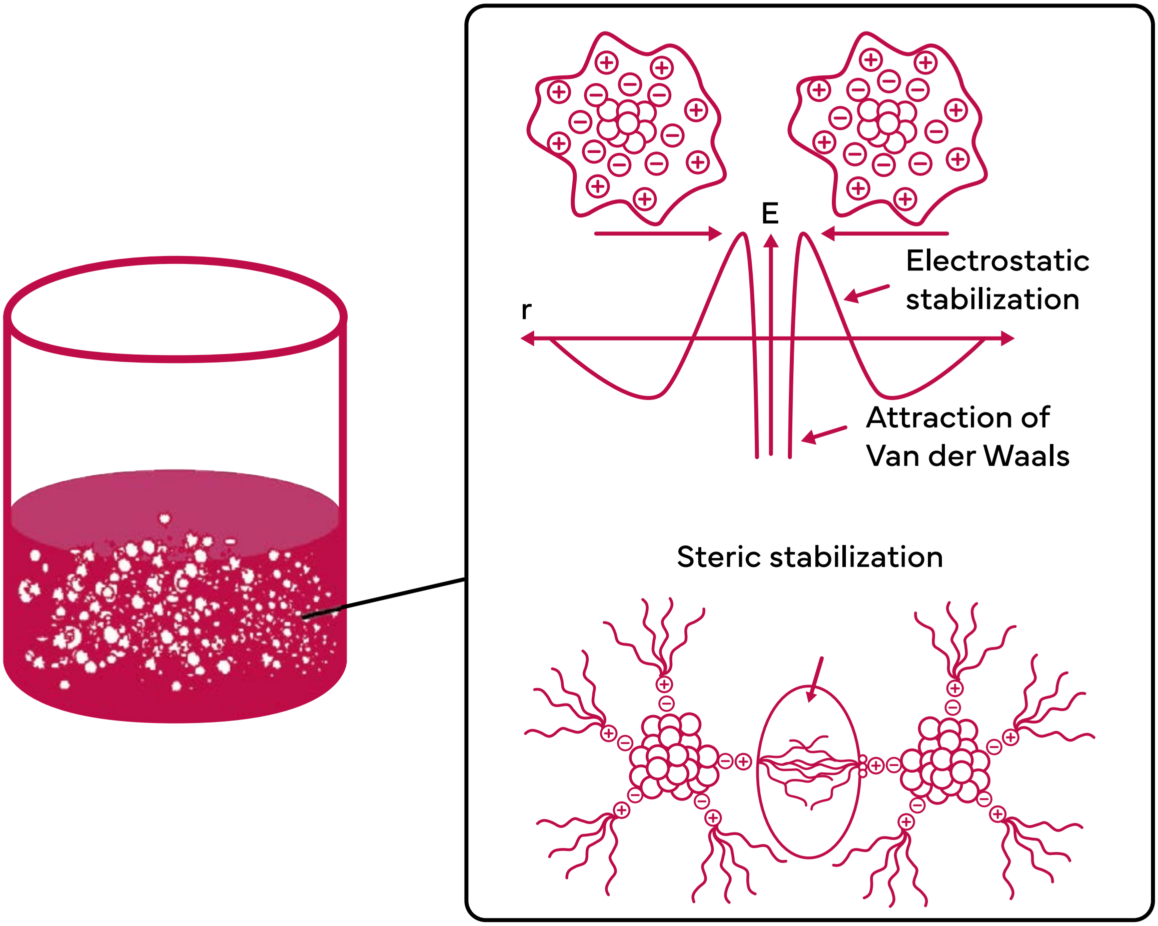


Figure 5.9: *Schematic showing the types of stabilization. Above, electrostatic, caused by stabilization between charges; below, steric, caused by repulsion between the molecular chains of the dispersants.*

Source: adapted from Shaw (2013).

For water-based systems, the type of dispersion required is usually electrosteric. This is because water is a high surface tension solvent, making the system very complex and difficult to stabilize and requires high-efficiency additives in dispersion. For this reason, dispersants are usually polymeric (high molecular weight) and anionic (with electric charge) (TADROS, 2011; ZENO, 2007). In addition, these products should have affinity groups to the pigment that will be dispersed to ensure efficiency over a longer period.

Another fundamental factor in ensuring adequate stability is the correct dosage of wetting and dispersing agents. The performance of the viscosity curve in studies, as previously discussed in item 5.2.1 of this chapter, is essential to determine the appropriate dosage for the formulation. Figure 5.10 schematically depicts how dosing a dispersing agent can affect the system's stability.

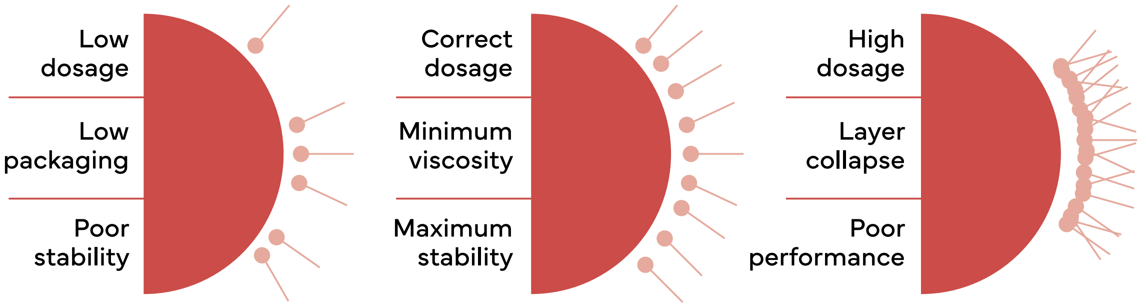


Figure 5.10: *Schematic showing the different dosing conditions — underdose, adequate dosage and overdose - of a dispersing agent on a pigment particle.*

The scheme on the left of Figure 5.10 illustrates an underdose scenario in which the dosage of dispersing agent is lower than necessary. Consequently, there is a low packaging or covering of the dispersant molecules around the pigment particle and a system with low stability. The one on the right depicts an overdose scenario. That is, the dosage of the dispersing agent is higher than necessary. Consequently, the pigment particle is poorly stabilized due to the collapse of the dispersing agent layer, causing a decrease in stability and performance. The middle one represents a suitable dosage scenario in which the best packaging of the pigment particle is obtained, corresponding to the point of minimum viscosity and maximum stability.

5.3 TYPES OF WETTING AND DISPERSING AGENTS

A type of wetting and dispersing agent can be chosen for each type of system. Table 5.1 presents some typical product characteristics for each type of technology (HEILEN, 2009; SHAW, 2013; TADROS, 2011).

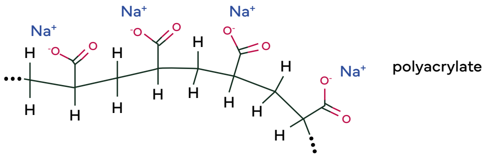
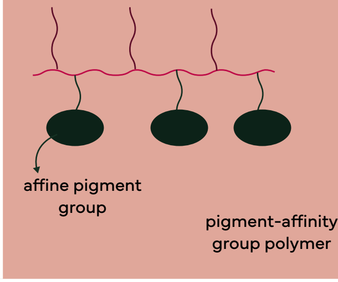
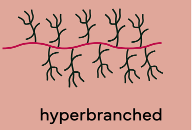
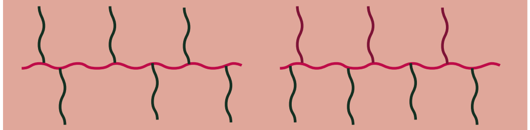
Type of product	Solvent-based	Water-based
Inorganic pigment	- Alcohol or alkoxylated fatty acids - Alkoxylated linear copolymers - Block and branched copolymers  	- Electrostatic stabilization - High molecular weight ionic surfactants  
Organic pigment	- High molecular weight molecules with pigment affinity groups - Block polymers with pigment affinity groups   	- Polymeric and copolymeric, by combining electrostatic and steric stabilization (required for less polar systems) 

Table 5.1: *Types of products by technology.*

5.4 CONCLUSION

Wetting surfactants play a crucial role in the dispersion process. For each filler and pigment, there is a need to use a surfactant with specific HLB, which will act to maximize its properties in the final paint.

The higher the concentration of pigments and fillers in the final paint, the more important the use of wetting and dispersing agents; increasing concentrations of these are often required. In addition to an adequate selection of wetting and dispersing agents according to the type of pigment to be dispersed and the application system, it is essential to carry out prior studies to determine the appropriate dosage of these additives in the system to optimize the stability and performance of the paints.

The concentration of pigments and fillers is measured using the Pigment Volume Concentration (PVC) parameter, the concept and calculation of which will be explained in the next chapter of this handbook.

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6 PVC and CPVC calculations in paint formulations

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6.1 PIGMENT VOLUME CONCENTRATION (PVC)

The pigment volume concentration refers to the percentage of pigments and fillers relative to the total solids (pigment/filler + resin and additives) in the cured paint film per unit volume.

$$PVC = \frac{V_p}{V_p + V_R} \times 100$$

V_p = pigment/filler volume

V_R = resin and additives volume

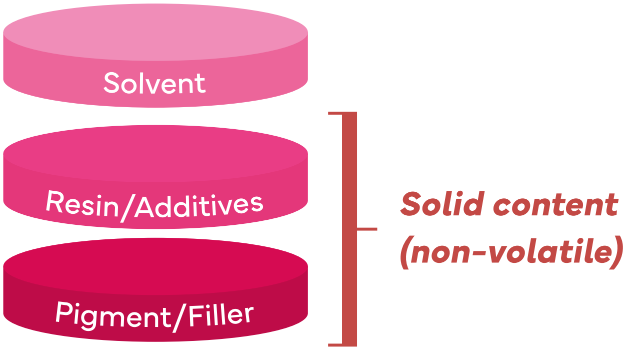

Figure 6.1: *Representation of the elements that form a paint. The volatile content (solvent) is not considered in the PVC calculation.*

The volumes of each component can be calculated using density (BEETSMA, 2014). To better illustrate it, we have below an example of PVC calculation for a matte paint formulation.

Components	Quantity (g)	
Water	1,943.5	
Sodium nitrite	5	
Sodium tripolyphosphate	7.5	
Thickener	10	
Neutralizing agent	5	
Dispersing agent	15	
Wetting agent	10	
Defoamer	10	
Bactericide	5	
Fungicide	5	**Fillers and pigments**
TiO_2	425	
Agalmatolite	425	
Precipitated calcium carbonate	525	
Kaolinite	525	
Calcium carbonate	109.9	
Defoamer	5	
Neutralizing agent	5	
Resin	800	**Resin**
Coalescent	44	
Thickener	120	

Table 6.1: *Typical matte paint formulation.*

Concerning fillers:

Solid component	Density (g.cm^{-3})	Volume (cm^3)
TiO_2	4.10	103.66
Agalmatolite	2.85	149.12
Calcium carbonate	2.67	196.63
Kaolinite	2.60	201.92
Calcium carbonate	3.00	36.63
Filler volume (cm^3)		687.96

Table 6.2 *Formulation of fillers and pigment.*

Regarding the resin:

Resin	
Mass of resin solution (g)	800
Solid content (%)	50%
Actual mass of resin (g)	400
Density (g.cm^3)	1.18
Resin volume (cm^3)	338.98

Table 6.3: *Resin data.*

Knowing all densities and solids content of the resin, we can calculate PVC as follows:

$$PVC = \frac{\overbrace{687.96}^{V_p}}{\underbrace{(687.96) + 338.98}_{V_p + V_R}} \times 100 = 67\%$$

ATTENTION

The value found of PVC is a simplification since the additive volumes were not considered.

Estimating the Quality Sectoral Program (QSP) classification through the PVC value in decorative paints is possible. Each type of paint has an acceptable PVC range, as the variation of this characteristic influences the opacity, brightness, durability, and rheology of the paints, which are determined by the program.

6.2 CRITICAL PIGMENT VOLUME CONCENTRATION (CPVC)

The critical concentration of pigment by volume refers to the PVC value in which the amount of resin is not sufficient to fill the interparticle spaces, and, as a consequence, air can be incorporated into the dry film, causing changes in several properties (FAZENDA, 2009). Thus, the CPVC index determines these properties' inflection points, as seen in Figure 6.2. The CPVC varies according to the size and shape of the particles (LEWARCHIK, 2014), as it is a direct result of their degree of packaging in the film formation.

The calculation of CPVC is made from the oil absorption (OA) of the pigment/filler, considering a non-flocculated dispersion in flaxseed oil. OA is expressed in grams of oil per 100 g of pigment.

$$CPVC = \frac{1}{1 + {(OA) \times (\rho)}/{93.5}} \times 100 = 53\%$$

Wherein:
ρ = pigment density
93.5 = 100 times the density of flaxseed oil

The absorption of flaxseed oil in TiO_2 is approximately 20 g of oil/100 g of pigment. Considering the density (ρ) of 4.10 g.cm^{-3}, the CPVC of this pigment is close to 53%:

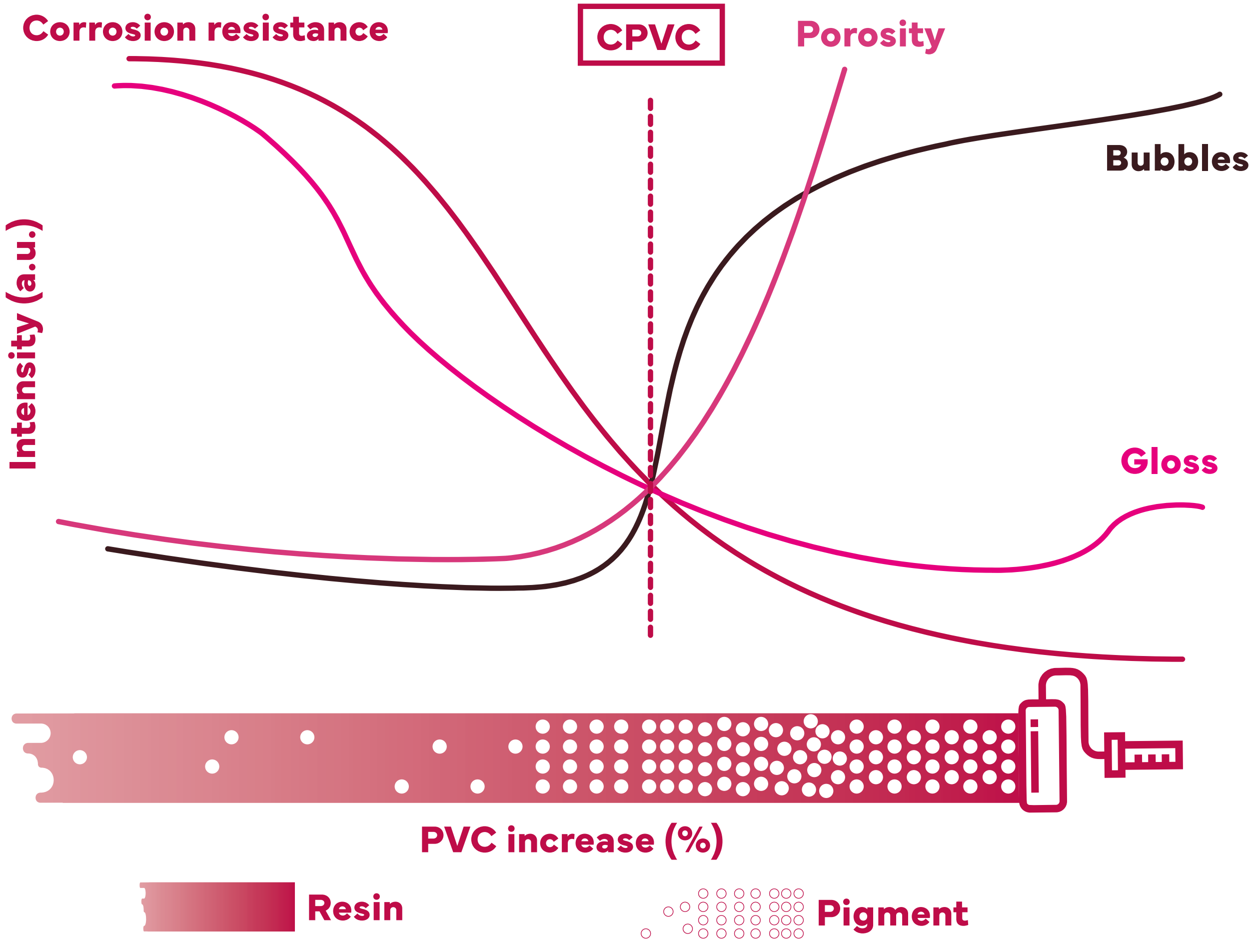

Figure 6.2: *Influence of PVC increase on paint film characteristics.*

Source: adapted from PSLC ([200-]).

The relationship between PVC and CPVC is known as λ (λ = PVC/CPVC). This parameter is important to define the type of finish desired in the paint, indicating how close the PVC is to the CPVC. Table 6.4 shows some λ values in some finishes (FAZENDA, 2009):

λ	**Finish type**
< 0.5	Glossy Enamels
0.5 a 0.8	Satin Finishing Paints
> 0.8	Matte Finishing Paints
0.5 a 1.0	Primers
> 1.0	Putty and Economic Paints

Table 6.4: *Types of finish and value of λ.*

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7 Application of surfactants in latex formulation: introduction to emulsion polymerization technology

Juliane Pereira Santos

7.1 OVERVIEW OF THE EMULSION POLYMERIZATION PROCESS

Emulsion polymerization is the main process of obtaining synthetic latex or emulsion polymer, the main component of water-based paints and adhesives (VANDERHOFF, 1993). In this process, radical initiators polymerize monomers (acrylic, methacrylic, vinyl, etc.) in aqueous medium. Surfactants are required to stabilize the system during polymerization, and the dispersed polymer particles formed.

A simplified view of the batch emulsion polymerization mechanism and its stages is depicted in Figure 7.1.

The beginning of polymerization (Figure 7.1 A) comprises droplets of monomers emulsified by surfactants in water, a fraction of water-soluble monomer, monomer-swollen micelles of surfactants, and water-soluble initiator.

When the temperature of the reaction medium reaches the decomposition temperature of the initiator (BLACKLEY, 1975) there is the formation of free radicals that initiate the polymerization of the soluble monomer molecules in the aqueous medium. It generates oligomeric radicals that grow to a particular molecular weight, before migrating into the micelles and starting the nucleation stage of the particles known in the literature as Step I (Figures 7.1A and 7.1B).

Micellar nucleation is predominant in polymerization containing monomers with low water solubility, such as styrene, which has a water solubility of around 0.03wt% at room temperature and an aqueous medium with surfactant concentration above CMC at polymerization temperature.

Polymerization containing monomers with high water solubility, such as vinyl acetate, which has a water solubility of approximately 2.5wt% at room temperature, follows homogeneous and coagulative nucleation mechanisms (TADROS, 2010). In this case, the radical oligomers grow until they lose solubility in water, because they are more soluble in this medium, and there is the adsorption of the surfactant on the surface of these precursor particles. Since they have a high surface area, these particles coagulate to form the primary nucleated particles. This particle nucleation mechanism may also be followed by styrene and methyl methacrylate if the polymerization occurs in an aqueous medium containing surfactant concentration below the CMC at the polymerization temperature.

There is a direct relationship between the number of nucleated particles, the conversion of the monomers to polymer, and the molecular weight of the polymer chains formed within the particles. In general, the higher the number of nucleated particles, the higher the conversion rate of the monomer to polymer and the molecular weight (LOVELL; EL-AASSER, 1997).

Because radical polymerization reactions are exothermic, it is important to control the number of nucleated particles to avoid conditions where the exotherm of the reaction medium, generated by the polymerization within the particles, is beyond the capacity of the cooling system to maintain constant the temperature of the medium.

In Step II, also represented by Figure 7.1B, polymerization proceeds within the particles. The monomer concentration is kept constant due to its diffusion from monomer droplets to the particles, resulting in the growth of the particles.

In Step III, polymerization proceeds within the monomer swollen particles (Figure 7.1C); however, the concentration of monomers begins to decrease within the particles, resulting in decreased conversion rate and polymerization termination.

The dispersion of polymer particles obtained at the end of the polymerization process, known as latex, is depicted in Figure 7.1 D.

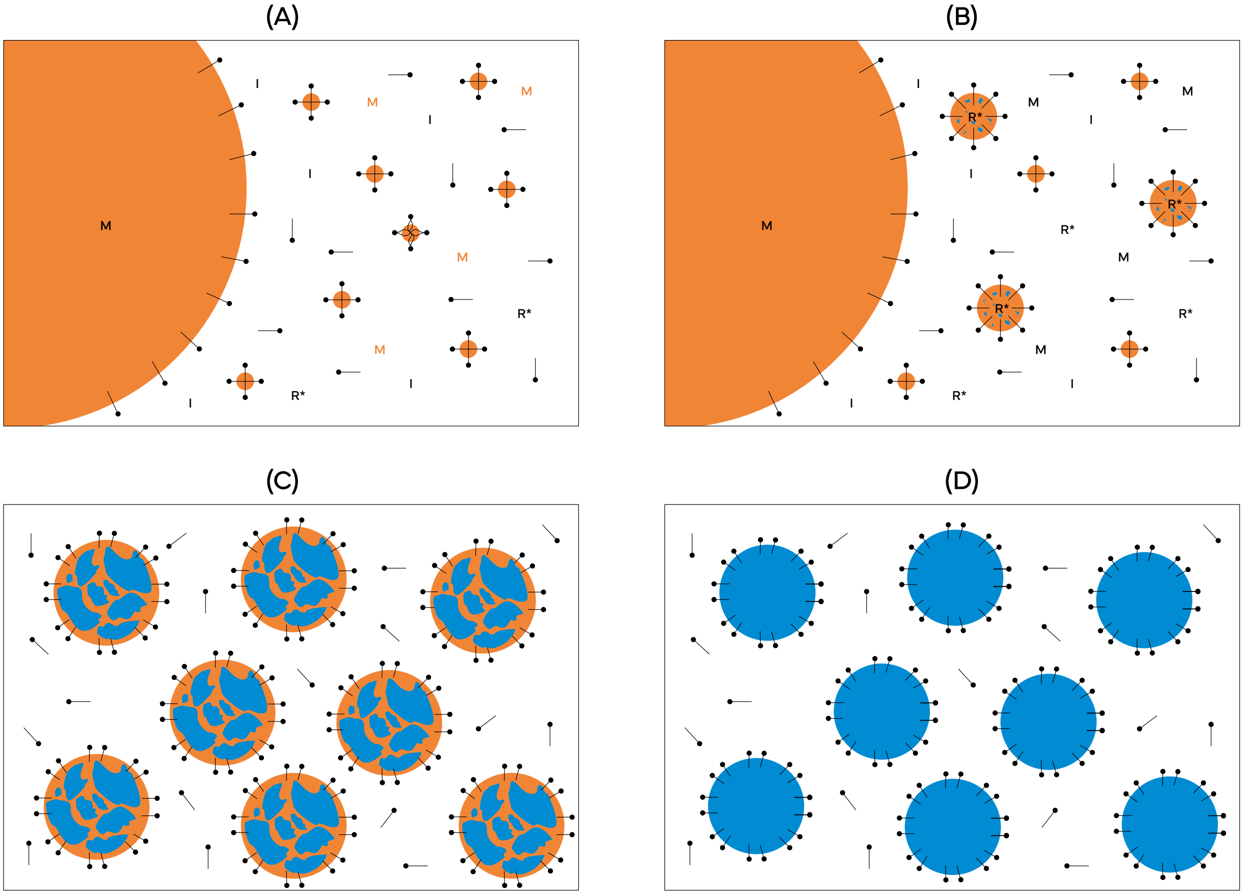

Figure 7.1 *Simplified scheme of the emulsion polymerization mechanism. The symbols I, M and R* represent the initiator, water-soluble monomer and radical formed in the aqueous medium.*

Latexes can be obtained by different emulsion polymerization processes (VANDERHOFF, 1993). Among them, it is worth mentioning the batch and semi-batch or semi-continuous polymerization processes, usually used in the polymerization of latexes used in paints and adhesives.

The batch polymerization process consists of adding all ingredients of the formulation, among which stand-out surfactant solution, monomer mixture and initiator solution, to the reactor at the beginning of the process and maintaining the polymerization in a certain condition of agitation and temperature until the conversion of the monomer to polymer is close to 100%.

The semi-batch process consists of adding to the reactor some ingredients, such as surfactant solution or seed batch. Along the process, with a defined flow rate, add critical ingredients to control the polymer composition, molecular weight and process exotherm, as monomer mixture or monomer pre-emulsion and initiator solution (LOVELL; EL-AASSER, 1997).

Emulsion polymerizations of latexes used in paints and adhesives, typically comprise the generation of an initial latex with solids content between 5wt% and 10wt%, termed seed, through batch process, as described in the topic of suggestive formulations. Subsequently, through a semi-continuous polymerization process, the seed polymers grow to generate latex with a solids content of around 50wt%. The main advantages of combining the two processes lie in being able to reproduce the particle nucleation step, which is the most difficult step to reproduce, along with the ease of controlling the polymer composition when using monomers with distinct reactivities (LOVELL; EL-AASSER, 1997), as well as controlling the process exotherm.

7.2 CHOICE OF SURFACTANT

The selection of surfactants is paramount to the development of an emulsion polymerization process and for obtaining a latex with particle size distribution and stability appropriate for each application (LOVELL; EL-AASSER, 1997).

