Transmittance Technique for Adjusting Properties in the Paint Industry

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Introduction

The paint industry is a vital part of the global economy, providing essential coatings for a variety of sectors, from construction to aerospace. However, compared to other industries, the sector has lagged in terms of automating quality control processes. Currently, the biggest bottleneck is the approval and adjustments of some critical properties that guarantee the quality of intermediates and final products.

The main conventional methods of analysis involve carrying out several manual operations, where the sample generally needs to be mixed with a standard base (in the case of tinting strength evaluation), applied to a chart or panel and subsequently dried in an oven before analysis. This procedure, in addition to requiring a lot of time, increases errors related to conventional reflection spectroscopy analysis.

With the aim of taking the paint industry to level 4.0, an innovative equipment was developed, called Transmicell V2, which allows automatic liquid control and adjustment (in natura sample) of crucial properties for quality assurance directly on the production line or in the laboratory.

Unlike conventional methods, the equipment is based on transmission spectroscopy, where the product's spectral curve carries information about each property, thus allowing measurement and comparison between batches and standards. With this new method it is possible to measure the wet hiding power of paints, the tinting strength (TS) of pigment dispersions and pastes, control the evolution of the dispersion in the grinding process and make color adjustments in translucent materials, such as wood stains. Studies are being carried out to use the technology also for the control and adjustments of effect pigments (metallic and pearlized), with promising previous results.

The high sensitivity and excellent GageR&R of this method makes it possible to detect very small variations between products that are often not detected in the reflection method. This allows approval limits to be narrowed, guaranteeing batch-to-batch quality and consequently a substantial reduction in raw material costs due to the possibility of reducing the amount of pigment in the formulation.

As the analysis is carried out with the sample still in liquid form and without the need for human interference, a reduced analysis cycle time is achieved, achieving higher levels of productivity, thus enabling the automation necessary to meet growing market demands. The equipment developed has two versions, one for quality control in the laboratory (offline) and another for process control (inline). The database developed in the wet control system can be used in both versions.

This work will present results and data from the use of this new technology in companies that have already adopted the method, demonstrating the benefits and gains from its use.

The Relationship of Transmission with Tinting Strength and Hiding Power

Most of the equipment that operates via transmission was developed to measure low opacity materials, preferably transparent, such as colored solutions analyzed in a UV-Vis spectrophotometer. In general, Beer's Law is valid in these cases, however, there is a restriction of application in the case of suspensions, dispersions, etc.

In the case of highly opacity pigmented materials, Beer's Law does not apply, as in this case there is a suspension of solid particles, finely divided in a liquid, where other optical phenomena occur, in addition to absorption, making their use impossible (QUINDICI, 2013).

In of particle suspensions, such as in paints and pigment pastes, in addition to absorption there is the phenomenon of light scattering, defined as the physical process in which a certain form of energy, when propagating in a linear trajectory, undergoes a change in the trajectory due to interactions with the environment through which it passes.

In inorganic materials (pigments and fillers) this effect is extremely intense and in organic materials it occurs with less intensity. Scattering is directly related to the size of the particles, their distribution in the medium, the refractive index of the medium, among others.

When analyzing a pigment dispersion, it is observed that the smaller the particle size, the greater the sum of the surface areas and the greater amount of light will be blocked by the particles, which is completely coherent in physical terms. According to Chen (2016), a pigment with acicular particles has greater absorption and dispersion of light and greater tinting strength compared to a pigment with spherical particles. This result is attributed to a greater surface area of the particles; therefore, it is possible to infer that a greater tinting strength is related to a lower light transmission. The same reasoning is valid in the case of wet hiding power analysis.

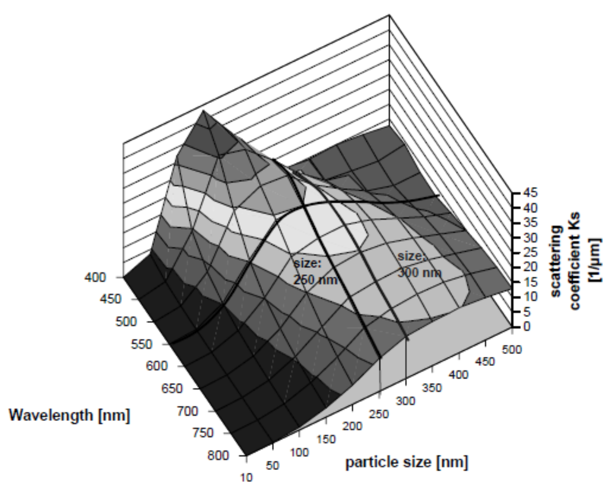

Figure 1 - Relationship of particle size to the interaction of light at different wavelengths.Tiarks (2003)

However, there are cases in which the opposite behavior is observed, where the light transmission is directly proportional to the tinting strength, generally in the case of organic pigments.

This is basically because the light directly passes through the dispersion of pigments so that there is less light-particle interaction, responsible for providing opacity to the medium.

This phenomenon is related to the size of the particle which, according to the literature (TIARKS, 2003), when smaller than approximately 200 nanometers present a reduction in the interaction with light, behaving like a translucent pigment, and therefore, providing low opacity when analyzed by transmission.

When the particle has a size of approximately half the wavelength of light, the opposite effect is observed, where a greater transmission at the peak corresponds to a high tinting strength.

Likewise, when the particle is very large, such as at the beginning of the pigment dispersion process, there is also low interaction due to the low surface area available. As the particle size is reduced to its ideal size, the opacity of the medium increases until it reaches a point of maximum interaction with