The micellar concentration of the surfactants and their ability to decrease the surface tension of the aqueous phase and adsorb onto dispersed phases are fundamental characteristics of the surfactants used in emulsion polymerization. They promote a decrease in interfacial tension and electrostatic and steric stabilities.

Anionic and nonionic surfactants are widely used in emulsion polymerization of conventional anionic latexes (LOVELL; EL-AASSER, 1997; TADROS, 2010). Usually, a single surfactant is insufficient to generate a latex that achieves all the requested requirements. Preferably, the anionic surfactants promote the mechanical stability of the latex through electrostatic stabilization of the particles. In contrast, the nonionic surfactants promote stability against electrolytes and freeze-thaw cycles through steric stabilization, in addition to contributing to the latex mechanical stability.

In emulsion polymerization process, it is typically used anionic surfactants containing sulfate, sulfonate, sulfosuccinate, or phosphate as anionic group, and sodium, potassium, or ammonium as counterion. Figure 7.2 presents examples of surfactants used in emulsion polymerization.

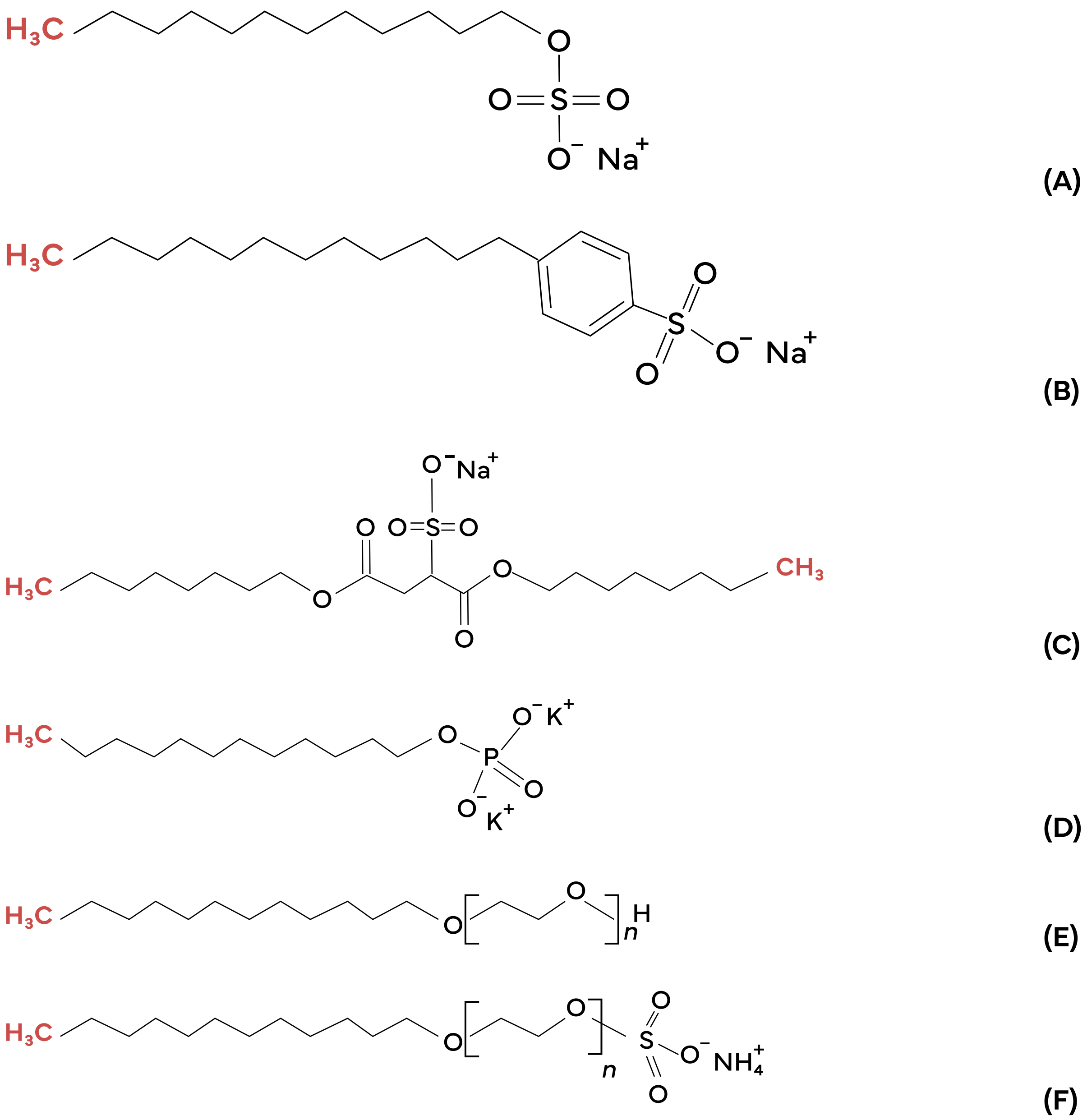

Figure 7.2: *Examples of surfactants that can be used in emulsion polymerization: sodium salt of sulfated lauryl alcohol (a), sodium dodecylbenzene sulfonate (b), sodium dioctyl sulfosuccinate (c), the potassium salt of phosphate lauryl alcohol (d), generic nonionic surfactant, n being between 7 and 40 moles of ethylene oxide (e) and ammonium salt of ethoxylated lauryl alcohol (f), being n equal to 2 to 30 moles of ethylene oxide.*

Ethoxylated anionic surfactants are also widely used in emulsion polymerization. This type of surfactant, containing at least 6 moles of ethylene oxide, combine the properties of anionic and nonionic surfactants and can be used as the only surfactant in the emulsion polymerization process. An example of sulfated ethoxylated surfactant (f) is also presented in Figure 7.2.

In emulsion polymerization, surfactants promote the emulsification of monomer droplets and solubilize monomers within micelles. They control the number of nucleated particles in Step I, the stability of particles throughout Step II and III, the distribution of particle sizes, the stability and surface tension of the final latex, and prevent clot formation in the reactor.

The relationship between the surfactant content and the number of particles is presented in Equation (1) (TADROS, 2010):

$$N \approx [S]^{0.6} \qquad (1)$$

Wherein:
N = number of particles
[S] = surfactant concentration

According to Equation (1), the number of nucleated particles increases with the surfactant concentration. It is important to note that this relationship is not linear, the exponent of the surfactant concentration is 0.6. Hence, starting from a reference latex, such as the latex described in topic 7.5, some relative surfactant contents estimated to increase or reduce the number of particles are presented in Table 7.1.

As the styrene-acrylic latex polymerization (largely used in the Brazilian market for architectural paints) is carried out predominantly at a temperature between 80°C and 85 °C, above the cloud point of the nonionic surfactant, the number of particles is preferably controlled by the anionic surfactant content. As a result, the surfactant contents mentioned in Table 7.1 refer to the anionic surfactant.

Number of particles	**Relative number of particles**	**Anionic surfactant content (mol/L) in the latex of topic 7.3**	**Anionic surfactant content (phm) in the latex of topic 7.3**
3.5×10^{17}	Reference	0.0345	2.52
5.3×10^{17}	50% increase	0.0678	4.95
7.0×10^{17}	100% increase	0.1095	8.00
1.8×10^{17}	50% reduction	0.0109	0.79
0.9×10^{17}	75% reduction	0.0034	0.25

Table 7.1: *Surfactant contents required to change the number of reference latex particles, such as styrene-acrylic latex described in topic 7.3.*

The stability of the latex particles depends on the type and content of surfactants used throughout the polymerization process. When one has unstable latex, a very common tendency is to increase the anionic and nonionic surfactant contents of the entire formulation before understanding which step is more prone to destabilization. In such cases, the ideal is to take latex samples throughout the process, determine the solids content, the density and the average particle size of the latex to estimate the number of particles to verify how the number of particles changes during the polymerization. From these data, it is defined whether it is necessary to increase the concentration of surfactants in the particle growth step to improve the surfactant coverage of the particles and their stability or to reduce the surfactant content in the seed step to reduce the number of nucleated particles and facilitate their stabilization in the particle growth step.

When the addition of bactericide and neutralizer desestabilizes the latex due to the low surfactant coverage of latex particles, it is possible increase the surfactant coverage of latex particles performing postaddition of surfactants. This postaddition is more effective for more hydrophobic latexes, for example, styrene-acrylic, where it is possible to increase the surfactant coverage of the particles with the postaddition of surfactants. This postaddition of surfactant is less effective in improving the stability of polar latexes, such as vinyl-acrylic, that present limited adsorption of surfactant on their surface (LOVELL; EL-AASSER, 1997).

Neutralization of latexes, such as styrene-acrylic and pure acrylic, containing carboxylic monomers is essential to ensure the electrostatic stability promoted by carboxylic groups in the form of carboxylates. However, this is a critical step that may favor partial latex coagulation. This may occur due to the high local concentration of the neutralizer during its incorporation into the latex, which causes an abrupt increase in the ionic strength of the medium, resulting in the compaction of the electric double layer, the reduction of the zeta potential, and the destabilization of the latex particles (FITCH, 1997). The tendency of neutralizing agents to destabilize latex particles depends on their ability to increase the medium's ionic strength and the cations' hydration strength. Preliminary studies of protein colloidal stability suggest that particle destabilization increases in the following order: $NH^{4+} < K^{+} < Na^{+} < Li^{+} < Mg^{2+} < Ca^{2+}$ (LOPEZ-LEON; JODAR-REYES; ORTEGA-VINUESA, 2003).

To prevent destabilization from increasing the ionic strength of the medium, one can increase the nonionic surfactant content of the latex to maximize steric protection. Another possibility is, whenever possible, to add diluted solutions of neutralizing agents.

7.3 REACTIVE SURFACTANTS

Conventional anionic and nonionic surfactants, despite being critical to ensure the stability of the latex particles during polymerization and the final latex, impact the latex film formation and the properties of the water-based coating films.

During the latex film formation, more specifically in Stage III of the coalescence of the particles, in which there is the diffusion of the polymer chains from one particle to another resulting in the disappearance of the domains of the particles, there is also the diffusion of the surfactants, preferably to the polymer-air surface and polymer-substrate interface and its segregation, forming hydrophilic domains distributed throughout the film. These hydrophilic domains are pathways for water to enter into the film and, thus, are primarily responsible for the low water resistance of latex films and water-based coatings containing conventional anionic and nonionic surfactants.

This is the main limitation of water-based coatings concerning solvent-based coatings, restricting the use of water-based coatings in more demanding applications, for example, environments with high relative air humidity that require coatings with high water resistance.

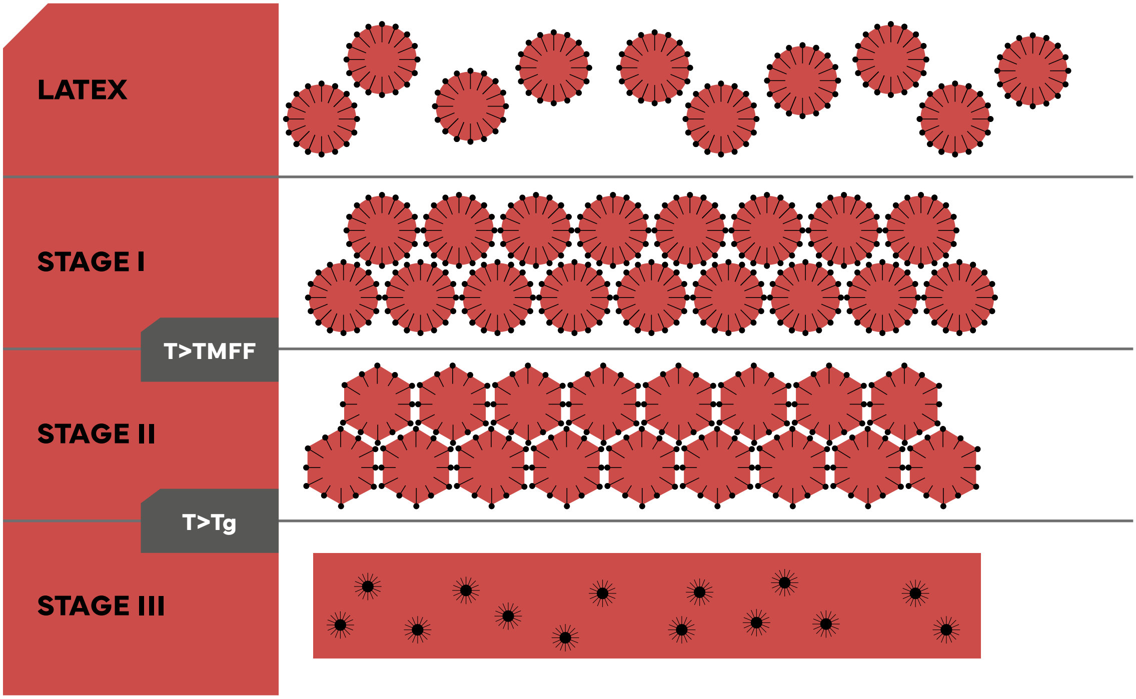

Figure 7.3: *Illustrates the migration of surfactants to interfaces and their segregation. Latex film formation stages and example of surfactant segregation in Stage III.*

A potential solution to this problem of low water resistance of water-based coatings lies in using reactive surfactants in the emulsion polymerization of latexes (GUYOT, 2004).

Reactive surfactants are unsaturated amphiphilic molecules that possess the same stability attributes as conventional surfactants (mentioned above), but form covalent bonds with the monomers used in emulsion polymerization mitigating migration and segregation of the surfactant in the latex film and improving water resistance of the final coating. An example of a hypothetical reactive surfactant is presented in Figure 7.4.

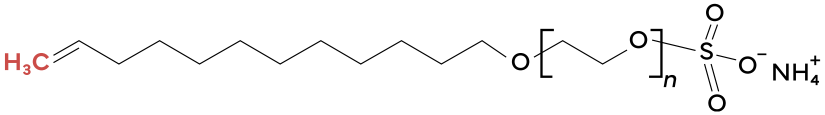

Figure 7.4: *Examples of generic reactive anionic surfactant.*

The use of reactive surfactants is also interesting from an environmental point of view since conventional surfactants are extracted from coatings applied externally by rainwater and taken to the environment, while the reactive surfactants incorporated into the polymer will not be extracted by rainwater and taken to the environment.

In the following section, it will be presented examples of suggestive formulations of styrene-acrylic latex, pure acrylic latex and vinyl-acrylic latex that illustrate some types of surfactants and stabilizing agents used in those polymerizations.

7.4 SUGGESTIVE FORMULATION OF STYRENE-ACRYLIC LATEX

Sulfated surfactant with low degree of ethoxylation, lower than 4 EO units, and nonionic surfactants with a degree of ethoxylation greater than 20 EO units free of alkylphenol ethoxylate (APEO) can be used in emulsion polymerization of styrene-acrylic latex. An APEO-free suggestive formulation of styrene-acrylic latex containing these surfactants will be described. The ingredients used for the different batches of the process are described in Tables 7.2 to 7.6. The reactor loading and typical properties of the obtained latexes are described in Tables 7.7 and 7.8, respectively. A video accompanying the polymerization process is available at the link: https://youtu.be/m1JV-cGU6R4.

Components	Mass (g)
Deionized water	507.0
Sodium bicarbonate @ 99 wt%	0.5
OXIMULSION® 1228 @ 28 wt%	8.0
Total	**515.5**

Table 7.2 *Emulsifier batch.*

Components	Mass (g)
Deionized water	476.5
OXIMULSION® 1228 @ 28 wt%	48.2
OXITIVE® 7110 @ 60 wt%	52.8
Styrene @ 99 wt%	625.0
Butyl acrylate @ 99.5 wt%	525.0
Acrylic acid @ 99 wt%	25.0
Total	**1,752.5**

Table 7.3: *Preemulsion batch.*

Components	Mass (g)
Deionized water	125.0
Potassium persulfate @ 99 wt%	3.75
Total	**128.75**

Table 7.4: *Initiator batch.*

Components	Mass (g)
Deionized water	37.5
T-butyl hydroperoxide @ 70 wt%	0.5
Total	**38.0**

Table 7.5: *Batch of oxidizing agent.*

Components	Mass (g)
Deionized water	37.5
Sodium formaldehyde sulfoxylate @ 98 wt% (SFS)	0.5
Total	**38.0**

Table 7.6: *Batch of reducing agent.*

Polymerization steps	Order of addition	Components	Mass (g)
STEP A	1	Emulsifier	210.5
	2	5 wt% Pre-emulsion	35.3
	3	5 wt% Initiator	2.6
STEP B	4	95 wt% Pre-emulsion	671.4
	4	95 wt% Initiator	49.4
STEP C	5	Reducing agent	15.4
	5	Oxidizing agent	15.4
STEP D	6	Defoamer	0.1
	7	Monoethanolamine (MEA)	Define
		Total	**1,000.1**

Table 7.7: *Reactor Loading.*

The polymerization of styrene-acrylic latex comprises several steps. In the first step, when occurs the nucleation of particles and the generation of seeds, the batch of emulsifiers is charged into the reactor, purged with N_2, and then heated to a temperature between 80-85 °C. Next, 5wt% of the pre-emulsion batch and 5% of the initiator batch are charged into the reactor. The N_2 flow rate is decreased, and the reaction is maintained for 30 minutes at 80-85 °C.

In step B occurs the seed growth. At this point, the medium temperature is maintained between 80-85 °C, and the continuous additions of the pre-emulsion batch and initiator batch are performed for 3.5 and 4.0 hours, respectively. After finishing the pre-emulsion and initiator batch additions, the polymerization is maintained for 30 minutes at a temperature of 80-85 °C.

Step C comprises the consumption of the residual monomers. In this part, the temperature of the reaction medium is reduced to 60-65 °C, and the batches of oxidant and reducer are gradually added for 30 minutes. Then, in step D, the latex is neutralized, the temperature of the medium is decreased to 30 °C and the reactor is discharged by passing the latex in a 200 mesh sieve previously weighted to quantify the clot content formed in the reactor.

Properties	Typical values
Clot content (ppm)	< 500
Solid content (wt %)	49.5 ± 1.2
Particle size (nm)	131.0 ± 10.3
Viscosity at 25 °C (cP)	338.0 ± 101.8
pH at 25 °C	8.5 ± 0.5

Table 7.8: *Typical properties of the obtained latexes.*

7.5 SUGGESTIVE FORMULATIONS OF PURE ACRYLIC LATEX

Because they are more polar, pure acrylic latexes present lower adsorption of conventional surfactants than styrene-acrylic latexes. As a result, they are more difficult to stabilize and can generate more clots in the reactor than styrene-acrylic latexes. The formulation of pure acrylic latex varies from region to region. In Europe, it is common to use a mixture of anionic and nonionic surfactants, while in North America, it is common to use only anionic surfactants. The following will describe a suggestive formulation of an APEO-free acrylic latex containing only an anionic surfactant with a high degree of ethoxylation. The ingredients used for the different batches in the process are described in Tables 7.9 to 7.14. The reactor loading and typical properties of the obtained latexes are described in Tables 7.15 and 7.16, respectively.

Components	Mass (g)
Deionized water	203.3
Sodium bicarbonate @ 99 wt%	3.4
OXIMULSION® 11230 @ 37 wt%	3.2
Total	**209.9**

Table 7.9: *Emulsifier batch.*

Components	Mass (g)
Deionized water	152.5
OXIMULSION® 11230 @ 37 wt%	18.5
Methyl methacrylate @ 99 wt%	246.6
Butyl acrylate @ 99.5 wt%	233.8
Methacrylic acid @ 99 wt%	9.8
Total	**661.2**

Table 7.10: *Pre-emulsion batch.*

Components	Mass (g)
Deionized water	1.2
Ammonium persulfate @ 99 wt%	13.3
Total	**14.5**

Table 7.11: *Initiator batch for seeds.*

Components	Mass (g)
Deionized water	1.5
Ammonium persulfate @ 99 wt%	43.3
Total	**44.8**

Table 7.12: *Initiator batch for seed growth.*

Components	Mass (g)
Deionized water	27.4
T-butyl hydroperoxide @ 70 wt%	1.7
Total	**29.1**

Table 7.13: *Batch of oxidizing agent.*

Components	Mass (g)
Deionized water	28.0
Sodium metabisulfite @ 99 wt%	1.2
Total	**29.2**

Table 7.14 *Batch of reducing agent.*

Polymerization steps	Order of addition	Components	Mass (g)
STEP A	1	Emulsifier	210.7
	2	5 wt% Pre-emulsion	33.3
	3	Initiator batch for seed	14.4
STEP B	4	Pre-emulsion	632.5
	4	Initiator batch for seed growth	44.8
STEP C	5	Reducing agent	29.1
	5	Oxidizing agent	29.0
STEP D	6	Ammonia @ 14 wt%	6.1
	7	Monoethanolamine (MEA)	Define
		Total	**1,000.0**

Table 7.15: *Reactor loading.*

In the first step of a pure acrylic latex polymerization, occurs the nucleation of particles and the generation of seeds. In this part, the batch of emulsifiers is added to the reactor, N^2 is connected to the reactor sky and the batch of emulsifiers is heated to a temperature between 78-82 °C. In the sequence, 5% of the pre-emulsion batch and the Initiator batch for seeds are charged into the reactor to generate the seeds. The N^2 flow rate is decreased, and the reaction is maintained for 30 minutes at a temperature of 78-82 °C.

In the second step, the seed growth, the temperature of the medium is maintained between 78-82 °C and the additions of pre-emulsion and initiator batches are performed for 3.5 hours. After finishing the pre-emulsion and initiator batch additions, the polymerization is maintained for 30 minutes at a temperature of 78-82 °C.

The final step comprises the consumption of the residual monomers, the temperature of the reaction medium is reduced to 60-65 °C and the batches of oxidant and reducer are added for 30 minutes. Subsequently, the temperature of the medium is decreased to 30 °C, the latex is neutralized, and the reactor is unloaded by passing the latex in a 200 mesh sieve previously weighted to quantify the clot content formed in the reactor.

Characteristics	Typical values
Clot content (ppm)	< 500
Solid content (wt %)	51.0 ± 1.0
Particle size (nm)	172.0
Viscosity at 25 °C (cP)	351.0
pH at 25 °C	9.0 ± 0.5

Table 7.16: *Typical properties of the obtained latexes.*

7.6 SUGGESTIVE FORMULATION OF VINYL-ACRYLIC LATEX

Vinyl-acrylic latexes are more polar than acrylic and styrene-acrylic latexes and, consequently, more difficult to be stabilized by conventional surfactants. Because of this, normally, these latexes are stabilized by a combination of anionic surfactant, nonionic surfactant and a protective colloid. The following tables will describe a suggestive formulation of an APEO-free vinyl-acrylic latex polymerized with an anionic surfactant with low degree of ethoxylation and a nonionic surfactant with a high degree of ethoxylation (degree of ethoxylation > 30), having hydroxyethylcellulose as a protective colloid. The ingredients used for the different batches in the process are described in Tables 7.17 to 7.23. The reactor loading and typical properties of the obtained latexes are described in Tables 7.24 and 7.25, respectively.

Components	Mass (g)
Deionized water	344.5
Sodium bicarbonate @ 99 wt%	2.3
NATROSOL 250 LR	1.7
OXIMULSION® 1228 @ 33 wt%	2.7
OXITIVE® 7140 @ 68 wt%	34.8
Total	**386.1**

Table 7.17: *Emulsifier batch.*

Components	Mass (g)
Vinyl acetate @ 99 wt%	424.0
Butyl acrylate @ 99.5 wt%	106.0
Total	**530.0**

Table 7.18 *Mixture of monomers.*

Components	Mass (g)
Deionized water	16.4
Ammonium persulfate @ 99 wt%	0.6
Total	**17.0**

Table 7.19 *Initiator batch of the seed generation step.*

Components	Mass (g)
Deionized water	26.0
Ammonium persulfate @ 99 wt%	0.7
Total	**26.7**

Table 7. 20: *Initiator batch of the seed growth stage.*

Components	Mass (g)
Deionized water	26.1
Sodium metabisulfite @ 99 wt%	0.6
Total	**26.7**

Table 7.21: *Batch of reducer of the seed growth stage.*

Components	Mass (g)
Deionized water	6.3
T-butyl hydroperoxide @ 70 wt%	0.5
Total	**6.8**

Table 7.22: *Batch of oxidizing agent to consume residual monomer.*

Components	Mass (g)
Deionized water	0.4
Sodium metabisulfite @ 99 wt%	6.3
Total	**6.7**

Table 7.23: *Batch of reducing agent to consume residual monomer.*

Polymerization steps	Order of addition	Components	Mass (g)
STEP A	1	Emulsifier	386.1
	2	2.5 wt% Mixture of monomers	13.3
	3	Seed initiator	17.0
STEP B	4	97.5 wt% Mixture of monomers	516.7
	5	Growth initiator	26.7
	6	Growth reducer	26.7
STEP C	7	Oxidizing agent	6.8
	8	Reducing agent	6.7
		Total	**1,000.0**

Table 7.24: *Reactor loading.*

The vinyl-acrylic latex polymerization comprises 3 steps. In the first step occurs the nucleation of particles and the generation of seeds. The batch of emulsifiers is prepared in the reactor at a temperature of 60, and then increased to 70 °C. The batch of ammonium persulfate and 2.5 wt% of the monomer mixture are added at once, and the addition of reducer starts after and lasts for a period of 4 hours. The reaction is maintained in this condition for 30 minutes.

In the second step, the seed growth, the temperature of the medium is maintained at 70 °C, and the addition of the mixture of monomers and a batch of ammonium persulfate take 3.5 hours. After finishing the additions of monomers, the batch of ammonium persulfate and the batch of reducer, the polymerization is maintained for 30 minutes at a temperature of 70 °C.

The third step comprises the consumption of the residual monomers. During the next hour, the oxidant and reducer are added in batches. Subsequently, the temperature of the medium is decreased to 30 °C and the reactor is unloaded by passing the latex in a 200 mesh sieve previously weighted to quantify the clot content formed in the reactor.

Characteristics	Typical values
Clot content (ppm)	< 500
Solid content (wt %)	55.8
Particle size (nm)	208
Viscosity at 25 °C (cP)	305
pH at 25 °C	4.8

Table 7.25: *Typical properties of the obtained latexes.*

7.7 CONCLUSION

Emulsion polymerization has the advantage of using water as a continuous phase, favoring thermal exchange and the control of the temperature in the process. In addition, it generates dispersion of polymeric particles with low viscosity and molecular weight in the order of 10^6 g/mol on a timescale of 4 to 6 hours and viscosity of the medium between 100 cP and 2,000 cP, in contrast to polymers obtained in solution typically performed using hazardous organic solvents that present molecular weight in the order of 10^3g/mol on a time scale often exceeding 12 hours. However, the colloidal stability of the latex particles is critical, and each monomeric composition requires a system of surfactants and process adjusted to generate latexes with optimal particle size distribution and stability, as well as generating low clot content.

Another point of attention is that the polymers obtained throughout emulsion polymerization are process dependent. As a result, latexes with the same monomeric composition synthesized at different temperatures can present distinct properties arising from differences in the distribution of monomers, level of crosslinking and molecular weight of polymer chains, as well as the size and stability of polymeric particles.

A limitation of the polymers obtained by emulsion polymerization using conventional surfactants is the lower water resistance in relation to the polymers polymerized in solution. This limitation has been gradually improved with the development of reactive surfactants and more appropriate processes to ensure the incorporation of reactive surfactants into the polymer.

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8 Application of surfactants in the formulation of emulsions of long in oil alkyd resins

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Alann de Oliveira Piagentini Bragatto**

8.1 OVERVIEW OF THE EMULSIFICATION PROCESS AND THE CHOICE OF SURFACTANT

Emulsions are easily described as a mixture of two immiscible liquids wherein the first liquid in the form of droplets, known as the dispersed phase, is dispersed in the second liquid, known as the continuous phase.

Emulsions are mainly divided into two types: water-in-oil (W/O) or oil-in-water (O/W). In both cases, emulsions are unstable and tend to separate phases over time, but it is possible to use surfactants or emulsifiers to prevent destabilization, increasing their shelf life.

The stability of an emulsion is directly related to the droplet size and distribution, such that the larger the size of the droplets or the wider their distribution, the more rapidly the emulsion tends to destabilize. This property is correlated with the preparation method used, the amount of energy supplied during the process, the degree of difference between the viscosities of the phases, and finally the type and content of the emulsifiers used (SANTOS, 2022).

The process of emulsifying a long in oil alkyd resin, with a viscosity up to 15000 cP at the emulsification temperature, is preferably carried out by the phase inversion methodology, generating stable oil-in-water emulsions with droplet sizes in the order of 200 to 400 nm and solids content between 50 – 70 wt%.

Figure 8.1 illustrates the phase inversion methodology that is based on the solubilization of the emulsifiers in the oil phase (continuous phase) followed by the gradual addition of water (discontinuous phase). Therefore, initially, the morphology of the emulsion is water-in-oil until it reaches the critical point at which the inversion occurs, modifying the morphology then to oil-in-water (HARTMANN, 2011; SANTOS, 2022).

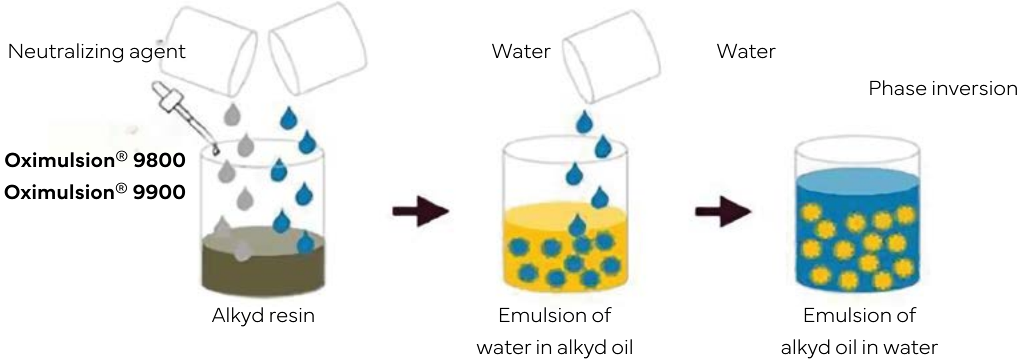


Figure 8.1: *Exemplification of the emulsification process of long in oil alkyd resins by the phase inversion methodology.*

Figure 8.2 illustrates the impact of the emulsifier content and type on the evolution of emulsion morphology as water is added to the oil phase. Figure 8.2a shows that the emulsion containing low content of a high HLB emulsifier initially generates a water-in-oil emulsion that, after the inversion point, converts it into an oil-in-water emulsion with larger droplet sizes. Figure 8.2b shows that, by using a higher content of a high HLB emulsifier, the initial water-in-oil emulsion evolves into multiple emulsions, where within each droplet of the water-in-oil emulsion, there is also formation of oil-in-water emulsion droplets. These multiple emulsions occur for intermediate water contents before the inversion point. After the inversion point, the obtained oil-in-water emulsion has smaller droplet sizes than the previous case with low emulsifier content, in Figure 8.2a.

Figure 8.2c illustrates that maintaining the use of high emulsifier content as in Figure 8.2b and reducing its HLB, the same phenomena occur, departing from a water-in-oil emulsion, evolving to multiple emulsions formed before the phase inversion point. However, the sizes of the oil droplets dispersed in the water phase of the multiple emulsions are smaller, resulting in an oil-in-water emulsion, after the inversion point, with droplet sizes smaller than those observed in the other two cases. These results suggest that optimizing emulsifier type and content makes it possible to form even smaller droplets, promoting an emulsion with greater stability (LEFSAKER, 2013).

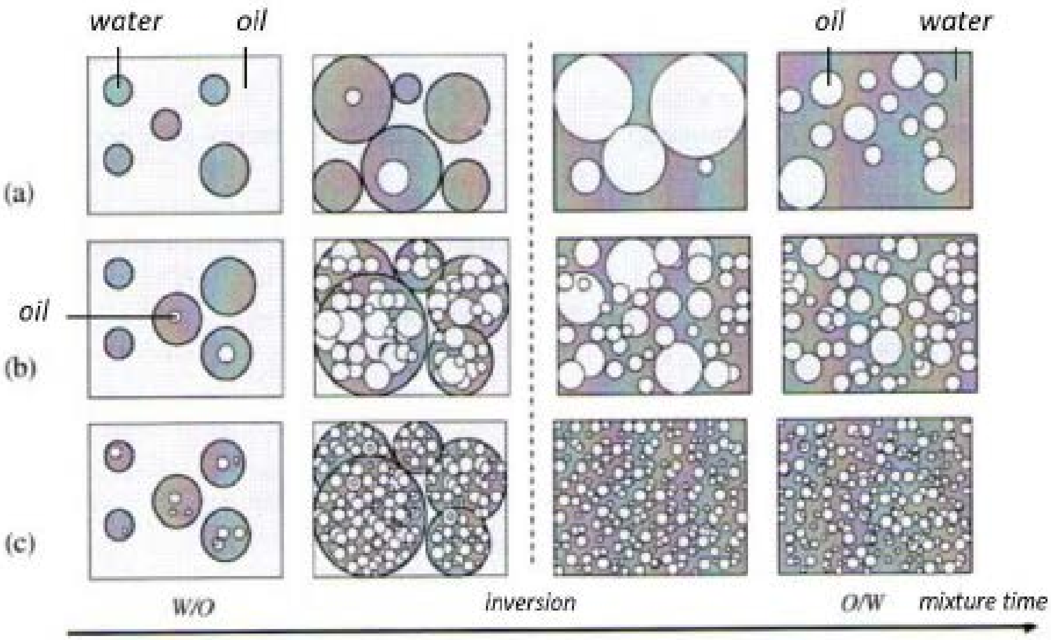


Figure 8.2: *Representation of the evolution of droplet size and morphology during the emulsion phase inversion; (a) low surfactant concentration with high HLB, (b) high surfactant concentration with high HLB, (c) high surfactant concentration with low HLB.*

Image taken and adapted from Hartamann, 2011.

In addition to the aforementioned cases, in situations where the oil phase, such as alkyd resins, exhibits a viscosity that matches or surpasses the one of water phase, phase inversion through multiple emulsion formation can occur and the respective emulsions are stabilized by at least two distinct emulsifiers (ASERIN, 2008).

To emulsify alkyd resins and obtain stable oil-in-water emulsions with droplet sizes less than 500 nm and solids content greater than 50%, it is recommended to use two emulsifiers, an anionic emulsifier, for example, a sulfonate or sulfate anionic emulsifier, and a nonionic emulsifier, typically a EOPO copolymer. Both emulsifiers are essential to reduce interfacial tension, allowing phase inversion to occur using mechanical agitation equipment that transfers low energy to the medium during the process (FERNANDEZ, 2004) and enabling the formation of emulsions with nanometric droplets. In addition, anionic emulsifiers promote electrostatic stability. In contrast, nonionic emulsifiers promote steric stability of the oil-in-water emulsion ensuring kinet stability and shelf-life appropriate for the application.

8.2 SUGGESTIVE FORMULATION OF AN OIL-IN-WATER ALKYD EMULSION

In order to formulate an alkyd emulsion in a 500 g round bottom flask, 150 g of resin and up to 8 wt%, i.e., approximately 12 g, of active surfactant relative to the resin is suggested. It is recommended to use a blend of OXIMULSION® 9900 (nonionic emulsifier) and OXIMULSION® 9800 (anionic emulsifier) and the use of triethanolamine (TEA 85%) as a neutralizer, calculated for the neutralization of the carboxylic groups of the alkyd resin and acidic group of the anionic emulsifier.

In addition, deionized water at room temperature is employed, adjusting its quantity to achieve solid content ranging form 40 to 70 wt% appropriate for transportation, storage, and final application. Based on studies with different resins, it was concluded that 55% solid content emulsions present high stability, in addition to viscosities below 2,000 cP and droplet sizes between 100 and 300 nm.

Considering the use of 150 g of resin and 12 g of emulsifiers, it is expected to produce approximately 314 g of emulsion for 55 wt% solid content as shown in Table 8.1.

Components	Equations
Alkyd resin	$m_{resin} = 150$ g
Neutralizing agent	Mass of neutralizers to neutralize the resin: $m_{TEA} = 0.448 \cdot$ Resin acidity index (*mgKOH/g*) Mass of neutralizer to neutralize the OXIMULSION® 9800 surfactant: $m_{TEA} = 0.524 \cdot m_{9800}$
OXIMULSION® 9900	$m_{9900} = 12.63 \cdot$ Percentage of nonionic surfactant in blend
OXIMULSION® 9800	$m_{9800} = 12.63 \cdot$ Percentage of anionic surfactant in the blend
Deionized water	Between 145 and 150 g for a solids content of 55 wt%

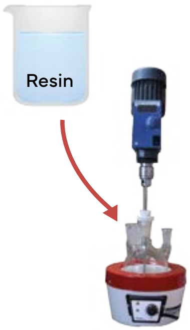
Table 8.1: *Emulsion formulation.*

It is worth emphasizing that, in carrying out the calculations of the amount of surfactants and neutralizer required, the total mass of the resin is considered. Based on our previous experience, it is possible to perform the emulsification and generate stable emulsion of alkyd resins with acid values ranging from 5 to 20 mg KOH/g.

8.3 PROCEDURE

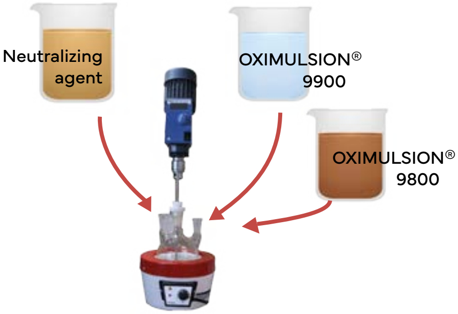
To determine the operating temperature of the process, the effect of temperature on the viscosity of the resin must be evaluated. It is recommended to perform the evaluation of viscosity in a Cone and Plate viscometer or in a rheometer. Typically, a process temperature in which the resin has viscosity between 5,000 and 15,000 cP is selected.It is not recommended to work at a temperature at which the viscosity exceeds 15,000 cP. Based on previous studies, emulsification processes at 80 °C have succeeded.

Part A - Addition of resin



Alkyd resin is added to the round bottom flask. It is recommended to monitor stirring during the temperature adjustment to prevent the incorporation of air bubbles into the resin.

Part B - Addition of raw materials



When reaching the operating temperature, add the total mass of the neutralizer (TEA 85) and wait 5 minutes.
Add the surfactants and wait 15 minutes. It is recommended to start with the addition of OXIMULSION® 9900 and then OXIMULSION® 9800.

Part C - Addition of water

Perform gradual addition of water using a pump for at least 30 min.
After the emulsion inversion, homogenize for 30 minutes and then discharge. The analyses mentioned in Table 8 are performed.

To identify the emulsion inversion point, use a beaker with water. Every 5-10 minutes remove a small amount of the product from the round bottom flask with the tip of a glass baguette and try to disperse it in water. The inversion point is verified when the emulsion aliquot is completely dispersed in water. Typically, the emulsion is expected to achieve the inversion point after adding 40 to 60 wt% of the total mass of water. If the whole amount of water is consumed before achieving the inversion point, more water can be added util achieving the inversion point, however, the target solid content will not be reached, resulting in an emulsion with lower solid content.

Part D - Characterization

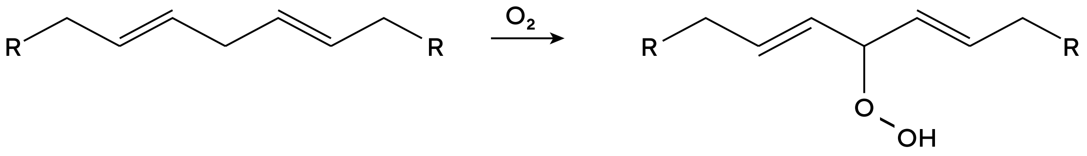
Properties	Typical values
Particle size (nm)	< 400
Solid content (wt%)	55.6 ± 1.5
pH at 25 °C	7.5 ± 0.5
Viscosity at 25 °C (cP)	2,000

Table 8.2: *Typical properties of the obtained emulsions.*

8.4 FILM FORMATION

The process of drying alkyd paints basically involves two main steps: physical drying and chemical drying, also called oxidative drying. During the first step of physical drying, the solvent in the system evaporates, and the resin particles coalesce. In oxidative drying, fatty acid chains in alkyd resin self-oxidize upon exposure to oxygen in the air. It leads to process start of radical formation, the crosslinking of the polymer chains, and the consequent increase in the glass transition temperature, Tg (GORKUM, 2005).

The mechanism of the reactions involved in the oxidative drying process is complex and is not yet completely elucidated. In a simplified way, the first step involves the auto-oxidation, by oxygen from the air, of a C-H bond present in the fatty acid chain that makes up the resin, generating a hydroperoxide. Subsequently, the hydroperoxide decomposes, generating free radicals, which are responsible for the process of polymerization, crosslinking, and effective film formation (MÜLLER, 2010). Figure 8.3 illustratively shows the described drying process.



$$\text{R-O-O-H} \longrightarrow \text{R-O}\cdot + \cdot\text{O-H}$$

$$2\ \text{R-O}^{\bullet} \longrightarrow \text{R-O-O-R}$$

Figure 8.3: *Main reactions involved in the oxidative drying process.*

Image adapted from Müller, 2010, Chapter 5 and Gorkum, 2005, Chapter 1.

The composition of the alkyd resin directly affects the efficiency of the drying process and film formation. The greater the degree of unsaturation (amount of carbon-carbon double bonds) in the fatty acid chain that makes up the resin, the more efficient the drying process will be (OYMAN, 2003). In addition, the type of double bond (isolated or conjugated) will also affect the performance in terms of drying, and the presence of conjugated double bonds tends to favor the drying process (MÜLLER, 2010).

Although the resin has an adequate composition in terms of the degree of unsaturation and type of double bond, the use of drying agents is essential for efficient drying and film formation.. Drying agents are composed of metal salts of organic acids and can be divided into:

- Primary dryers, redox catalysts or surface dryers - catalyze the process of decomposing hydroperoxides to generate free radicals. Because they act as catalysts, they are not effectively consumed during the process of drying and film formation. Cobalt is the most commonly used metal due to its high efficiency. However, its use has been questioned due to possible toxicological problems. Alternatives such as manganese and iron salts can be used. However, they have lower performance than cobalt salts concerning drying time and evolution of surface hardness (WU, 2004).
- Secondary, real or coordination dryers - act by forming salts between carboxyl or hydroxyl groups present in the structure of the alkyd resin, promoting the ionic crosslinking process (MÜLLER, 2010). The use of secondary dryers is important, especially as the thickness of the applied paint layer increases, to ensure effective film drying and not only superficial drying. Zirconium, aluminum or barium salts can be used as secondary dryers, with the use of zirconium salts being more common.
- Auxiliary dryers - the mechanism of action of this type of dryer is still unknown, but it is suggested that its use potentiates the action of primary dryers. In this case, potassium, lithium, and zinc salts can be used.

The premises established to obtain an efficient drying process in alkyd systems are valid for alkyd solvent-based paints and water-based paints produced from alkyd emulsions. However, some details related to the drying process and selection of additives used in the formulation and the emulsification process of the resins must be known to obtain an efficient drying process and a film formation suitable for the final application.

The first important factor to mention is that water-based paints formulated from alkyd emulsions tend to exhibit a longer drying time than solvent-based alkyd paints. This factor can be explained because water acts as a strong complexing agent with different metals that are used as primary dryers, such as cobalt and manganese. The formation of these complexes will cause a loss of the catalytic effectiveness of the dryer, and the oxidative drying process will only start after water evaporation (OYMAN, 2003).

Because of this factor, the use of dryers commonly used in solvent-based systems may not be suitable for water-based systems. In this case, it is preferred to use drying agents emulsified in water that are soluble in organic solvents (WEISSENBORN, 2000).

Moreover, the concentration of drying agents demanded for water-emulsified alkyd systems generally tends to be higher than the same system diluted in organic solvent. Another factor that helps to understand the difference in drying between solvent-based and water-based systems is the difference in oxygen solubility in the medium. As oxygen is less soluble in water than other organic solvents, in water-emulsified systems, the oxygen availability in the medium tends to be lower than in systems composed of organic solvents, thus generating a longer drying time (HURLEY, 1982).

To ensure a good efficiency of the paint formulated from an alkyd emulsion, the selection of emulsifiers and neutralizers used in the emulsification process and their concentrations must be carried out carefully, as mentioned in the previous items of this chapter. Studies demonstrate that the emulsifiers used in the resin emulsification process can affect the partition of drying agents between the polymeric phase and water. Consequently, it is preferred to use emulsifiers that favor the partitioning of the drying agent in the polymeric phase, so it favors the drying time and the film formation process. In addition, the pH range and the chemical nature of the neutralizing agent may also affect the drying process.

In this case, to optimize the efficiency of the drying agents, it is preferable that the system has a pH greater than 7 and to avoid the use of neutralizing molecules which can act as complexing agents with the metals that make up the drying agent (ÖSTBERG, 1994).

In addition to the careful selection of drying agents to optimize the drying process, as mentioned above, the selection of additives and other components that will be used in the formulation of the water-based alkyd paint must also be carried out reasonably so as not to impair the film formation process. Here are the main points of attention:

- Wetting and dispersing agents: the use of molecules with predominantly ionic character, such as anionic wetting agents and polyacrylate-based dispersing agents, should be avoided. This class of molecules tends to act as a complexing agent with the metals used in the composition of the drying agent, causing a loss of the efficiency of the film drying process (WEISSENBORN, 2000).
- Thickening agents and rheological modifiers: to minimize impacts on the final properties of the film, it is preferable to use associative thickeners, such as hydrophobically modified urethane ethoxylates, HEUR. Thickeners based on hydrophobically modified alkali-soluble emulsions, HASE, should be avoided.
- Neutralizing agents: as mentioned earlier, for the emulsified resin, it is preferable to work at pH values greater than 7 to favor the partition of the drying agent in the polymeric phase. In addition, neutralizers that can act as complexing agents with the metal of the drying agent should be avoided (ÖSTBERG, 1994).
- Anti-skin agent: unlike solvent-based alkyd systems, for paints formulated with emulsified alkyd resin, the use of anti-skin agents in the formulation is not recommended.

Finally, regarding the paint formulation and production process, it is not recommended to add the emulsified alkyd resin to the grinding paste before the dispersion process. For better performance in terms of drying and quality of the formed film, it is recommended to incorporate the drying agents directly into the emulsified alkyd resin and then add to the formulation in the letting down step.

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Part 4

Main defects in paints

9 Main defects in paints

Henrique César Liviero | Thiago Cavalheiro Magri

If there is a certainty for every professional who works in the coatings market, it is that one day we will encounter some kind of defect. This defect may have a single cause or be a conjunction of factors. Still, in fact, it is a crucial competence of every professional in the area to know how to identify, understand, and deal with this problem to solve it better, which is often essential for the success of any product development or production correction, for example.

The intention of this work is to identify some common defects in paints and indicate probable solutions - probable precisely because, in addition to having several causes for a defect, we may have a cause that we never thought possible until that moment. Therefore, it is imperative to have an open mind and know how to identify and fully understand the formulation so that, knowing the impact of each item, the professional can identify the causes and solutions for a given defect.

9.1 LOSS OF ADHESION

Paint failure example of adhesion loss.

Loss of adhesion is an easy-to-view defect. Basically, it occurs due to a lack of anchor points at the interface between the paint film and the surface on which it was applied. This surface can be a metallic substrate, plastic, vitreous or even another film, such as a base coat.

The ASTM D3359 standard is the main methodology used for the evaluation of adhesion. However, it is quite prone to errors. Whenever possible, prefer methods that directly evaluate the adhesion strength of the film on the substrate (pull-off methods), such as the method described in ASTM D4541.

Possible actions	
Water-based liquid paints	**Solvent-based liquid paints**
In masonry: check surface preparation, such as sanding and cleaning. **In metal**: be careful with the cleaning and preparation of the surface (it must be free of dirt and oil). Systems with very high polymer Tg can potentiate the problem.	**Refinish**: check surface preparation and layer compatibility (primer + base coat + varnish). **Beware of high-hardness formulations!** Flexibilizing agents and adhesion agents (polysiloxanes or phosphates) can be used in many cases, mainly in polyurethane-based systems.

9.2 CRATERS


Paint film defects - Craters.

The formation of craters ("fish eyes") is directly linked to the difference in interfacial tension between the film and its substrate, which confers greater difficulty in wetting. The craters are easily identifiable as malformations of circular shapes and with well-defined edges. Generally speaking, surfactants help solve the problem.

In addition to contaminants on the surface of the substrate, among the probable causes, we can have incompatibility between the components of the formulation. Typically, the best way to identify is to make a mixture of all formulation components without fillers and pigments (just the "varnish"). If the solution formed becomes cloudy, mixtures should be made until the incompatible components are identified. In this case, the ideal is to isolate the component and replace the product if it is impossible to correct it with additives. The following is a list of possible formulation components with the potential to cause the crater problem:

- Silicones: mainly defoamers and unmodified silicones (silicone oils). The latter class is extremely harmful; even small concentrations can lead to large defects. This is why many paint factories have abolished its use.
- Solvent composition: during evaporation, the solubility of the system may change, causing precipitation of polymer fractions and even additives.
- Pigments with dispersion problems: this problem can be easily identified through visual analysis (usually, the crater is accompanied by an opaque point in the center of the depression).
- Modifying resins (for example, flexibilizing agents): to identify this situation, it is important to make applications of the paint without pigments and fillers (only the "varnish" of the formulation). After drying the film, if there are apparent turbidities, it is important to identify and replace the incompatible component.

Possible actions	
Water-based liquid paints	**Solvent-based liquid paints**
In masonry: check the preparation of the surface, sanding, cleaning and substrate condition. **In metal**: beware of oiliness on the surface and general cleaning; also, pay attention to silicone additives in the formulation. **Spray**: check for oil contamination in the compressed air line. In many cases, changing the air filter is necessary.	**Refinish**: check surface preparation and incompatibility between layers (primer + base coat + varnish) since additives that migrate to the film's surface may favor the problem. As a general rule, the surface tension of the top layer always has to be lower than the bottom layer. It is important to use additives that lower the surface tension, but the excess in lower layers can lead to problems. Often, for example, it is better to decrease these additives' concentration in primers than increase them in finishes. **Spray**: Check for water contamination in the compressed air line. In many cases, changing the air filter is necessary. In cases of quick-drying paints (acrylic lacquers, for example), it may be necessary to decrease the air pressure to avoid generating dry particles, which act as contaminants of the wet film.

9.3 BOILING

Boiling is easily identifiable by the formation of bubbles of varying sizes on the film's surface. It occurs when there is an increase in the surface viscosity of the film, preventing the evaporation of volatile substances. The ideal is to have a balance in the evaporation rate, using light and heavy solvents that allow the mobility of the paint components throughout the drying or curing process.

Paint film presenting blisters.

Possible actions	
Water-based liquid paints	**Solvent-based liquid paints**
Ambient cure: check paint preparation, especially regarding the solvents' dilution and evaporation rate, maintaining the film's mobility throughout the drying process. **Greenhouse cure**: pay attention to the variation in curing temperature. High TG polymers can dry quickly, sealing the surface before full evaporation of the formula solvents. **Urethane system**: attention to the formation of CO_2 by reaction between isocyanate and water. Give preference to solvents whose urethane grade does not exceed the 500-ppm water limit in the formulation.	**Refinish**: check the preparation and dilution of the paint. Small concentrations of heavy solvents in the formulation can assist in solving the problem without significantly altering the average evaporation rate of the paint.

9.4 ORANGE PEEL

It is a film-leveling defect in which the surface becomes so uneven that it looks like an orange peel. In addition to the visual aspect being significantly impaired, it can also affect brightness and other properties.

Paint film example of orange peel aspect.

DID YOU KNOW?

In some cases, orange peel is desirable as it improves the coverage of defects (e.g., scratches) on the surface.

Possible actions	
Water-based liquid paints	**Solvent-based liquid paints**
In metal: surface oiliness and using incompatible raw materials in the formulation may favor the problem. Leveling additives help with correction.	**Refinish**: check surface cleanliness and layer compatibility (primer + base coat + varnish). The correct drying of the primer is important. Pay attention to the adjustment of the application, such as the viscosity and pressure of the gun, for example. Typically, a very light solvent composition favors the problem.

9.5 SAGGING

Sagging is the tendency of the paint to flow downward forming a thicker lower edge on the surface that is being coated and easily perceived immediately after application. The probable causes are paint rheology, application viscosity, layer thickness, and open time, among others.

Paint sagging after application.

Water-based and solvent-based liquid paints
Low system viscosity and high applied layer conditions are more favorable to sagging. In such cases, rheological conditions such as thixotropy or increased viscosity may adjust the defect. In masonry and repainting a surface, situations in which we apply under angular structures, the defect can be potentiated; for these cases, there are application techniques that minimize the problem.

9.6 CRACKING

It is a type of film malformation that occurs during application or drying, mainly caused by a lack of paint coalescence. Coalescence is a condition that promotes optimal compaction and distribution of the polymer so that it forms a regular film.

Paint film presenting cracks.

Possible actions
Water-based liquid paints
In masonry: attention to the coalescence of the paint. The concentration of coalescent should be sufficient to ensure film formation at the application temperature (which can reach 0 °C in some regions of Brazil).

9.7 OVERSPRAY

Commonly known as "dry hit paint", it is a defect that happens in applications through a compressed air gun. It is easy to identify since the film looks uneven, without coverage and shine.

Paint application with overspray issue.

Possible actions
Water-based and solvent-based liquid paints
Check the adjustments of the application gun, such as opening and pressure. Very light solvents may favor the problem. In these cases, we can use heavier solvents or cosolvents in the formulation, adjusting the defect.

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10 Methodology for evaluating dirt pick-up resistance

Nina Yumi Suzuki Dantas | Thiago Cavalheiro Magri

Decorative paints are susceptible to degradation due to sun exposure and dirt adsorption on their surface. To prevent the appearance of the paint from being impaired, it must be formulated in such a way as to ensure its resistance to dirt pick-up. To ensure the efficiency of this property of the paint, the following suggested test is performed.

What we call "dirt" is actually the result of paint film adsorption of dust particles, smoke and pollution, or contact with people and objects. This effect can be observed mainly in external decorative paintings, as they are exposed to weathering and dirtiness of the environment (LAUER et al., 2006). However, the dirty aspect is obviously undesirable for paint. In addition to compromising the appearance of the surface, it will also generate higher maintenance costs and reapplication of the paint. So, it is necessary, in addition to formulating paints that are resistant to dirt pick-up, to evaluate this property in the final paint through a methodology that analyzes the tendency of an accelerated aged paint film to pick up dirt, which will be presented below.

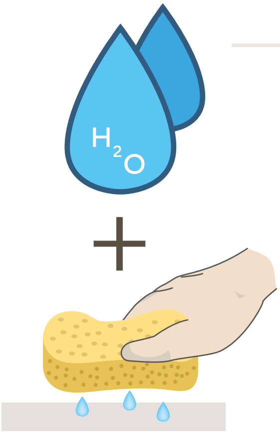
Painting the wall of a house can be simulated by applying a paint film in a glass plate. (150 µm aperture extender).

A standard solution of iron oxides is prepared to carry out the test always with the same "dirt". However, it is also possible to use other types of pigments, such as carbon black (BARDMAN et al., 2003).

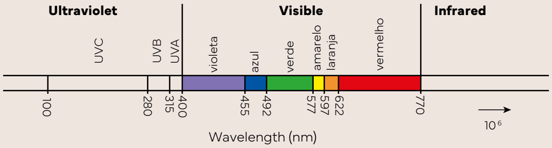
TIP

Standardize to minimize variables in the test: the amount of dirt applied, amount of water for removal, number of sponge-passes over the dirt, etc.

After applying a standard dirt dispersion and subsequent drying on the paint surface, the dirt is removed only with a sponge and water.



To represent the aging caused by UV radiation from the sunbeams over the years, a UV camera (QUV of Q-Panel, for example) is used. Normally, UVB lamps are used, which cause faster degradation of their shorter wavelength. However, it is preferable to use UVA lamps, which better simulate the actual wavelengths emitted by the sun.

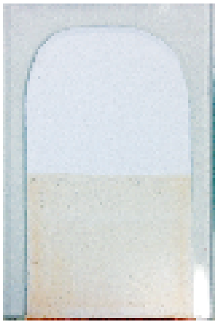


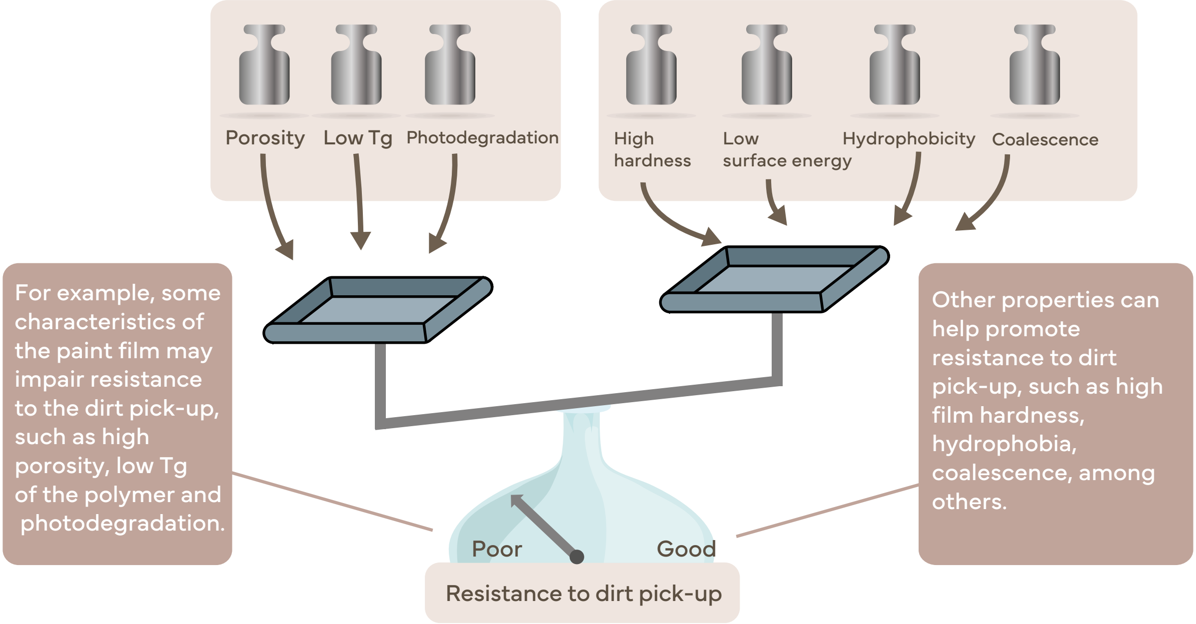
RESULT

An example of a satisfactory result is one in which the surface where was applied dirt is practically clean. In contrast, the poor result is visually observed by the permanence of color even after removing the dirt, indicating that there was a dirt pick-up.

The result is obtained with a spectrocolorimeter by the total color difference between the dirty part and the white part

$$\Delta E = \sqrt{(\Delta L^2) + (\Delta a^2) + (\Delta b^2)}$$





For example, some characteristics of the paint film may impair resistance to the dirt pick-up, such as high porosity, low Tg of the polymer and photodegradation.

Other properties can help promote resistance to dirt pick-up, such as high film hardness, hydrophobia, coalescence, among others.

Therefore, knowing the importance of paint being resistant to dirt, promoting this property in its formulation is necessary. It is necessary to pay attention so that other properties of the film are not compromised, thus seeking an optimal balance.

Figure 10.1: *Methodology for analyzing the dirt pick-up trend of an aged paint film.*

11 Methodology for evaluating leaching in paint films

Thiago Cavalheiro Magri

Leaching (also known as staining) is one of the main problems found in any decorative paint formulation. Technically, it can be defined as the phenomenon of extraction of water-soluble components (additives and part of the pigment employed) from the paint film through contact with water (moisture or rain). Water has the role of solubilizing and extracting these components from the film. This negatively impacts the look of the paint, especially its color and gloss.

This defect is related to several components of the paint formulation.

- **Coalescent**: directly impacts the formation of the film, where a poorly coalesced film will have numerous defects in its structure that will be paths for water permeation and extraction of hydrophilic species.
- **PVC:** affects the packaging of particles and, consequently, the paths available in the film. **Surfactants:** essential in all water-based paint and present in latex, wetting agents, and dispersants.
- **Pigment:** the type of pigment (more or less hydrophilic) and how well it is dispersed.

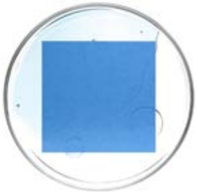
The most traditional methodologies for leaching, such as ASTM D7190, involve the visual evaluation of the film before and after water is applied on its surface. Therefore, it is always subject to the visual interpretation of the performer of the analysis. In the methodology proposed below, developed internally, the phenomenon of leaching is evaluated by two quantitative parameters: 1) surface tension of water and 2) color variation within the CIELab colorimetric space. Due to this reason, it is a more precise form and less dependent on the evaluation of the executor because these parameters are measured by equipment.

STAGE 1

Paint film preparation

- Thickness: 400 µm
- Substrate: PVC Leneta
- Area: 25 cm²
- Temperature: 5 ± 2 °C
- Drying time: 1 day
- After drying, cut 3 specimens of 5 cm x 5 cm

STAGE 2



Immersion in water in the Petri dish

- Mass of water: 20 g
- Water temperature: 25 ± 5 °C
- Surface water tension: 72 mN/m
- Immersion time of paint film: 2h
- Drying time of paint film: 7 days
- Drying temperature of paint film: 25 ± 5 °C

STAGE 3

Water analysis

- Measurement of surface tension of immersion water

STAGE 4

Measurement of the color difference of the paint film

- Before immersion in water
- After immersion in water

ΔE

Adjustments to the methodology can be made as needed. For example, in Stage 1, the drying temperature may be room temperature, and the drying time of the film may be reduced, simulating conditions closer to "early rain resistance". In Stage 2, the immersion time of the film in water can also be adjusted.

Color assessment is very common in the paint market. However, the concept of water surface tension and its relation with leaching is not so trivial. When immersing the film in water, water-soluble substances will migrate to that water, especially surfactants not well anchored in the film. Therefore, the surfactant will fulfill one of its primary roles of reducing the water surface tension.. This reduction in the water surface tension is directly correlated to the amount of surfactant that migrated. It is important to mention that the water surface tension used in this methodology is close to 72 mN/m at 25 °C.

Surface tension (mN/m)					
Sample	**Specimen**	**1**	**2**	**3**	**Average**
Coalescent 1	A	40.5	40.4	40.6	40.5
	B	40.2	40.1	40.1	40.1
	C	40.5	40.7	40.6	40.6
		Average			**40.4**
Coalescent 2	A	44.2	44.5	44.3	44.3
	B	44.6	44.9	44.7	44.7
	C	44.1	44.2	44.2	44.2
		Average			**44.4**

Table 11.1: *Water surface tension assessment from the three film specimens of two formulations with coalescing variation.*

In this example, considering the same paint formulation, where only the type of coalescent of the formula was varied, it is possible to affirm that the formulation with Coalescent 1 is proner to leaching than the one with Coalescent 2 because there was a greater reduction in the water surface tension and, consequently, a greater migration of surfactants.

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Part 5

Experiment planning methodology for paint development

12 Introduction to experiment planning

Rafael C. J. P. S. Salvato | Fabrício Guilhermino Pereira

12.1 INTRODUCTION

Experimentation traditionally employed by chemists on a laboratory scale consists of changing a single component of a formulation or process factor at a time, given the difficulty of understanding the effects of these variables on complex formulations of commercially employed paints combined with risk aversion in developing new products.

However, this approach is recurrently time-consuming and costly, hardly compatible with the competitiveness scenario and, therefore, with the pressure for efficiency added to the differentiation of the current globalized world. It is in this antagonistic environment that experimental statistical planning, popularly known as "experimental design" or DOE, finds its differentiating factor, being fundamental for the research and development centers of the paint and coatings industry to more effectively assist their companies in meeting the success criteria for launching new products on the market (Figure 12.1).

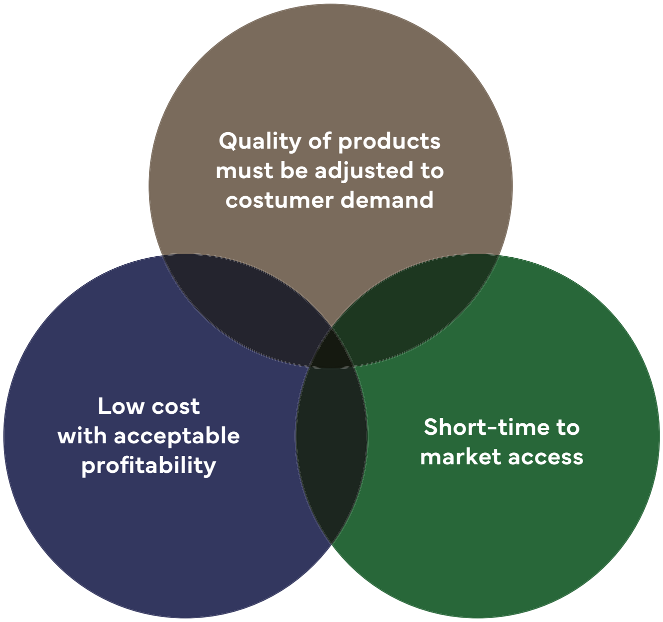


Figure 12.1: *Success criteria of modern research and development centers for launching new products on the market.*

Source: adapted from Rössler (2014).

Thus, the objective of this brief chapter lies in the attempt to bring to a simple and uncomplicated language all the potentiality of planning experiments for the day-to-day life of paint formulators.

12.2 EXPERIMENTAL STATISTICAL PLANNING AND ITS MAIN BENEFITS

The approach proposed by the planning of experiments based on the use of statistical tools has been gaining a lot of space in the recent decades in academic and industrial circles (SILVA, 2013; BARRIOS, 2014; PILZ, 2016), as it allows the user to create and validate models obtained in practice and that describe what was found in the experiments carried out, directing them to the specific universe of the problem in question (Figure 12.2).

This facilitates the interpretation of the data based on the fundamentals of basic statistics and allows the creation of a rationale to improve the results obtained (called "responses") by optimizing the variables (called "factors") that influence a given product or target process of a study.

In addition, using experiment planning makes it possible to perform fewer laboratory tests than the classical approach, often reducing the cost of developing formulations and products significantly (see Chapter 11). An illustrative comparison of this reduction is shown in Figure 12.3.

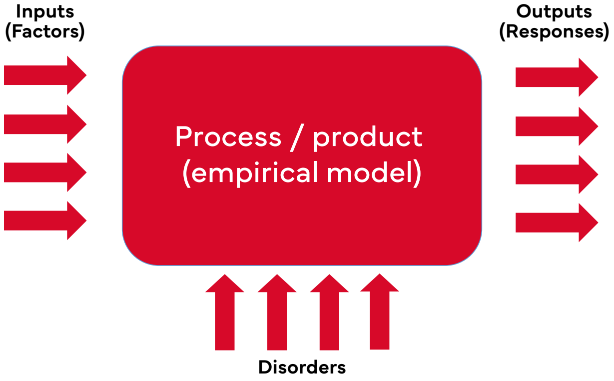


Figure 12.2: *General aspect of any model that describes a process or product, with typical nomenclatures in experimental statistical planning (in parentheses).*

Source: adapted from Tracton (2006).

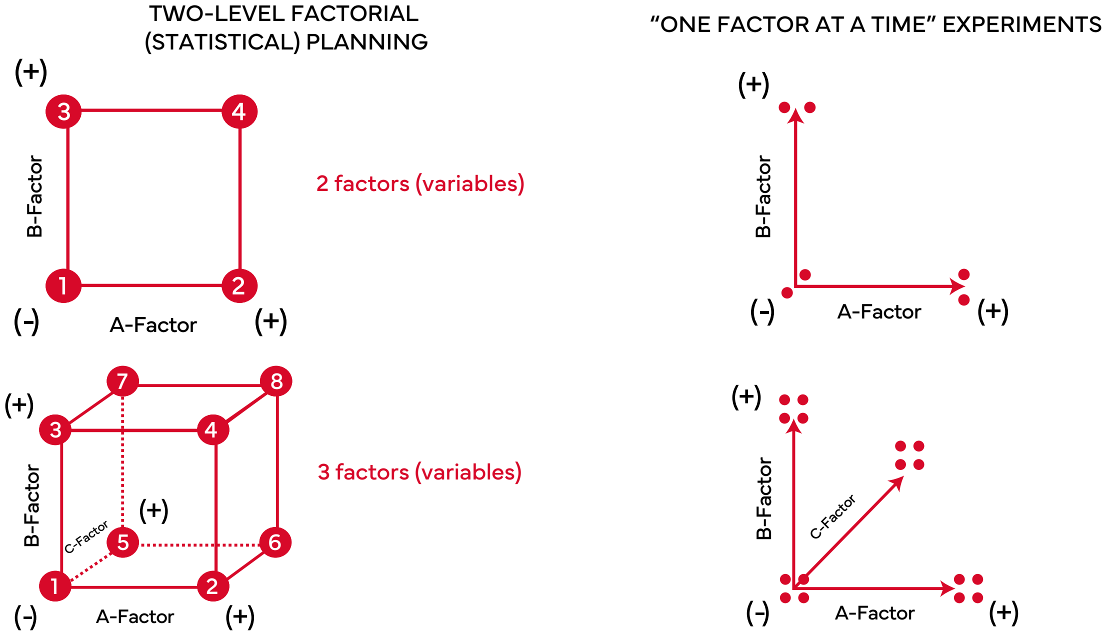


Figure 12.3: *Comparison of the number of experiments required to evaluate the effect of factors in planning two-level factorial-type statistical experiments versus the traditional "one factor at a time".*

Source: adapted from Rössler (2014).

Although more widespread, the experimentation strategy of changing a single component of a formulation or process factor at a time presents several other problems besides the high number of experiments and the time taken to perform the entire study. One is that this type of approach does not provide some important information, such as the combined effect of the interaction of these variables (synergy), a recurring reality in the processing and formulation of paints, in which a myriad of ingredients with different affinities and natures are simultaneously used.

In addition, the variability and uncertainties conferred by low-precision manual performance evaluation methods, which represent the vast majority in the paints and coatings universe, increase the difficulty in identifying the type of contribution (positive or negative) of a given component or factor under evaluation during the development of a new formulation. This set of interferences is the so-called "disturbances" present in Figure 12.2.

12.3 SIMPLIFYING EXPERIMENTAL STATISTICAL PLANNING AND DIRECTING ITS USE TOWARD THE DESIRED OBJECTIVE

The strategy of planning experiments, often referred to in the market as DOE, can be simple and straightforward. In summary, DOE shows its value mainly in the following cases when:

- The effect of the variables is not fully known, or there is a very large number of them to assess, and a scan is necessary to find the few and particularly relevant variables;
- The relevant variables are known, but its is still necessary to find the ideal region to operate a certain process or a more cost-effective one to adjust a product (or formulation).

ATTENTION

Before starting the planning of statistical experiments, it is essential to have minimal knowledge of the system, especially to choose the limits of the variables. It is recommended to perform initial tests in the "classic" way for completely unknown systems.

A different type of strategy is recommended for each of the cases mentioned. Furthermore, the nature of the variables must be considered to choose the type and strategy to use. In the paint universe, there are two:

- Components that integrate a given formulation (example: ingredients as a rheology modifying additive in a paint).
- Factors affecting a given process (e.g., reactor temperature in an alkyd resin synthesis).

Factor-type experimental statistical designs are often employed to map relevant factors (scanning methods). There are several options for optimization, but those involving response surface methodology are the most used for optimization in products and processes present in the daily life of research and development centers in paints and coatings. Both will be discussed below.

12.4 FACTORIAL PLANNING AND THE USE OF SCANNING EFFECTS OF FACTORS AND INTERACTIONS (SCREENING)

Factor planning involves simultaneous adjustments in the levels (values) of the experimental factors (variables). The most commonly used of these is the two-level one, which is coded as low (recurrent notation "-") and high (recurrent notation "+"), as previously shown in Figure 12.3.

The reason for popularizing two-level factorial planning is that this type is simpler, besides the fact that it involves a substantially smaller number of experiments compared to those of higher levels, as seen in Figure 12.4.

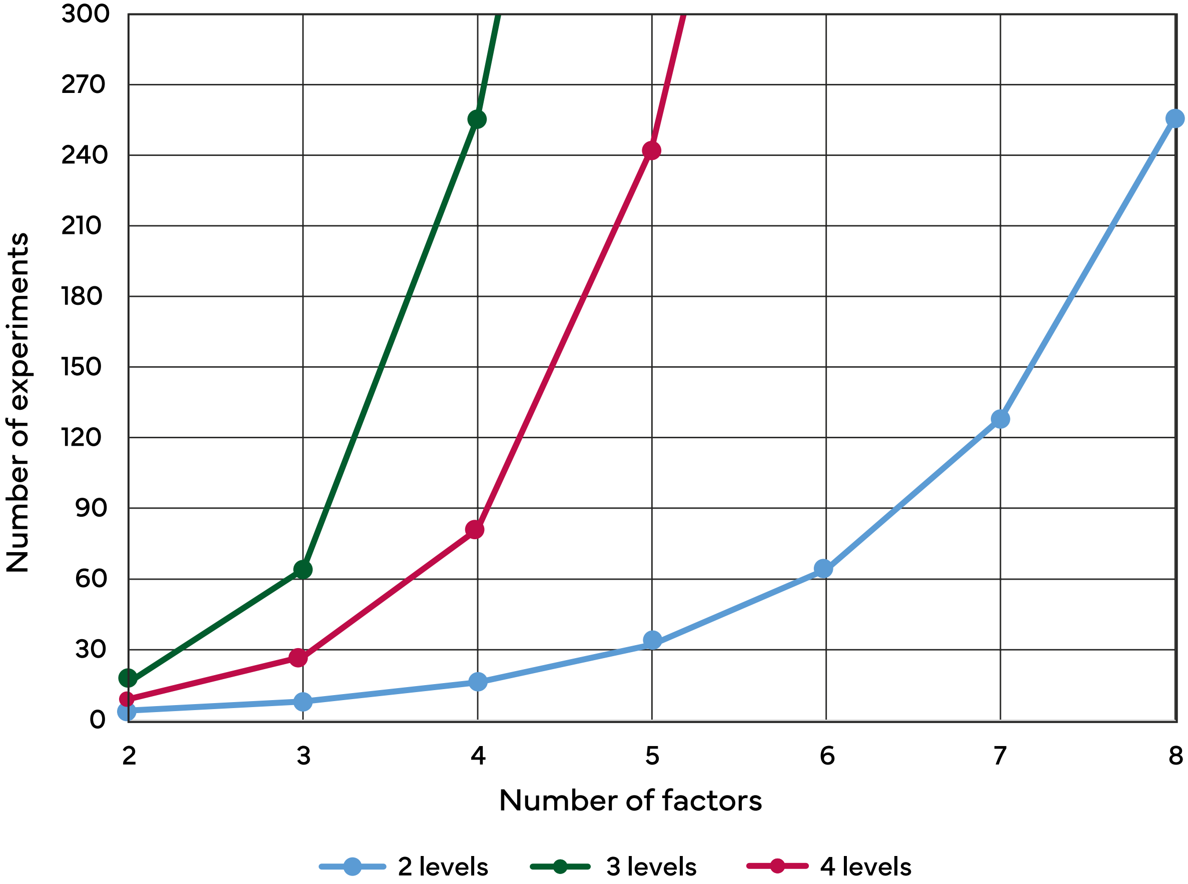


Figure 12.4: *Comparison of the number of experiments required as a function of the number of factors for factorial planning with 2, 3 and 4 levels.*

Theoretically, we can have as many factors as we want in two-level planning. In practice, even for this type, when we have more than 4 or 5 factors under evaluation in the study, the number of experiments to carry out factorial planning starts to get high, as can be seen in Figure 12.4.

When factorial planning goes through all possible combinations, it is called "full" or "complete" factorial planning. In this context, we have all the interaction effects of the variables. For cases of more than two factors, we can simultaneously interact with several factors, the so-called interactions of higher orders (NETO; SCARMINO; BRUNS, 2010).

Typically, in the preliminary stages of scanning, determining the interactions among factors of order greater than two (that is, of more than two variables at the same time) is not so important since the main objective is not to know in depth all the details, but rather what the effects of the factors are and which are significant. An "elegant" alternative to reduce the number of experiments is to work with incomplete plans in intentionally chosen positions, which is called fractional factorial planning, as shown in Figure 12.5.

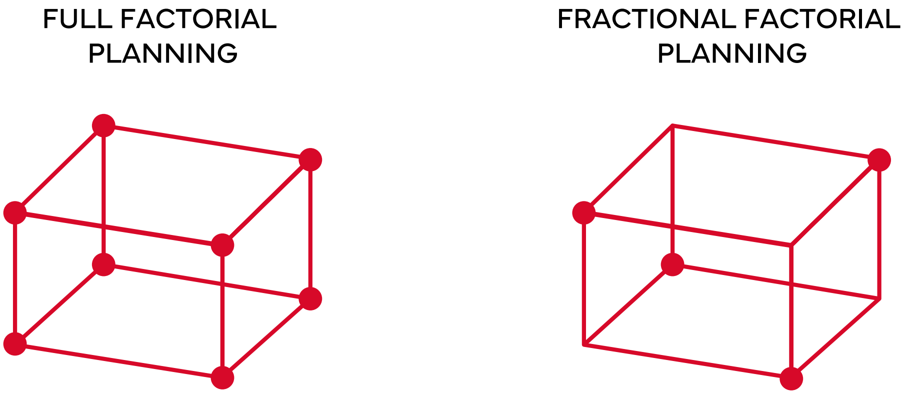


Figure 12.5: *Comparison of the number of experiments required in a complete factorial design (two-level and three-factor) versus a fractional factorial design (half-fraction).*

Source: Neto, Scarmino and Bruns (2010).

In these cases, the selective withdrawal of points reduces the resolution of the planning, precisely forgoing trying to obtain information about interactions of higher orders, which are less frequent and sometimes negligible. There are practical table templates that can be used regularly to choose the best option for the study, in which is presented estimates of the number of experiments according to the number of variables and the resolution of the two-level factorial planning (see Table 12.1).

	Number of factors										
Number of tests	2	3	4	5	6	7	8	9	10	11	12
4	Full	III									
8		Full	IV	III	III	III					
16			Full	V	IV	IV	IV	III	III	III	III
32				Full	VI	IV	IV	IV	IV	IV	IV
64					Full	VII	V	IV	IV	IV	IV
128						Full	VIII	VI	V	V	IV

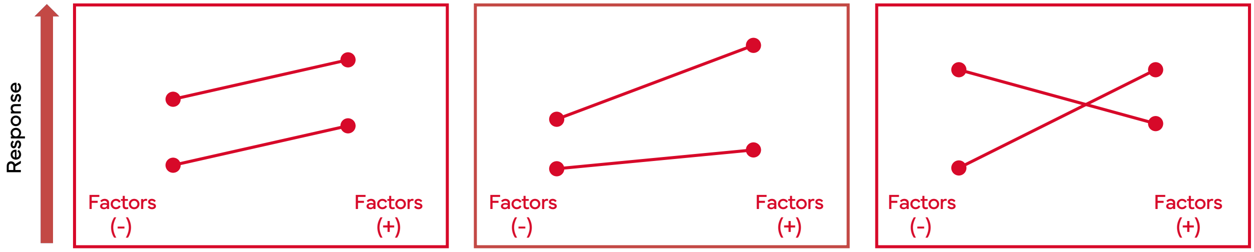
Table 12.1: *Two-level factorial planning resolution matrix according to the number of experiments and factors.*

Source: adapted from Tracton (2006) and Neto, Scarmino and Bruns (2010).

Obviously, one can pay a price for employing these alternatives if the interactions of higher orders are not negligible. Additionally, the interpretation becomes more complicated the greater the reduction in resolution. Thus, the table indicates in suggestive colors which are the safest resolutions (in green), those that require attention (in gray) and the riskiest in terms of obtaining information about the process (red). Succinctly and practically, it is only considered appropriate to use those that fit the red colors when it is already known in advance (due to previous work or based on experience) that the experiment does not present significant interactions between the factors under evaluation or even that they are first order (the result of the combination of two factors only) if they exist. In these cases, one can choose them without compromising the result of the study and still obtain a reduction in the minimum number of tests required to complete it.

The greatest use of factorial planning is to map or "sweep", in a sample space, the effects of factors (variables) to determine those that are relevant, as well as identify if there are interactions (synergism) between them, employing as few tests as possible.

A practical and simple way to verify if there are interactions between the factors in experiments involving factorial planning is to make a graphical evaluation in interaction diagrams, as shown in Figure 12.6.



No interaction
=
the same slope

Low interaction
=
distinct slope, but the same trend

Strong interaction
=
distinct slopes and trends

Figure 12.6: *Types of interaction between factors (variables) and a graphical evaluation of them in two-level factorial planning. Source: adapted from Rössler (2014).*

In these diagrams, if a line is horizontal, it means that the factor it represents does not affect the response. If the line is not horizontal, the factor represented affects the response, and the greater the slope, the greater the effect. In addition, there is a visual qualitative idea of how the various factors under evaluation interact with each other.

As important as this is to determine or even obtain an estimate of the experimental error or disturbances (variables unknown or external to the factors under evaluation) that influence the responses. Thus, duplicate experiments (commonly called "replicates" or "repetitions") are often carried out, with the aid of basic statistics, to enable making the Analysis of Variance (ANOVA) and determine the confidence interval for the experiment.

Performing duplicates at all points can bring difficulties for experiments involving many factors due to the total number of trials required to complete the evaluation. In these cases, an alternative strategy is employed to estimate the experimental error, including central points in the experimental design and making several repetitions in it. A breakdown of this alternative strategy will be presented in the following subtopic, which deals with optimization methodologies in which it is widely used.

An essential and quantitative evaluation of these effects of the experiment's factors on each response is the quality of the adjustments of the data to the empirical linear model, as well as the evaluation of the significance and impact of the main effects. Usually, this data is provided by statistical software as soon as the data is entered and an analysis of it is performed. Typically, the important information that results from this analysis is compiled and presented in Table 12.2.

	Linear Model Adjustment	**Analysis of variance (F)**	
Responses	Pearson's correlation coefficient (R^2)	Effects (isolated factors)	Interactions
One line for each of the outputs under evaluation at work	Numeric, from 0 to 1. The larger and closer to 1, the better the fit of the experimental data to the model	It's numerical and should be compared with critical F (extracted from basic statistics tables, depending on the size of the experiment and the degree of confidence desired). If they are greater (effects and/or interactions), it indicates that they are statistically significant.	

Table 12.2: *Presentation of relevant data for quantitative evaluation of adjustment to the linear model and analysis of variance in factorial plans.*

A graphical form widely used to verify whether the effects of the factors or their interactions are directly significant is the Pareto diagram for normalized responses, as shown in Figure 12.7.

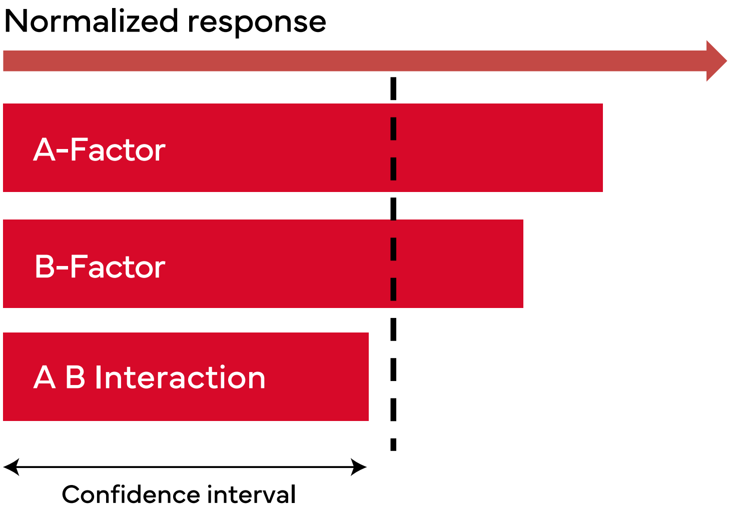


Figure 12.7: *Significance assessment of the effects of isolated factors (variables) or interactions (combinations) by the Pareto graphical method. The confidence interval can be approximated by multiplying the standard deviation of the measurements by two.*

In the evaluation by this graphical method, the effects can be easily compared and classified. Additionally, the dotted line indicates from which point the effects of factors or interactions begin to be representative (significant) of the results obtained in the experiments, exceeding the confidence interval. In statistics, this range typically equals twice the standard deviation (in which 95% of events are included). In simpler language and using an analogy, in this case, it can be said that if it exceeds the dotted line, the effect visualized by the factor or interaction in question tends to be greater than the errors induced by the disturbances (variables external to the experiment).

Using the basic principles presented in this work and the friendliest software available on the market, two-level factor planning becomes simple and practical. Because of this, more and more applications for them are popularized every day to facilitate development work, whether in the production of water-based acrylic resins, either in the emulsification of alkyds by phase inversion or in the evaluation of complex interactions of dispersants with fillers.

Important note: theoretically, it's possible to do both the planning of factorial experiments and the processing of statistical data manually or even in Excel spreadsheets, according to the step-by-step presented by several textbooks. In practice, most of the time, software available on the market, such as MiniTab, Statistica or JMP, is used to facilitate and accelerate this stage, ensuring the quality of the data and the graphical presentation for the interpretation of the results obtained.

12.5 RESPONSE SURFACE METHODOLOGY AND THEIR USE IN PRODUCT AND PROCESS OPTIMIZATION

If in a previous work of a product and/or process development (involving a complete two-level factorial type of planning) one of the situations listed below is present, it is recommended to insert additional points at intermediate levels, called "central points" (recurrent notation "0"):

- It is imagined that the optimum point is close or, still, it is clear that it is within the factors of previous experimental work universe.
- There is a lack of data fit to the linear model (intrinsic to two-level planning).

In these cases, the central point serves as a third point for the factors, enabling a quadratic model and accommodating curvatures, as seen in Figure 12.8.

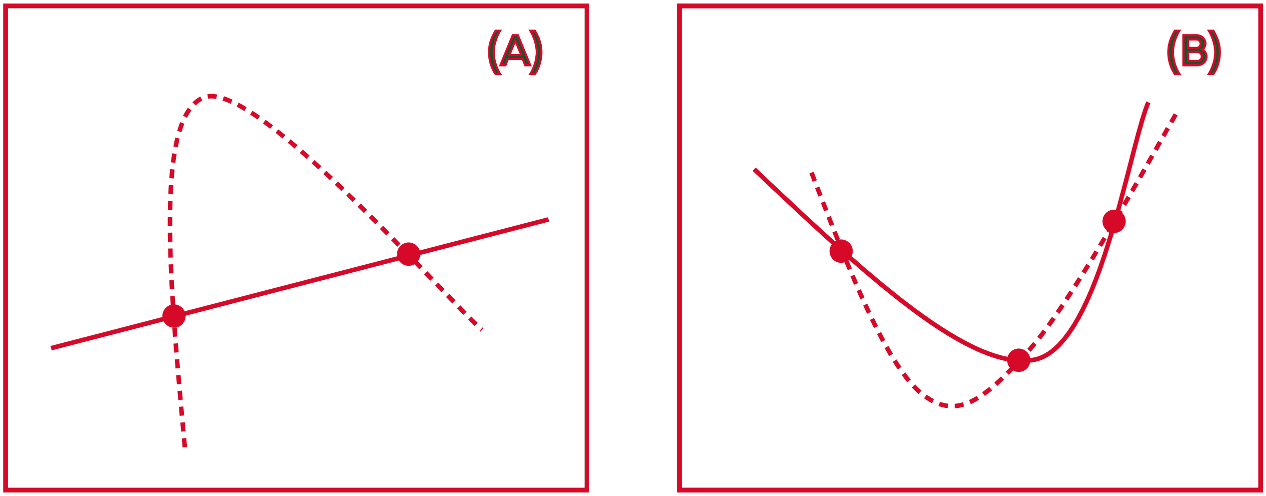


Figure 12.8: *Comparison of the linear model with two levels (A) and the quadratic model with the addition of the central point (B).*

Source: Tracton (2006); Neto; Scarmino; Bruns (2010); Myers; Montgomery; Anderson-Coook (2009).

Obviously, with three points, you can draw a curve, but still, the ability to describe a curve's actual inflection point is low, representing a "maximum" point (or even a minimum, as in the case of Figure 12.8B). Therefore, in optimization approaches, it is necessary to have more points to build a "mesh" that can generate a surface with a satisfactory resolution to find the desired "optimum" point. An elegant alternative typically proposed is to take advantage of a previously performed two-level factorial design and add to it not only the central point but also four new equidistant points, as shown in Figure 12.9. These plans are called "star type" plans, rotated, or even central composite plans (CCD) (TRACTON, 2006; NETO; SCARMINO; BRUNS, 2010; MYERS; MONTGOMERY; ANDERSON-COOOK, 2009).

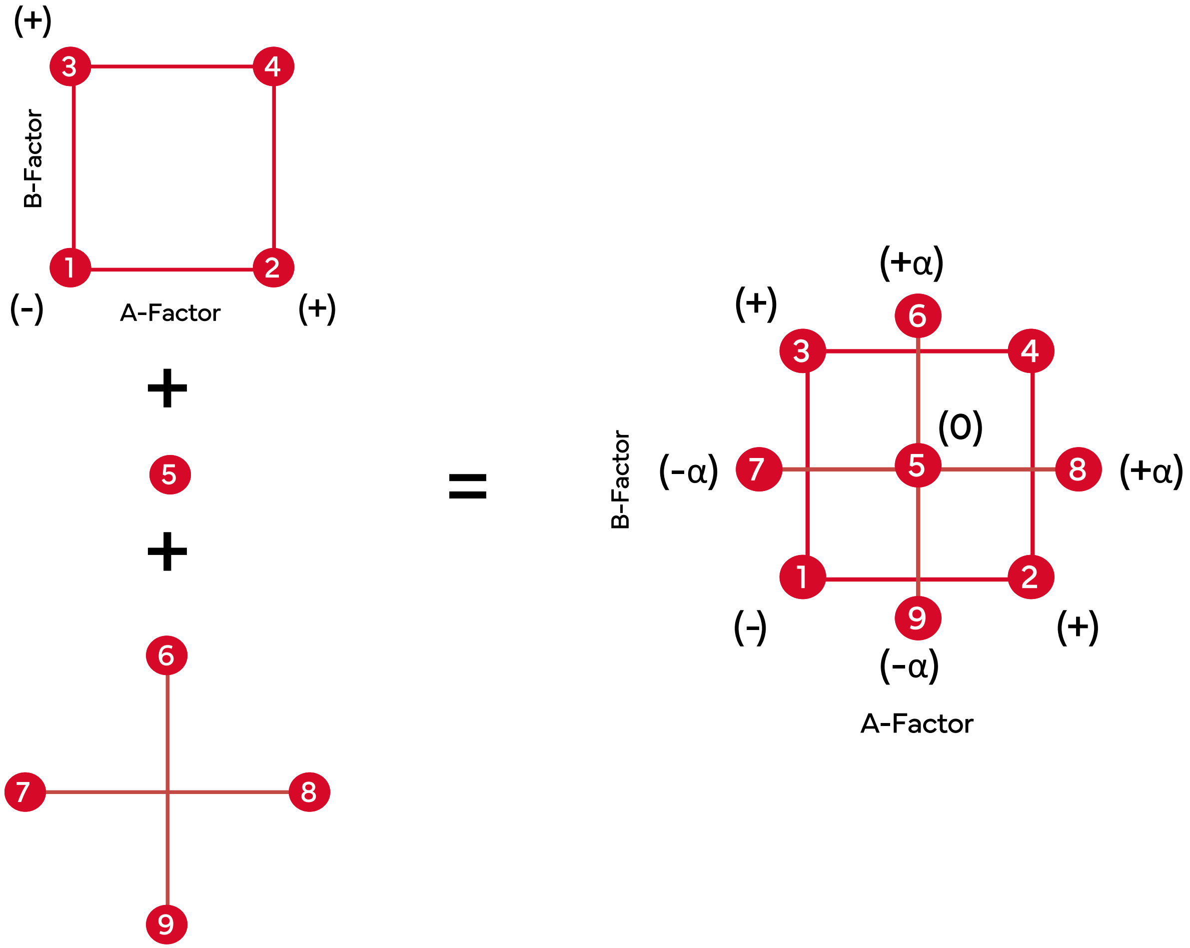


Figure 12.9: *Two-factor central composite planning (CCD) construction rationale.*

Source: Tracton (2006); Neto; Scarmino; Bruns (2010); Myers; Montgomery; Anderson-Coook (2009).

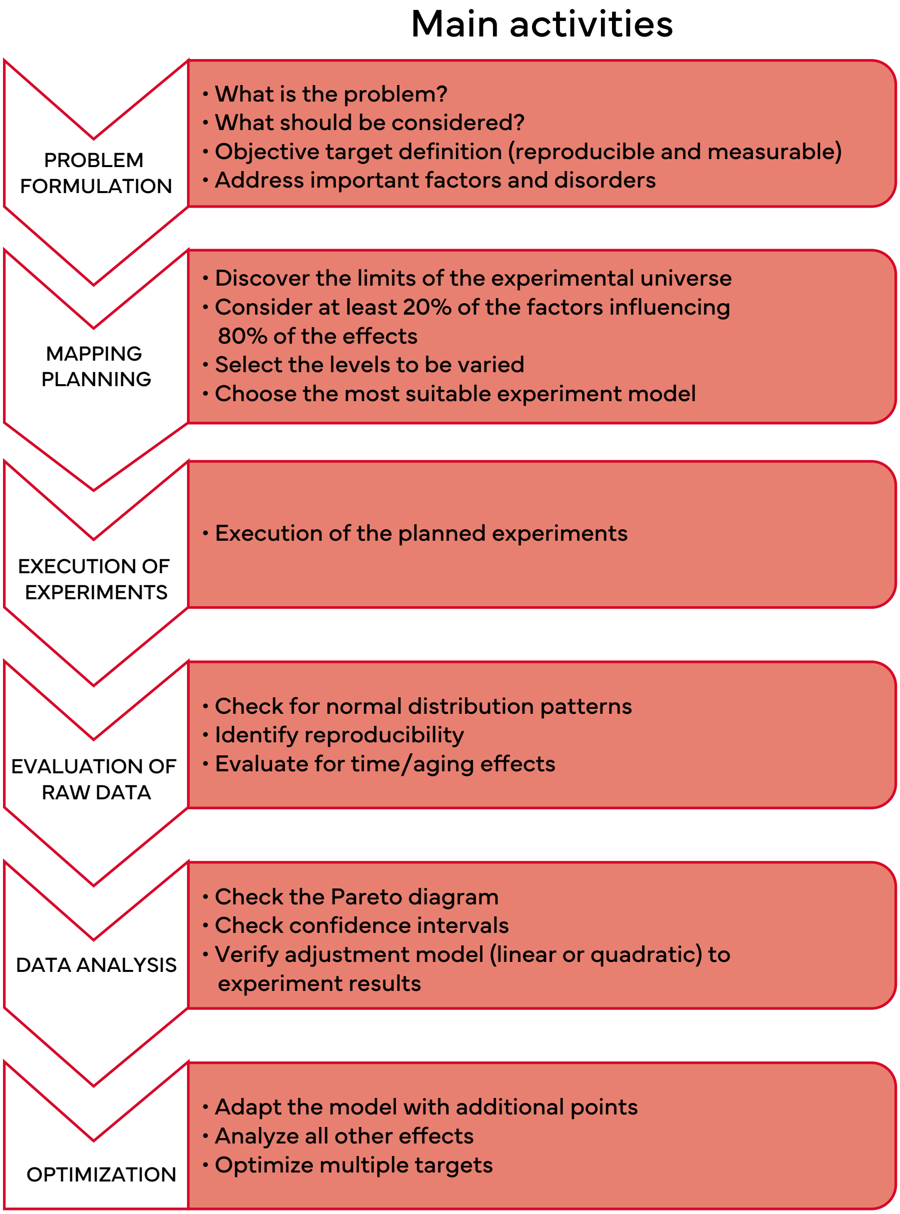
Often, when replicated multiple times, the central point also represents an alternative to an error estimate involving fewer experiments other thanreplicating all points of a given planning, especially in CCD.

The main benefit of using these types of response surface methodology is identifying the optimum points where the desired processing objectives or achievement of product specification in development can be obtained. Additionally, this is achieved by conducting a small number of experiments, evaluating the study of the influence effect of several variables simultaneously on the observed responses, with empirical and statistically validated data. This situation is relevant because, in addition to the high number of factors (variables) that an optimization study involves, synergism is often observed between them and without the aid of statistical tools. This evaluation, both qualitatively and quantitatively, becomes complex (NETO; SCARMINO; BRUNS, 2010; MYERS; MONTGOMERY; ANDERSON-COOK, 2009; SILVA, 2013).

There are several specialized books on this topic, as other approaches are possible regarding response surface methodology (such as mixture planning, which is widely used in formulation optimizations). Due to the existence of particularities and a wide range of options, it is recommended to consult and view case studies directed to paints and coatings in the literature (RÖSSLER, 2014; NETO; SCARMINO; BRUNS, 2010; MYERS; MONTGOMERY; ANDERSON-COOK, 2009).

12.6 PRACTICAL GUIDE REGARDING THE STRATEGY OF USING DOE IN PRODUCT AND PROCESS DEVELOPMENT PROJECTS

As previously mentioned, both in the literature and on the websites of software providers, there are technical notes available with instructions and answers to questions related to the practice of performing work with DOE for beginners in these environments. However, the success in using DOE in development projects implies having an assertive strategy and clarity of the main activities and methods available for each of them, and what is essential at each stage. Otherwise, the desired speed and the quality required when using this type of tool can be compromised. Thus, the final part of this chapter presents, in Figures 12.10 to 12.12, summarized schemes addressing these main points, step by step to be used as a practical guide.



Main activities

PROBLEM FORMULATION	• What is the problem? • What should be considered? • Objective target definition (reproducible and measurable) • Address important factors and disorders
MAPPING PLANNING	• Discover the limits of the experimental universe • Consider at least 20% of the factors influencing 80% of the effects • Select the levels to be varied • Choose the most suitable experiment model
EXECUTION OF EXPERIMENTS	• Execution of the planned experiments
EVALUATION OF RAW DATA	• Check for normal distribution patterns • Identify reproducibility • Evaluate for time/aging effects
DATA ANALYSIS	• Check the Pareto diagram • Check confidence intervals • Verify adjustment model (linear or quadratic) to experiment results
OPTIMIZATION	• Adapt the model with additional points • Analyze all other effects • Optimize multiple targets

Figure 12.10: *Main activities in each phase within a strategy typically adopted in projects when using statistical planning of experiments in product/process development.*

Source: adapted from Tracton (2006).

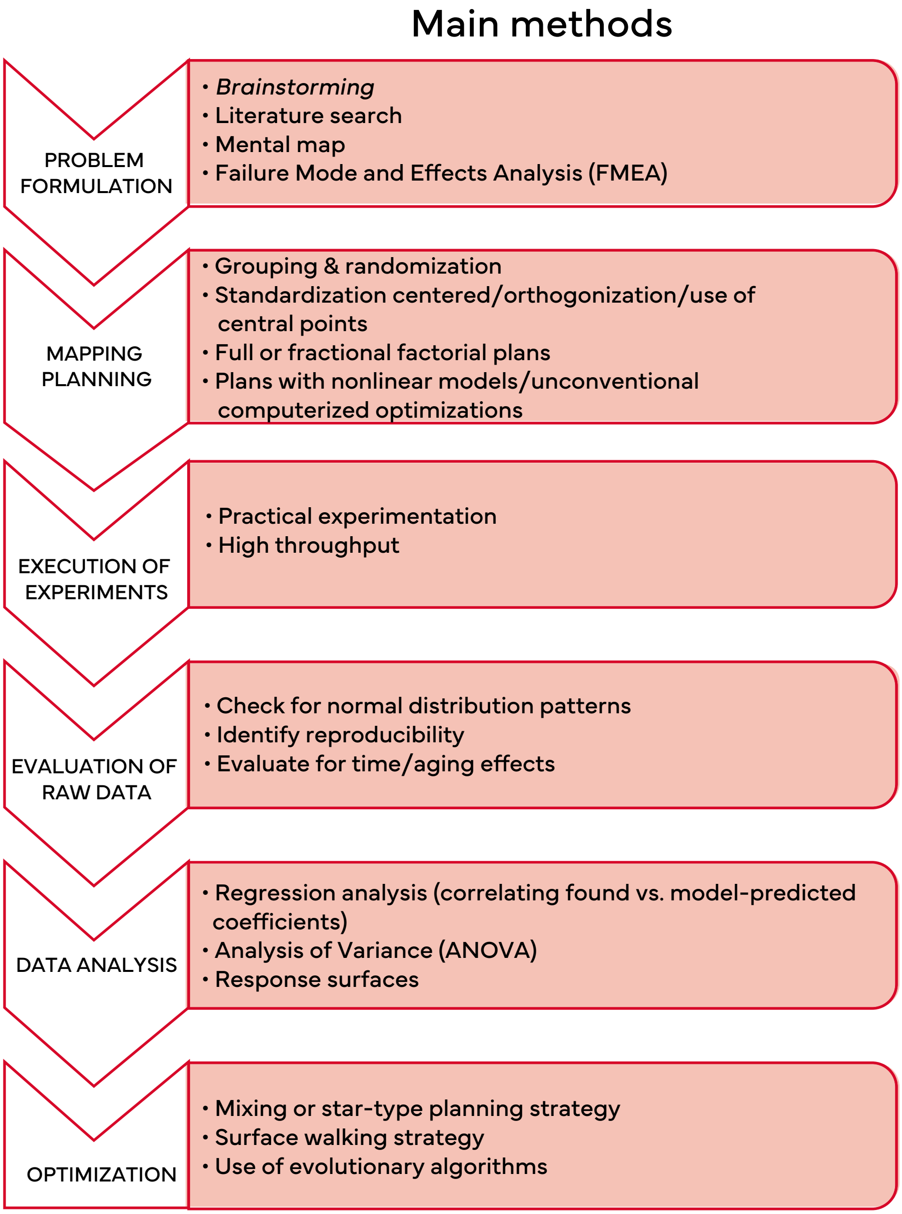
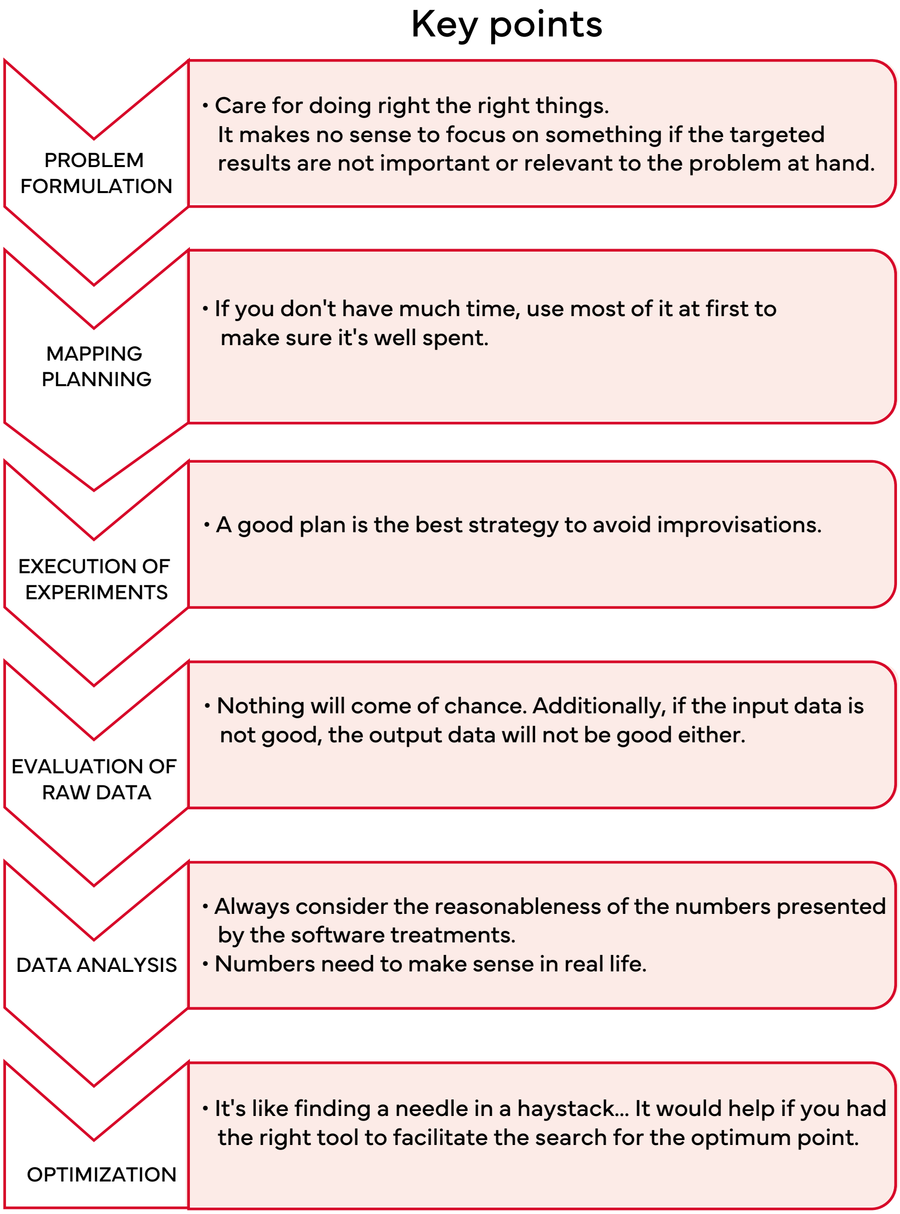


Figure 12.11: *Main methods in each phase within a strategy typically adopted in projects when using statistical planning of experiments in product/process development.*

Source: adapted from Tracton (2006)



Key points

PROBLEM FORMULATION	• Care for doing right the right things. It makes no sense to focus on something if the targeted results are not important or relevant to the problem at hand.
MAPPING PLANNING	• If you don't have much time, use most of it at first to make sure it's well spent.
EXECUTION OF EXPERIMENTS	• A good plan is the best strategy to avoid improvisations.
EVALUATION OF RAW DATA	• Nothing will come of chance. Additionally, if the input data is not good, the output data will not be good either.
DATA ANALYSIS	• Always consider the reasonableness of the numbers presented by the software treatments. • Numbers need to make sense in real life.
OPTIMIZATION	• It's like finding a needle in a haystack... It would help if you had the right tool to facilitate the search for the optimum point.

Figure 12.12: *Main points in each phase within a strategy typically adopted in projects when using statistical planning of product/process development experiments.*

Source: adapted from Tracton (2006).

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13 Adjustment of rheological behavior of decorative paints using design of experiments

Natália Freitas de Paula | Juliane Pereira Santos

13.1 INTRODUCTION TO RHEOLOGY

One of the most important characteristics of a paint is its rheological behavior, which is related to the deformation and flow of matter. Inadequate rheology directly affects the most important characteristics of the paints (BHAVSAR, DAVE, PARMAR, 2012).

For a paint to be produced with ideal properties in applicability and storage, one must pay attention to the viscosity parameter, which is adjusted by using additives known as rheological modifiers or thickeners in its formulation. The thickener must control the viscosity over a wide range of shear rates (PEIFER, 2006) to obtain a complete profile, indispensable for optmizing the thixotropic behavior of paints that comprises viscosity reduction as an increasingly shear rate is applied, and viscosity recover, after a certain period of time, when the shear rate is cessed.

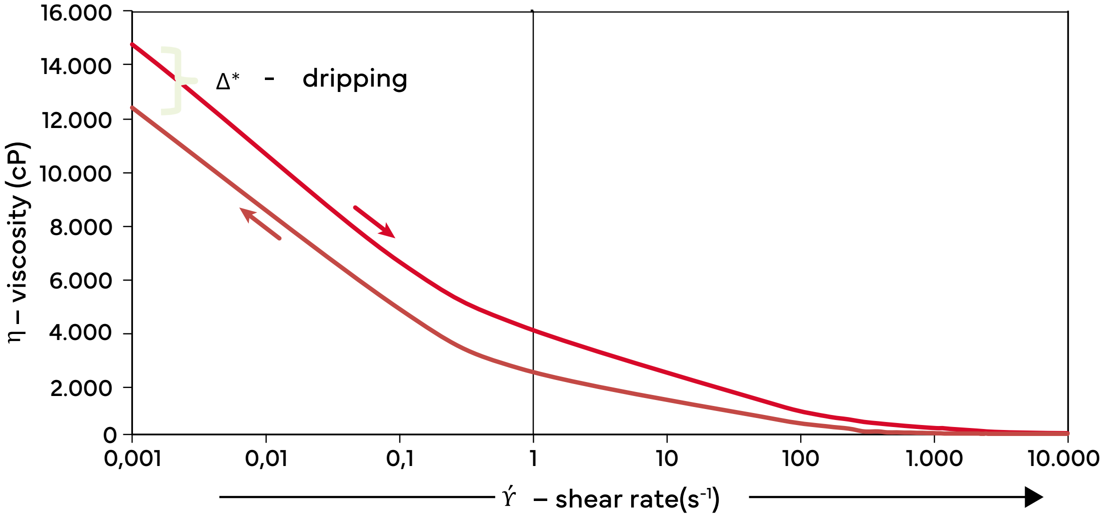


Figure 13.1: *Thixotropic flow behavior.*

This behavior can be seen in Figure 13.1, where there is an upper shear curve and a lower recovery curve (ELEMENTIS, 2008). This variation between these curves corresponds to thixotropy. If this recovery happens slowly, the applied product has a dripping defect (SUPRA, [201-]). An optimized viscosity at a given shear rate is essential for production, storage and, application of paints.

For each shear rate, there is a desirable viscosity range to be adjusted (TADROS, 2010), correlated to the performance and application of the material. From the standard (ASTM D7394-08), it is clear that for medium shear regions, the ideal paint viscosity ranges from 90 to 110 KU. At low shear, there are typical viscosity values that can be found in Table 13.1. Table 13.2 presents typical values regarding the performance of decorative paints at high shear rates.

Table 13.1 shows that the low shear is related to the performance of the paints still inside the package, which can cause sedimentation, and also to the paint already applied to the substrate. Table 13.2 shows that at high shear rates, the performance is related to drag brush and film build properties, that is related to the applicability and construction of product layers without causing dripping.

Viscosity (poise)	Paint performance
< 100	Dripping
100 - 150	Excellent leveling
150 - 250	Very good leveling
250 - 500	Good leveling
500 - 900	Low leveling
900 - 1,500	Poor leveling and high sedimentation
1,600 - 2,400	Very poor leveling and medium sedimentation
> 2,400	Low sedimentation

Table 13.1: *Viscosity values typical of performance-related architectural paints for low shear rates.*

Source: ASTM D7394-08.

Viscosity (poise)	Paint performance
< 0.5	Very low drag brush/film build
0.5 - 0.75	Low drag brush/film build
0.75 - 1.0	Medium drag brush/film build
1.0 - 1.5	Medium-high drag brush/film build
1.5 - 2.0	High drag brush/film build
2.0 - 2.5	Very high drag brush/film build
> 2.5	Very high for brush or roller application

Table 13.2: *Viscosity values typical of performance-related architectural paints for high shear rates.*

Source: ASTM D7394-08.

13.2 METHODOLOGIES FOR ADJUSTING RHEOLOGICAL BEHAVIOR

The choice of rheological modifier for each formulation must be evaluated according to its chemical characteristics. Moreover, its cost must also be considered since this additive has a relevant influence on product performance, and more than half of the expenses in new product development is consumed in rheology optimization (ELEY, 2012). Table 13.3 shows the types of thickeners most used in paint formulations.

	Thickener
ASE	Alkali swellable thickener
HASE	Hydrophobically modified alkali swellable thickener
HEUR	Hydrophobically modified ethoxylated urethane thickener

Table 13.3: *Types of thickeners most commonly used in paint formulations.*

Source: Auschra et al. (2015).

Typically, in a formulation, two thickeners are used, one to correct the viscosity at low shear and the other acting on the correction of the viscosity at high shear. The characteristics of a paint related to each shear region can be seen in Figure 13.2.

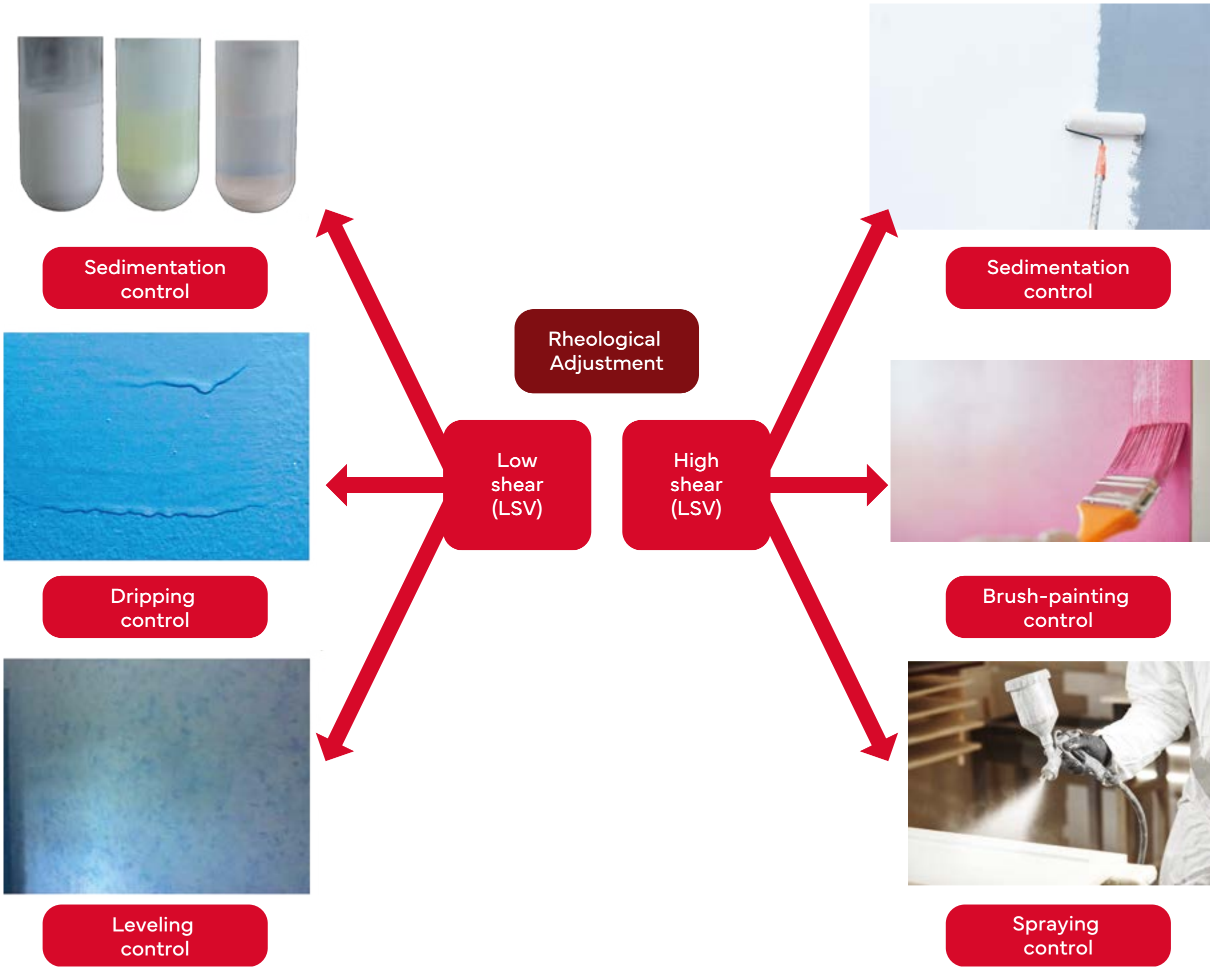
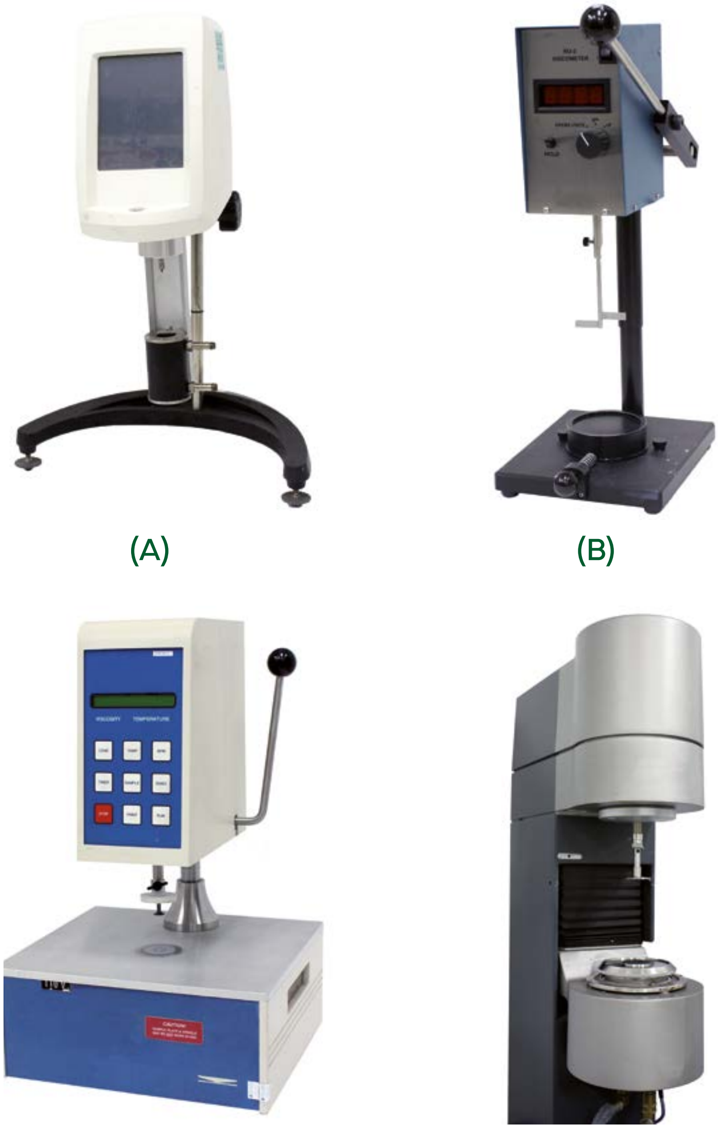


Figure 13.2: *Characteristics to be optimized in a paint formulation in the LSV and HSV regions.*

The viscosity in each shear range is measured with specific equipment. The Brookfield type viscometer (Figure 13.3A) simulates Low-Shear Viscosity (LSV); the Stormer (Figure 13.3B) is used for Mid-Shear Viscosity (MSV); and the ICI (Figure 13.3C) for High-Shear Viscosity (HSV). Rheometers (Figure 13.3D) can also be used to perform viscosity flow curves covering a wide range of shear rates.



(A) (B)

(C) (D)

Figure 13.3: *Equipment for viscosity measurement at different shear rates.*

Figure 13.4 illustrates a viscosity low curve, three shear rate regions as well as the paint properties related to them and the equipments used for measuting the viscosity in each shear rate region. High viscosity at low shear rates allows a product with good in-can stability and dripping resistance. At the same time, leveling is controlled with lower viscosities in the low-shear region. This contradiction is met using the proper additive, which provides high viscosity to avoid the problem of dripping and sufficient thixotropy for good leveling properties. On the other hand, medium shear is associated with the aesthetic appearance of the liquid paint to the consumer and its reaction to agitation or soft balance. High shear refers to the quality of the application. A paint with high viscosity in this region, implies a product with good resistance to brush painting or roller painting, while low viscosity indicates good behavior if applied with spray.

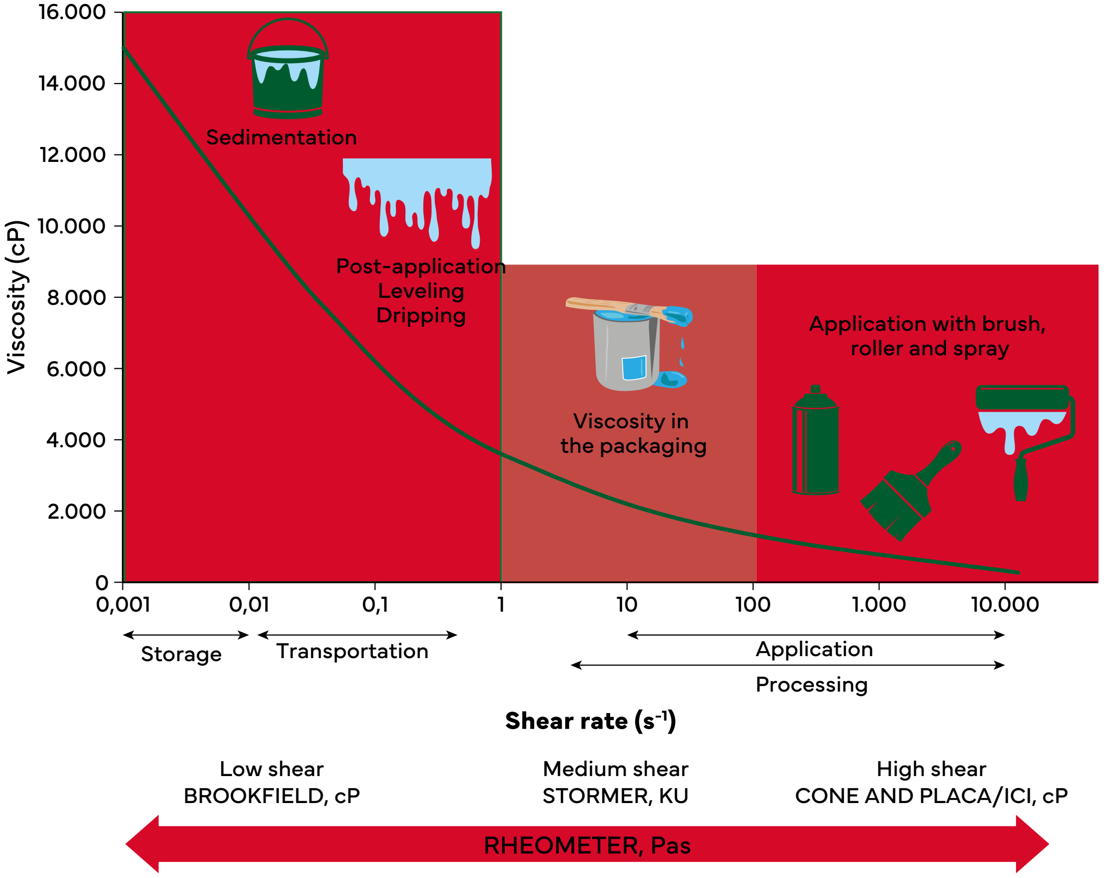


Figure 13.4: *Shear regions related to characteristics and processing of paint and respective equipment for viscosity measurement.*

The methodology for adjusting the rheological behavior of paints is applied according to ASTM D7394-08, Standard Practice for Rheological Characterization of Architectural Coatings Using Three Rotational Bench Viscometers. It can be best observed in Figure 13.5.

Figure 13.5: *Rheological behavior adjustment sequence for decorative paints based on ASTM D7394-08.*

13.3 RHEOLOGICAL ADJUSTMENT METHODOLOGY USING DESIGN OF EXPERIMENTS (DOE)

Statistics has been widely applied in research and development in recent years to improve productivity and quality or even optimize existing methodologies. The design of experiments can be very well applied in optimizing the rheological behavior of paints, mainly because the conventional adjustment method mentioned above can sometimes become very laborious and require a lot of time from those who perform it. This difficulty of "manual" adjustment may come from possible negative interactions between the thickeners used or even the influence of the two types of thickeners, on both low and high shear viscosities.

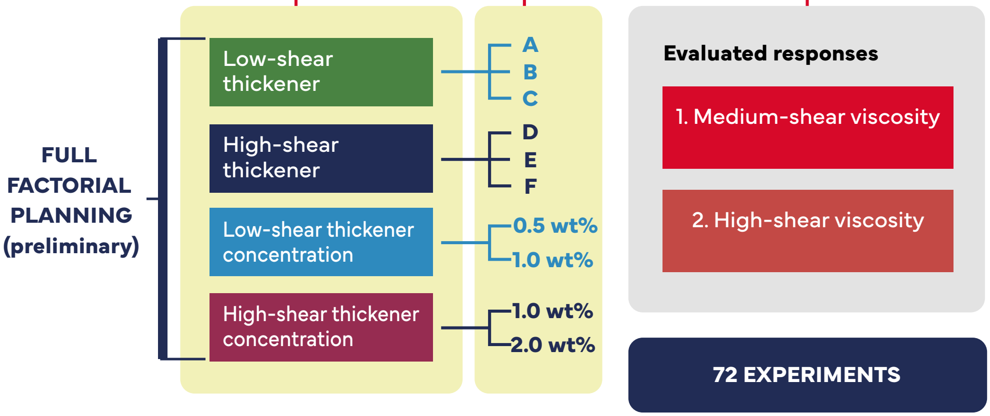
For example, we will describe a case study for evaluating and validating the best pair of thickeners to be used in a semi-gloss decorative paint formulation to promote a system with target viscosity of 100 KU and 150 cP in medium shear and high shear, respectively. The design of experiment planning and subsequent validation were done using MiniTab® software. The factorial planning used can be better visualized below.

1. It was used a complete factorial in which the factors evaluated were thickener type and concentration used in the formulation.

2. The planning was carried out and all possible combinations between factors and their levels were experimentally evaluated in the laboratory.

3. The concentration levels were chosen based on previous studies, considering that the high shear thickener is used in a higher concentration in comparison to the low shear thickener in the formulation.

4. The measured responses were viscosities at medium and high shear.



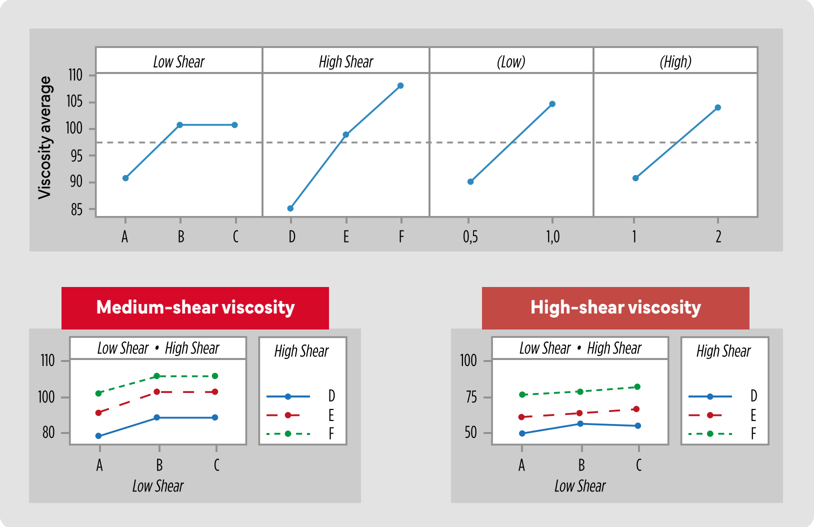
FULL FACTORIAL PLANNING (preliminary)

- Low-shear thickener: A, B, C
- High-shear thickener: D, E, F
- Low-shear thickener concentration: 0.5 wt%, 1.0 wt%
- High-shear thickener concentration: 1.0 wt%, 2.0 wt%

Evaluated responses

1. Medium-shear viscosity
2. High-shear viscosity

72 EXPERIMENTS



5. From this study, it was extracted the factors and interactions statistically significant in the responses and the most efficient pair of thickeners when used together. It can be observed that two low shear thickener, B and C, were more efficient for increasing the viscosity of the paints.

Factorial planning example for rheology study.

Source	GL	SQ (Aj.)	QM (Aj.)	F-value	P-value
Model	36	16,292.2	465.49	1,436.58	0.000
Linear	6	15,250.8	2,541.79	7,844.37	0.000
Low Shear	2	1,572.8	786.39	2,426.93	0.000
High Shear	2	6,489.3	3,244.63	10,013.44	0.000
[Low]	1	3,885.2	3,885.21	11,990.36	0.000
[High]	1	3,303.5	3,303.49	10,195.08	0.000
2-factor interactions	13	915.8	70.44	217.40	0.000
*Low Shear * High Shear*	4	55.1	13.77	42.51	0.000
*Low Shear * [Low]*	2	136.5	68.25	120.64	0.000
*Low Shear * [High]*	2	24.0	11.98	36.96	0.000
*High Shear * [Low]*	2	95.5	47.77	147.43	0.000
*High Shear * [High]*	2	603.0	301.51	930.51	0.000
*[Low] * [High]*	1	1.7	1.65	5.09	0.030
3-factor interactions	12	122.8	10.23	31.59	0.000
*Low Shear * High Shear * [Low]*	4	36.1	9.03	27.86	0.000
*Low Shear * High Shear * [High]*	4	59.0	14.75	45.53	0.000
*Low Shear * [Low] * [High]*	2	12.7	6.36	19.63	0.000
*High Shear * [Low] * [High]*	2	15.0	7.49	23.11	0.000
4-factor interactions	4	2.9	0.72	2.21	0.087
*Low Shear * High Shear * [Low] * [High]*	4	2.9	0.72	2.21	0.087
Error	36	11.7	0.32		
Total	71	16,303.9			

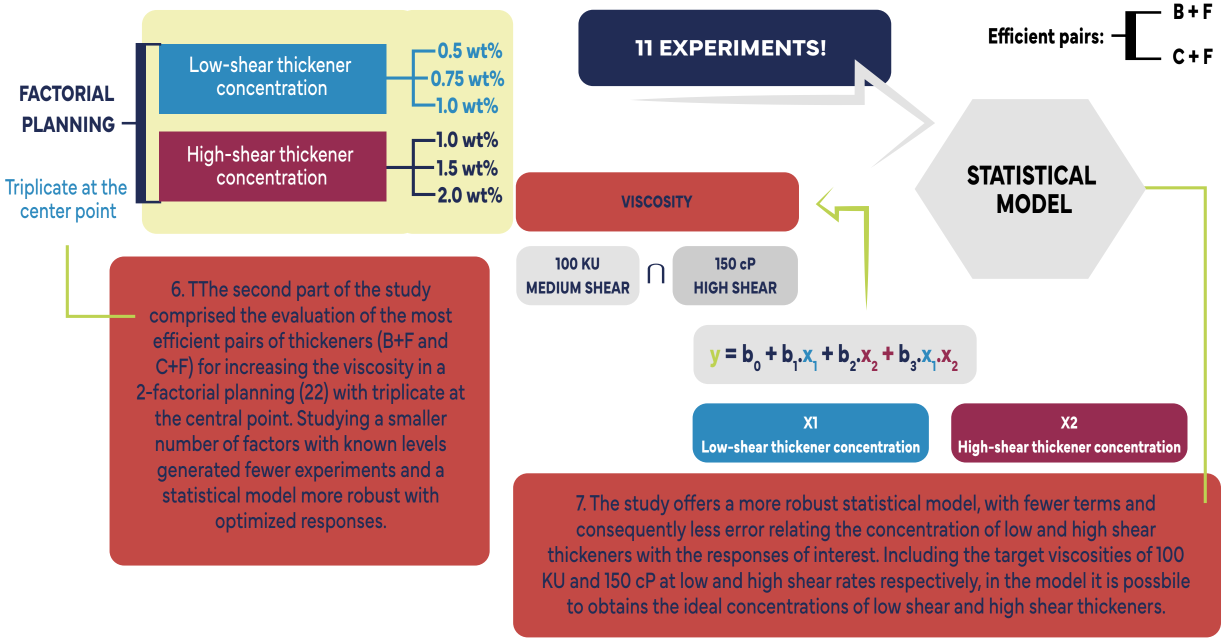
Significant!

Significant!

Significant!

Not significant!

P-value greater than 0.05 is not included in the model



Efficient pairs: B + F / C + F

FACTORIAL PLANNING

Triplicate at the center point

Low-shear thickener concentration: 0.5 wt%, 0.75 wt%, 1.0 wt%

High-shear thickener concentration: 1.0 wt%, 1.5 wt%, 2.0 wt%

11 EXPERIMENTS!

STATISTICAL MODEL

VISCOSITY

100 KU MEDIUM SHEAR ∩ **150 cP HIGH SHEAR**

$$y = b_0 + b_1.x_1 + b_2.x_2 + b_3.x_1.x_2$$

X1 Low-shear thickener concentration

X2 High-shear thickener concentration

6. TThe second part of the study comprised the evaluation of the most efficient pairs of thickeners (B+F and C+F) for increasing the viscosity in a 2-factorial planning (22) with triplicate at the central point. Studying a smaller number of factors with known levels generated fewer experiments and a statistical model more robust with optimized responses.

7. The study offers a more robust statistical model, with fewer terms and consequently less error relating the concentration of low and high shear thickeners with the responses of interest. Including the target viscosities of 100 KU and 150 cP at low and high shear rates respectively, in the model it is possbile to obtains the ideal concentrations of low shear and high shear thickeners.

Factorial planning example for rheology study.

13.4 CONCLUSION

The main difference between the manual adjustment method and the one that uses the design of experiments is that the first presents only one solution proposal, with a chance of not being reproducible if the same formulation is prepared in a second moment. The application of statistical methods offers solutions with several possibilities of combinations between the factors involved and the response of interest, and there is the possibility of choosing the one that best meets essential requirements, such as cost. However, the disadvantage of this methodology is that the model presented as a solution of possibilities cannot be considered universal. That is, each system evaluated requires a specific study, such as the design of experiments carried out. To illustrate it, Table 13.4 shows the difference between the results of thickener concentrations that were used in a manual rheology adjustment based on ASTM D7394-08 and using the design of experiment methodology. The explanation for the higher demand of thickeners in the first experimental design, compared to the manual adjustment and second design carried out, is of the higher complexity of the first model generated and, consequently, greater error due to the presence of a large number of terms. The terms of the model are a consequence of the factors and interactions that were statistically significant. It can be seen that the performance of the second experimental design for rheology adjustment required about 18 wt% less thickeners in the formulation compared to the adjustment performed by the ASTM standard. Thus, it is possible to verify that performing a preliminary study, in this case, the complete factorial (3 x 3 x 2 x 2), even if it is laborious for requiring a high number of experiments, it was an important step for maximum optimization of the resources of our study. Experimental design with prior knowledge of response trends and fewer factors, generate more robust models and, therefore, fewer errors due to the fewer terms present. Other studies have also shown significant reduction of thickeners in paint formulation optimizaing the rheological behavior using DOE methodology. In these studies, there was a reduction of about 26% and 43% of thickeners in the paint.

Methodologies	Total concentration of thickeners in the formulation (wt%)
Manual adjustment	2.06
Adjustment with doe 3X 3X 2X2	3.00
Adjustment with doe 2x2	1.70

Table 13.4: *Concentration of thickeners for optimizing rheological behavior of paint formulation obtained from different methodologies.*

Remembering that rheology is not the only property required to be adjusted in a paint formulation. Due to this, after the optimization of the rheological behavior of the product, it is still necessary to evaluate essential properties such as wet scrub resistance, hiding power, gloss, and hardness to validate whether the composition suggested by the methodologies mentioned above also maintain those properties appropriate for a high-quality product.

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Part 6

Safety in the laboratory

14 Safety in the paint development laboratory

Brandon Lucas da Silva

14.1 RISKS PRESENTED BY ACTIVITIES IN PAINT DEVELOPMENT, QUALITY CONTROL AND APPLICATION LABORATORIES

The activities in paint development, quality control and application laboratories present several health risks due to handling chemical agents in resins, solvents, pigments, mineral fillers, oils and additives.

These chemical agents can cause hazards in various processes:

- weighing of raw material;
- dispersion;
- grinding;
- completion and dilution;
- neutralization, acidification or alkalinization;
- preparation of substrate;
- sanding of substrates and primers;
- application of paints.

14.1.1 Weighing of raw material

When weighing the raw material, exposure to toxic products, corrosives, irritants, etc. occurs, such as solvents, alkalizing, pigments and others. Therefore, we must pay attention to wearing gloves appropriate to the type of product handled.

Another important precaution is using respirators, popularly called masks, with filters for organic vapors and acid gases.

14.1.2 Dispersion

During the dispersion process, we need to be aware of the risks that arise from rotating equipment use. Some precautions we should be aware of:

- Always keep your hair tied back.
- Possibility of pressing hands and fingers.
- Possibility of inhalation of organic vapors and dust.
- Be aware of moving parts of the equipment, and the risk of gloves or lab coats being stucked and causing injuries.
- Grounding the equipment to prevent accumulation of static electricity due to the movement of the liquid in the container.
- Do not clean the equipment under operation. It is recommended to unplug it to avoid accidental starting of the equipment.
- Do not perform temperature checks with equipment under operation (stirring). If necessary, use digital infrared thermometers.

14.1.3 Grinding

In grinding, horizontal and vertical mills are used to reduce particle size. In both horizontal and vertical mills, pay attention to grounding and respiratory protection as Volatile Organic Compounds (VOC) are released. *Do not forget* to de-energize the equipment during cleaning.

14.1.4 Completion and dilution

The main risk factors in this step are VOC emission and solvent contact, which have the following associated risks:

Contact with solvent in liquid form:

- Can irritate the skin and eyes.
- Can be fatal if swallowed or if they penetrate the airways.

VOC:

- Repeated and prolonged exposure may cause organ damage.

Both:

- In some cases, they may present a risk of carcinogenicity.
- They are flammable.

ATTENTION

Flammable versus corrosive: never mix flammable liquids with corrosive as they are incompatible.

14.1.5 Neutralization, acidification or alkalinization of paints

This process is carried out in the paint laboratory, usually using volatile bases such as NH_4OH (ammonium hydroxide) and acids such as acetic acid, sulfuric acid, etc.

In this process, there is a risk caused by the manipulation of corrosive chemical agents, which can cause damage to the respiratory system and burns if they come into contact with the skin.

14.1.6 Preparation of substrate for application

To sand carbon steel panels, it is necessary to degrease the part which comes bathed in oil. In this step, we must select solvents with lower risk. Table 14.1 deals with the solvent formulation.

Solvent	Volume
Sec-butyl acetate	40%
Methyl ethyl ketone (MEK)	40%
Anhydrous ethanol*	20%

*** Do not use hydrated alcohol, as it favors the oxidation of the part.**

Table 14.1: *Suggestion of cleaning thinner.*

Pure MEK solvent is not ideal because, as it has a fast evaporation rate, it does not maintain contact with the part for long and, therefore, does not remove the residue as well. By placing sec-Butyl acetate, which is a medium evaporating solvent, the solution stays in contact with the oil longer and removes it more easily.

14.1.7 Sanding of substrates and primers

Another step in which there are chemical risks is sanding the steel-carbon panel and the primer layer, in which suspended solids are released in the form of metal and primer dust.

ATTENTION

One should not tilt the sander during sanding in any way, as this can produce sparks and generate a fire outbreak in the laboratory.

Note: For carbon steel sanding, it is recommended to use the "thicker" P80 sandpaper, as it creates deeper cracks that ensure a good anchorage of the paint, avoiding adhesion problems.

A sander paired with a vacuum cleaner can be used to collect dust that would be dispersed in the atmosphere, so the risks of inhaling these specks of dust are minimized.

14.1.8 Spray Gun application

The following are the risks associated with the application: the generation of liquid particles and the release of VOC from solvent evaporation. Therefore, it is necessary to use respirators for organic vapors combined with a particulate filter, which can retain liquid particles.

Before applying, check if the exhaust cabin filters are saturated. If so, the exhaust efficiency is impaired, generating a lot of over-spray, which is the paint mist that returns to the applicator.

14.2 RISK CONTROLS

14.2.1 Safety Data Sheet (SDS)

The Safety Data Sheet (SDS) is the first safety item in a paint development laboratory and must be read thoroughly before handling any chemical agent. One of the main parts to read carefully to is the "Hazard Identification" section.

2. HAZARDS IDENTIFICATION

Classification	Flammable liquids, Category 2 Acute toxicity - Oral. Category 5 Skin corrosion/irritation, Category 3 Serious eye damage/eye irritation, Category 2 A Specific target organ toxicity - single exposure, Category 3 (central nervous system).
Appropriate labeling elements	
• Hazard Pictograms	 
• Signal Word	DANGER
• Hazard Statements	H225 Highly flammable liquid and vapor. H303 May be harmful if swallowed. H316 Causes mild skin irritation. H319 Causes serious eye irritation. H336 May cause drowsiness or dizziness.

In this section, we can see what hazards the product presents and the level of these hazards, such as flammability, which is classified as category 3. This classification is related to the flash point and the boiling point, according to Table 14.2.

Category	Criteria
1	Flash point < 23 °C and initial boiling point < 35 °C
2	Flash point < 23 °C and initial boiling point > 35 °C
3	Flash point > 23 °C and < 60 °C
4	Flash point > 60 °C and < 93 °C

Table 14.2: *Criteria for flammable liquids.*

Source: Adapted from United Nations (2013).

Note: The lower the flash point temperature, the greater the product's flammability. It is also important to note the danger and precautionary phrases that show other risks, such as skin and eye irritation, among others. Another important section is "Exposure Control and Personal Protection."

8. EXPOSURE CONTROLS AND PERSONAL PROTECTION

Control parameters	
• TLV-TWA (ACGIH)	200 ppm
• PEL-TWA (OSHA)	200 ppm: 590 mg/m^3
• TLV-STEL (ACGIH)	300 ppm
• LT(NR15)	155 ppm, 460 mg/m
• Odor Threshold	0.21 mg/m3 0.07 ppm
• IDLH	3000 ppm
• Biological Exposure indices (ACGIH)	Methyl ethyl ketone in urine 2 mg/l End of shift
Engineering Control Measures	In closed environments, this product should be handled keeping proper exhaust (general diluter or local exhauster)
Individual Protection Measures	
• Eye Protection	Side shields or wide vision safety goggles
• Skin Protection	PVC apron. It is recommended to adopt safety boots/shoes
• Hand Protection	Gloves made of butyl rubber
• Breathing equipment	In case of emergency or contact with high concentrations of the product, wear an air-supplied mask or self-contained breathing apparatus. It is recommended to wear a face mask with organic vapors cartridge in case of exposure to vapors/aerosols

In this field, we can see which Personal Protective Equipment (PPE) is suitable for handling the product.

14.2.2 Collective Protection Equipment (CPE)

Within the paint development laboratory, we have several pieces of equipment that protect more than one individual. Below are some examples and recommendations.

14.2.2.1 Laboratory fume hood

Activities in the laboratory that require the use of laboratory fume hoods: handling of solvents, resins, acids, bases, cleaning of panels, spatulas, containers, etc.

Usage tips:

- Keep the fume hood clean and organized.
- Do not leave large objects in front of the fume hood, obstructing the air intake.
- Do not use the fume hood to store reagents and other items permanently.
- When not in use, keep the fume hood closed.
- Turn on the fume hood a few minutes before starting work.
- Do all work that may generate dangerous gases or vapors inside the fume hood.
- Work with the front glass closed or with the opening as recommended by the manufacturer.

- Try to position the sources of vapors and gases further down the fume hood.
- Never place the head inside the fume hood in operation.
- If you need to handle something inside the fume hood, wear suitable PPE: glasses, gloves, safety boots etc.
- Keep the fume hood on for a few minutes after finishing the work.
- Regularly check the efficiency of the fume hood, for example, its noise level, lighting, and exhaustion (average air speed with open doors according to current regulations).

When bench hoods are available, activities that generate vapor release (VOC) and dust release can be carried out. For example, raw material weighing, paint dilution, solids weighing, carbon steel panel degreasing, primer sanding, etc.

Always check with the safety team if there are periodic checks on the efficiency of the exhaust system.

Check the possibility of installing an exhaust hood in the sinks so that it is possible to wash laboratory utensils, flasks and other materials that release organic vapors and acid gases.

When handling chemicals, wear wide-vision safety goggles as they prevent liquids from entering from any direction Common safety glasses are recommended only for activities that pose a risk of solids projection.

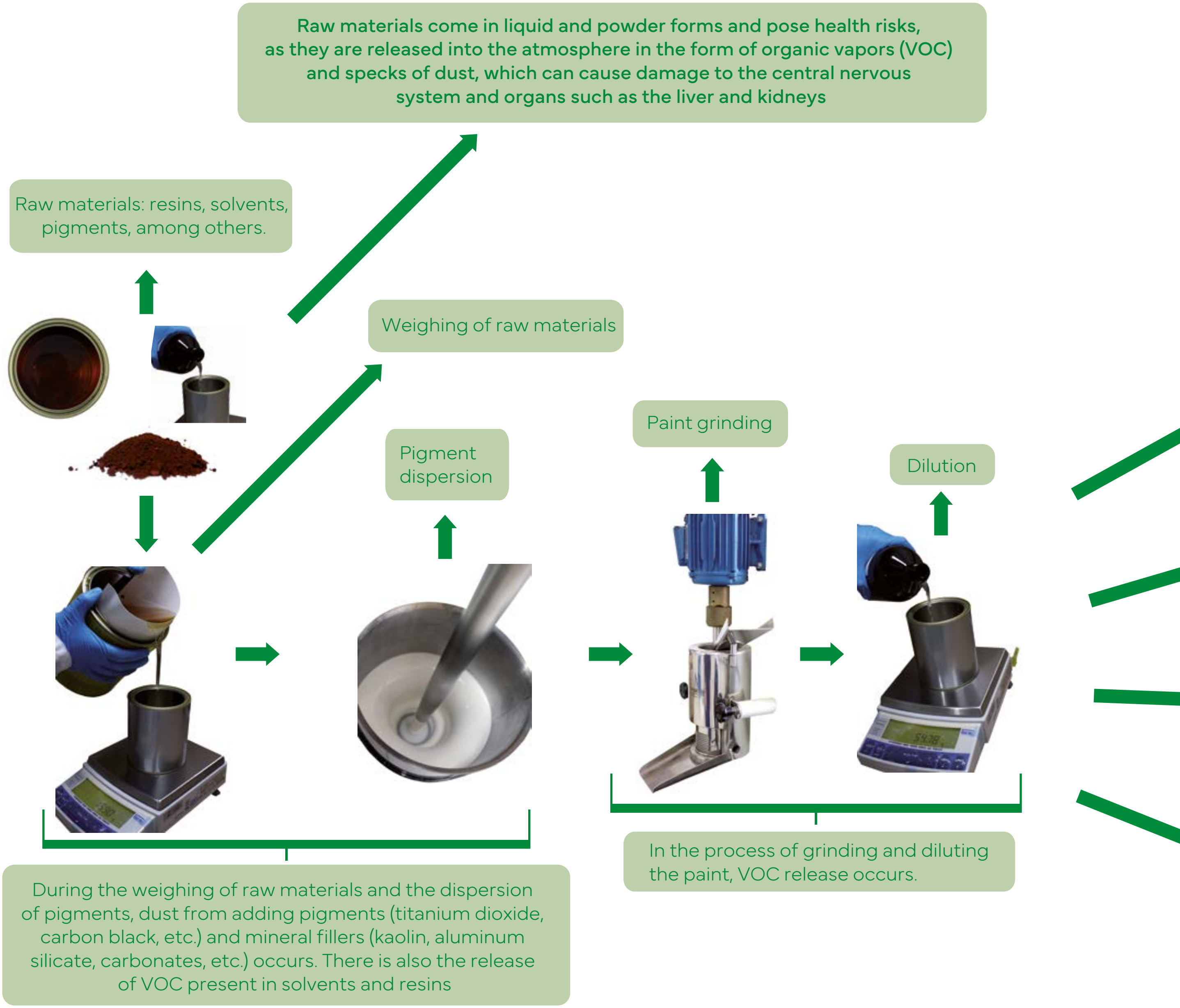
Use facial or semi-facial respirators with filters suitable for organic vapors, acid and particulate gases for handling solvents, acids, and bases, weighing raw material, dispersion of pigments, application of automotive paint, application of varnish on wood, etc.

The company, through environmental monitoring, will determine the type of filter most suitable for each activity.

It is recommended to use a complete face shield when working with corrosive liquids, skin-irritating solvents, etc.

Wear appropriate clothing, such as lab coats or long-sleeved uniforms. Give preference to closed boots instead of safety shoes with laces, as they offer better protection against chemical spills. When handling chemicals, wear suitable gloves that offer resistance to the type of product being handled.

14.3 PAINT MANUFACTURING PROCESS IN THE LABORATORY



Raw materials come in liquid and powder forms and pose health risks, as they are released into the atmosphere in the form of organic vapors (VOC) and specks of dust, which can cause damage to the central nervous system and organs such as the liver and kidneys

Raw materials: resins, solvents, pigments, among others.

Weighing of raw materials

Pigment dispersion

Paint grinding

Dilution

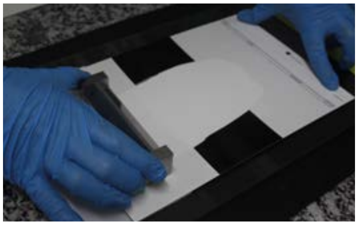
During the weighing of raw materials and the dispersion of pigments, dust from adding pigments (titanium dioxide, carbon black, etc.) and mineral fillers (kaolin, aluminum silicate, carbonates, etc.) occurs. There is also the release of VOC present in solvents and resins

In the process of grinding and diluting the paint, VOC release occurs.

Main risks related to paint preparation and application.

Applications

In spray gun application, paint mists are formed by the rupture of the particle of the solvents and the release of VOC by their evaporation.



In the process of applying paint with a brush, roller or an extender, VOC release occurs.

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15 Safety in the emulsion polymerization process in the development laboratory

Robson André Pagani

15.1 INTRODUCTION

In the chemical industry, every process must be very well evaluated for the risks involved to ensure the safety of the process and workers. The following are some aspects related to the safety of the emulsion polymerization process, focusing on a laboratory scale. This process involves the reaction of hazardous products with potential exotherms and should be evaluated with great attention.

15.2 SUMMARY OF PROCESS CONDITIONS

On a laboratory scale, the emulsion polymerization process is usually carried out in glass or stainless-steel reactors. Reactions occur at medium temperatures, and condensers are used to prevent evaporation loss during the process due to the volatility of the raw materials used. Mechanical impellers ensure good stirring of the entire loaded mass, avoiding deficiency of the reaction and/or lack of control. The process lasts approximately four to eight hours and takes place under normal atmospheric pressure conditions.

15.3 PROCESS RISK ANALYSIS

Based on the guidelines of the regulatory standard NR-1 and the Occupational Health and Safety Assessment Series (OHSAS) 18001, it is essential that, before carrying out any type of activity - or, in this case, process -, a study is carried out to identify and characterize hazards and damages to assess occupational safety and health risks and define the relevant control actions.

Tools, such as Preliminary Hazard Analysis (PHA) and Task Risk Analysis (TRA), can be used for this type of assessment. Figure 15.1 presents a suggested header of the items contained in a TRA. During the preparation of this document, each step of the process must be evaluated.

<table>
<tr><td colspan="13">TRA - TASK RISK ANALYSIS</td></tr>
<tr><td>NO.</td><td colspan="4">COMPANY:</td><td colspan="2">UNIT:</td><td colspan="5">DATE:</td><td rowspan="2">REVISION:</td></tr>
<tr><td colspan="4">PLACE OF ACTIVITY:</td><td colspan="8">PREPARED BY:</td></tr>
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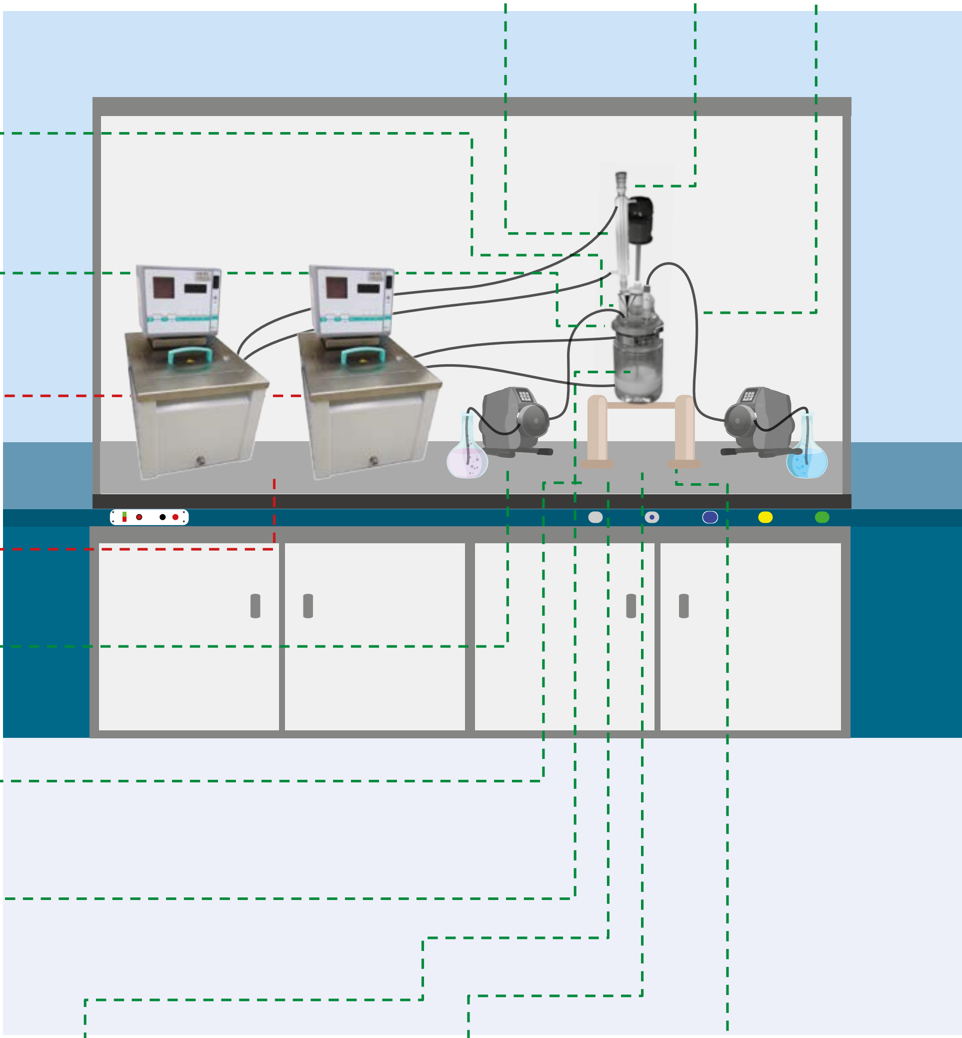
Figure 15.1: *Example of a TRA header.*

15.4 WHAT IS THE SECURITY LEVEL OF THE POLYMERIZATION PROCESS THAT I AM CURRENTLY RUNNING OR THE NEW PROCESS I AM GOING TO RUN?

The following checklist, in line with the preparation of the TRA, may assist in answering this question. Evaluate every detail, and do not underestimate the potential risk of exposure and/or accident of any step to be performed. Notably, the operator must be in good physical and emotional condition in addition to all items concerning process equipment, safety, and related documents.



Latex styrene acrylic polymerizations have less exotherm, making them easier to control. However, vinyl acrylic latex polymerizations present a greater exotherm, generating high monomers reflux since vinyl acetate's boiling point is equal to 72.5 °C. Therefore, this type of reaction must be very well controlled so that the condenser does not project products at high temperatures.

Is it known as the basic thermodynamics of the reaction?

Whenever possible, perform temperature control using PT-100 type sensors with software communication to constantly monitor temperature changes.

Is the equipment used calibrated and in good condition?

Will the execution be carried out within a classified area?

Is the temperature control system capable of rapid cooling if the exotherm is elevated? There are reactors equipped with Peltiersystems that have excellent thermal exchange capacity, making the process more stable and safer.

Is there exhaustion at product and process handling sites?

Whenever possible, use metering pumps for the controlled addition of the pre-emulsion and the initiator, avoiding lost of control. In addition, reactors with more advanced automation systems allow the use of metering pumps automatically driven via software, contributing significantly to the optimization and safety of the process.

The use of glass reactors facilitates the evaluation of the entire process progress, mainly viscosity changes, clot formation and cleaning.

Evaluate the compatibility of pipes and hoses used.

Is the compatibility between the products in contact known?

Is there a possibility of generating undesirable intermediaries?

In some processes, due to the formation of a large amount of clot, the temperature sensor can be dragged, causing it to become entangled in the impeller, often locking the agitator motor. For this reason, a pit should be properly positioned to avoid such drag.

Is the procedure to be used described in detail? It is crucial to reinforce the RPIs that need to be used in the different stages of the process.

Is the safety data sheet (SDS) of the products handled known to those involved in the process?

Are the personal protective equipment specified in the safety data sheets available, in good condition and being used correctly?

In case of absence of exhaustion on site, using masks for organic vapors becomes fundamental for the safety of all those involved in the processes.

Is the intended storage location suitable for chemical compatibility, containment, exhaustion, and temperature?

Handling must be carried out away from heat and/or ignition sources due to the flammability of various raw materials.

Is the destination of the generated waste adequately defined?

Is cargo handling being performed ergonomically?

Are resources for extinction/mitigation of possible accidents available and easily accessible?

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Part 7

Life cycle assessment in paint development

16 Life cycle assessment (LCA)

Fábio Rosa

16.1 INTRODUCTION

Climate change and declining natural resources are increasingly worrying people. Of the various factors linked to these problems, population growth and increased industrial production are the ones that most impact the environment across the planet. This has driven the industry and the most diverse sectors to seek sustainable development.

According to the World Commission on Environment and Development definition, sustainable development is the one capable of meeting the needs of the current generation without compromising the ability to meet the needs of future generations. It is a development that does not deplete resources for the future.

Therefore, one of the ways to reduce environmental impacts, whether as individuals, companies, or organizations, is to use life cycle assessment as a subsidy for choosing a product or service from a sustainability point of view.

For example, what is better for the environment: using a disposable coffee filter or cloth? Using a disposable glass or using water and detergent to wash a glass? Producing water-based paint or solvent-based paint? To consistently answer these questions, we have a powerful ally in Life Cycle Assessment (LCA).

LCA is a tool that quantitatively analyzes all possible impacts related to the life cycle of products and services, ranging from the extraction of natural resources, through all links related to the production chain, to distribution, use and final disposal. LCA, therefore, is an excellent alternative for evaluating the environmental performance of a product or service, assisting in decision-making based on the environmental variable.

16.2 LIFE CYCLE ASSESSMENT (LCA) IN PAINTS

LCA is a fundamental technique for the paint segment, capable of assessing the environmental performance of a product by determining the environmental impacts throughout the life cycle, from the extraction of natural resources (cradle) to their disposal (tomb). In Figure 16.1, we have an example of the life cycle of an original automotive paint.

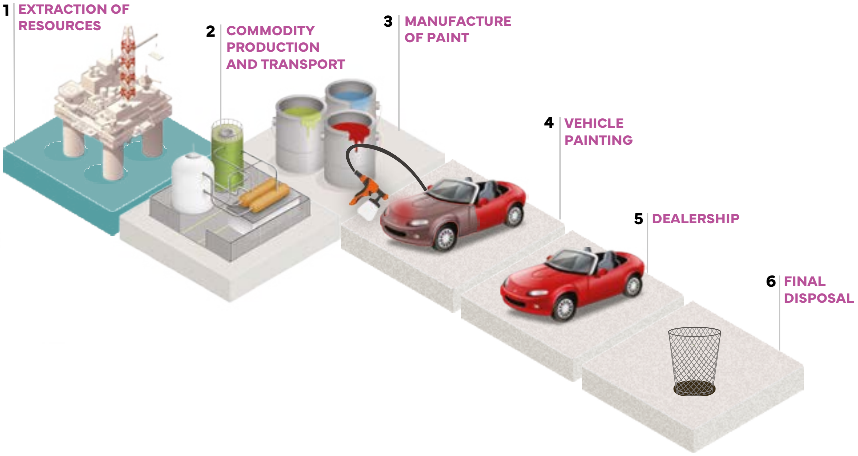


Figure 16.1: *Schematic of the life cycle stages for vehicle painting.*

The analysis can be done according to different categories of environmental impacts, which are divided into effects on the environment, depletion of abiotic resources and effects on man.

Effects on the Environment

Abiotic resource depletion

Effects on man

Figure 16.2: *Environmental aspects for measuring the impacts of a product.*

The importance acquired by the LCA in the contexts of environmental management and pollution prevention meant that, the methodological structure that constitutes it, ended up being standardized by the International Organization for Standardization (ISO) in the 14040 family of the ISO 14000 series. The following technical standards were released in this collection:

- ISO 14040: Environmental management - Life cycle assessment - Principles and framework (2006)
- ISO 14044: Environmental management - Life cycle assessment - Requirements and guidelines (2006)

16.2.1 LCA study: comparison of original automotive paint with different diluents

The study example relates to the life cycle assessment of a solvent-based technology automotive paint (base coat) diluted by both a diluent A and a diluent B.

The diluent for the automotive base coat guarantees the performance in the application and the proper finishing of the vehicle paint, in addition to being used in the cleaning of pipes and equipment of the paint system in the automotive industry.

As shown in Table 16.1, diluents A and B are composed of a mixture of solvents containing natural alcohol esters (isopentyl acetate, sugarcane derivative) or esters of synthetic alcohols (sec-butyl acetate) or aromatic solvent (xylene).

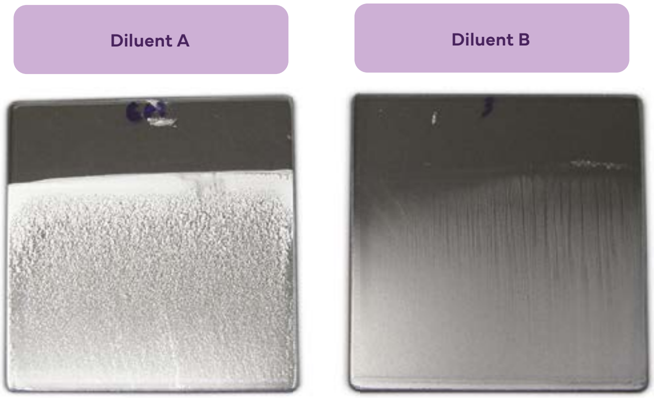
Component	Diluent A (% mass)	Diluent B (% mass)
Xylol	55	0
Sec-Butanol	10	0
Sec-butyl Acetate	35	68
Isopentyl Acetate	0	32
Total	**100**	**100**

Table 16.1: *Diluent formulations for* base coat *used as a comparative in the study.*

Both diluent A and diluent B meet the main technical attributes, proven by solubility parameters, evaporation rate, electrical resistivity, and high efficiency in cleaning painting equipment.

Figure 16.3 compares diluents A and B in an efficiency laboratory test, which consists of cleaning a glass plate impregnated with silver paint before drying, simulating the cleaning process in the vehicle assembly industry.

The test results indicated that the volume of solvent required for the total cleaning of the glass plate was twice lower for diluent B. The superior yield of diluent B was also proven on an industrial scale at the vehicle manufacturer.



Decreased cleaning efficiency

Increased cleaning efficiency

Figure 16.3:: *Laboratory simulation of the cleaning of paint impregnated on a glass plate.*

The LCA study was carried out with the Simapro software and with the Ecoinvent database based on the technical performance of diluents A and B. The Ecoinvent database is recognized worldwide and contains the values of the environmental loads associated with the life cycle of many products, processes, energy systems, transport, and waste disposal, among others.

The comparative evaluation was based on environmental performance for painting a medium-sized car using the electrostatic painting technique.

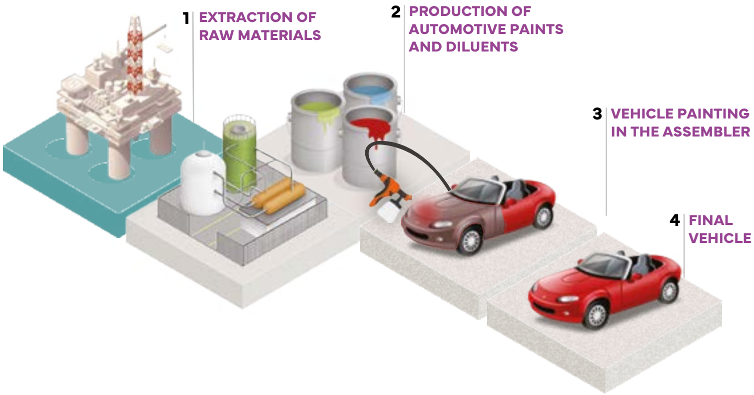


Figure 16.4: *LCA: evaluation steps in studying diluents A and B of automotive paint.*

16.3 CRITERIA AND DEFINITIONS FOR CARRYING OUT THE LCA STUDY

16.3.1 Scope

The study compared diluents A and B for the dilution of automotive paint and for the cleaning of paint pipes and painting equipment in a vehicle manufacturer in the State of São Paulo (Brazil). The study followed the methodology referring to ABNT NBR ISO 14040 and 14044 (both 2006).

16.3.2 Technical requirements

- Product systems: comparison of diluents A and B used for paint dilution and cleaning of pipes and equipment in paint lines at the vehicle assembler.

- Function: dilution of basecoat and cleaning of equipment and pipelines.
- Functional unit: the amount of diluent for diluting the basecoat and cleaning equipment and pipes for painting a medium-sized black car.
- Technical performance coefficient.

Figure 16.5: *Functional unit for the study of LCA.*

Painting a medium-sized black car consumes 1.6287 L of diluted paint with the following preparation of a more diluent paint mixture:

- 60% by mass of concentrated paint
- 40% by mass of diluent A or B

The volume of diluent required for cleaning equipment and piping varies depending on the diluent. Considering painting for one medium-sized black car:

- Diluent A = 1.6846 L
- Diluent B = 1.5780 L (mass 10% lower than diluent A due to greater cleaning efficiency)

16.3.3 Study boundaries

All processes associated with the production of each solvent from the cradle to the factory gate were established, including the transport of the components used in each formulation to the respective solvent-producing unit, transport to the place where the painting occurs and also the production of utilities (such as industrial water, boiler water, steam and electricity) involved in the various processes. The operations of preparing the diluted paint and its application to the vehicle were also considered.

16.3.4 Data quality

Data regarding the production of diluent A come from the Ecoinvent database, which was obtained from secondary sources. Data on the production of diluent B were obtained directly from the raw material manufacturer, that is, from primary sources. As for temporal and geographical coverage, the study was conducted in 2012 involving the States of São Paulo and Rio Grande do Sul (Brazil).

16.3.5 Exclusion criteria

Environmental aspects whose cumulative contributions in terms of mass and energy were below 1% and loads of negligible environmental relevance according to ABNT NBR ISO 14044 were excluded from the life cycle inventories (LCI).

16.3.6 LCA study impact categories

The analysis was performed considering the environmental impact categories shown in Figure 16.6.

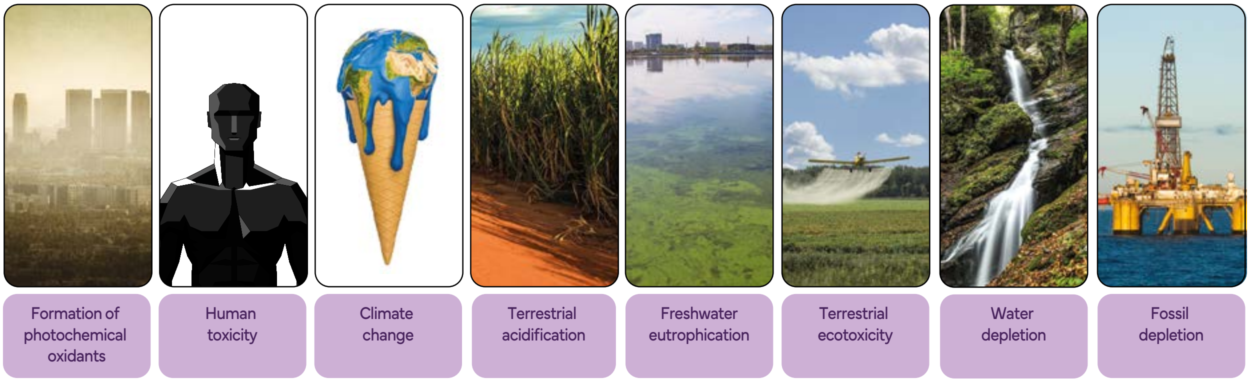


Figure 16.6: *Environmental impact categories.*

16.4 RESULTS

Table 16.2 summarizes the environmental performance of diluent A and B used in painting a medium-sized car painted at the automaker and cleaning equipment and pipelines.

Impact category	Unit	Diluent A	Diluent B
Formation of photochemical oxidants	kg NMVOC (non-methane volatile organic compounds)	1.31	0.40
Human toxicity	kg 1,4-DB eq (1,4 dichlorobenzene)	3.66	3.39
Climate change	kg CO_2 eq	82.23	82.16
Terrestrial acidification	kg SO_2 eq	0.09	0.10
Freshwater eutrophication	kg P eq (phosphorus)	0.003	0.004
Terrestrial ecotoxicity	kg 1,4-DB eq (1,4 dichlorobenzene)	0.05	0.06
Water depletion	m^3	0.22	0.23
Fossil depletion	kg oil eq	8.33	8.85

Table 16.2: *Comparison of environmental performance between diluents A and B for the purpose of a painted car, used in Brazil. Caption: eq = equivalent.*

The Figure 16.7 summarizes the environmental performance profiles with standardized data.

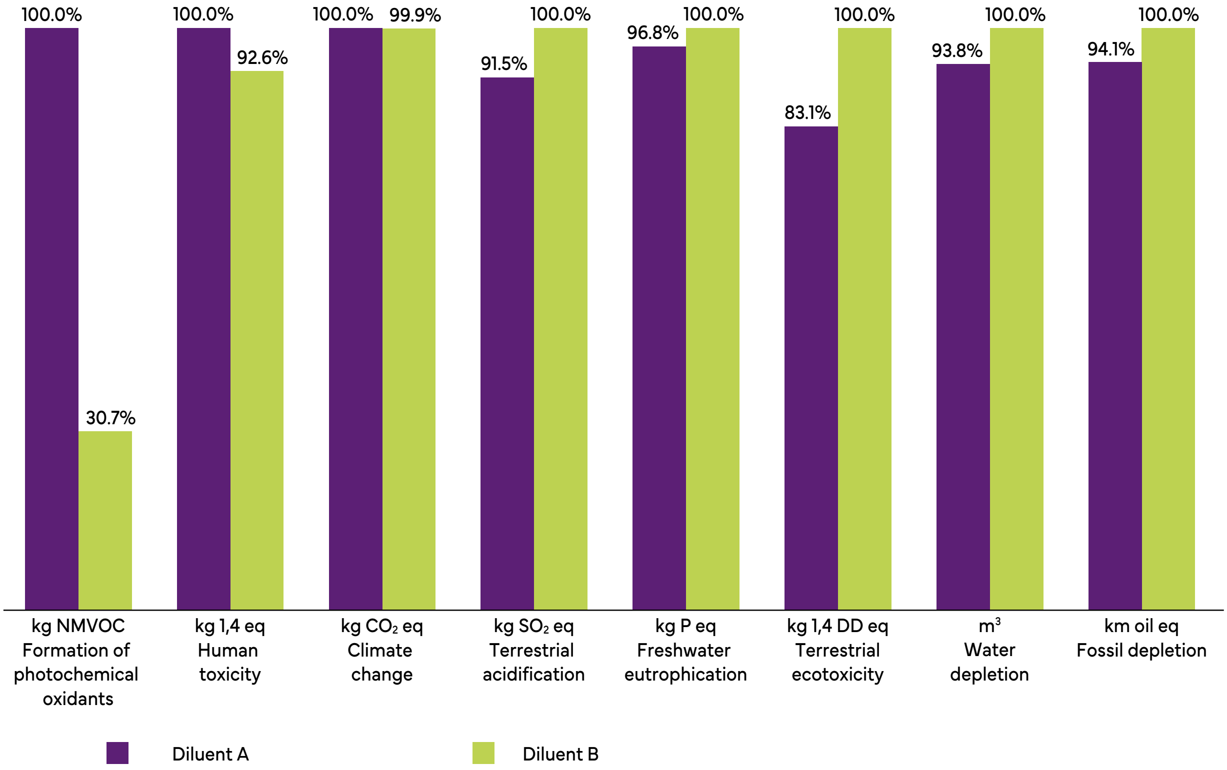


Figure 16.7: *Comparison of environmental performance between different formulations of solvents for the purpose of a painted car, used in Brazil, normalized data.*

The comparative assessment of environmental performance demonstrates that diluent B performs better regarding impacts relative to human toxicity and the formation of photo-oxidants relative to diluent A.

The evaluation of photo-oxidant formation showed that diluent B performs 68% better than diluent A, which the characteristic composition of each formulation can explain.

The impact categories related to climate change, and the depletion of fossil resources, demonstrated equivalent or very similar results for diluents A and B.

In the impact categories related to terrestrial acidification, aquatic eutrophication, terrestrial ecotoxicity and water depletion, diluents A and B showed similar results. In addition, absolute contributions have low values, less expressive than the values of the other categories.

As a conclusion, the analyses performed with the LCA study comparing diluents A and B for the dilution of automotive base coat allow us to conclude that diluent B has less impact on the environment because its use causes less photo-oxidant formation and less human toxicity. In the other environmental impact categories, diluents A and B have similar environmental performance.

16.5 LCA STUDY: COMPARISON OF DECORATIVE PAINT WITH DIFFERENT COALESCENTS

In this example, the LCA study compares ULTRAFILM® 5000, a coalescent from renewable source, with 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, both used in an architectural paint formulation.

The function of 'protecting a surface against weathering, preventing its wear and tear' has been established. Considering the context, the Functional Unit became: 'protect a surface of 50 m^2 against weather, avoiding its wear and tear, over 5 years'.

Each liter of paint is sufficient to protect 18 m^2 of surface per coat, requiring three coats of paint to obtain a proper surface finish, and both coatings have identical technical performances in the application stage and under normal exposure conditions, the durability of the two paints after application is 5 years.

Considering these assumptions, the Reference Flow corresponds to 8.30 l of paint, being common for both analyses.

Concerning the composition of the Product Systems, the only difference between the productive chains of the paints with ULTRAFILM® 5000 and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate is in the processing of the coalescents.

All processes associated with the production of each coalescent from the cradle to the factory gate were established, including the transport of the components used in each formulation to the respective coalescing production unit, transport to the place where the painting takes place and also the production of utilities (such as industrial water, boiler water, steam and electricity) are involved in the various processes.

The geographical coverage considered obtaining ULTRAFILM® 5000 at Coatzacoalcos, in Mexico, and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate in Longview, Texas (TX).

The formulations and applications of the paints took place in McCarran City, Nevada (NV).

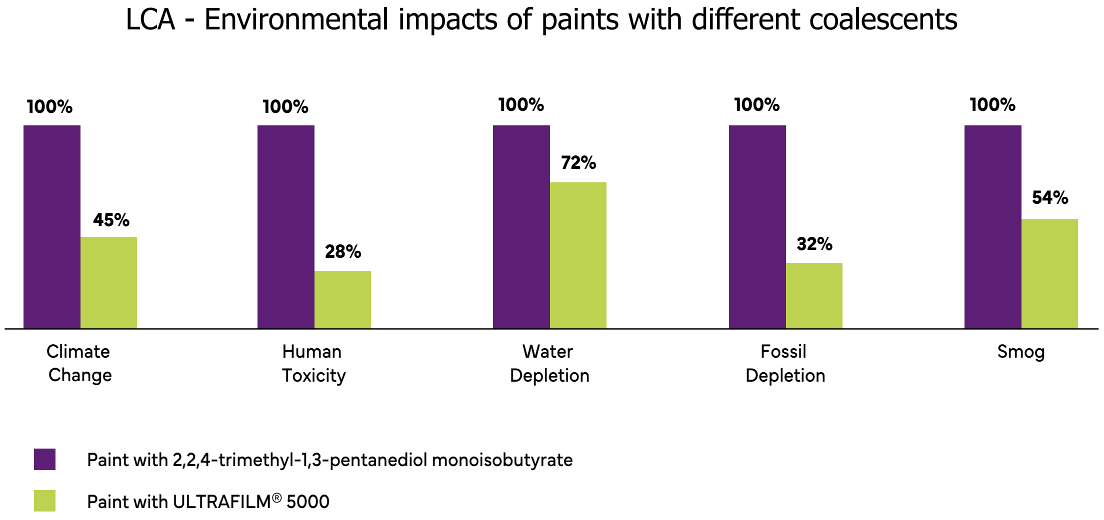


Figure 16.8: *Environmental profile of paints with different coalescents.*

As a conclusion, the results generated by the LCA study demonstrate that ULTRAFILM® 5000 has a superior environmental performance than the 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate with better results in all impact categories studied, namely climate change, human toxicity, water depletion, fossil depletion and smog (impact due to VOC emissions).

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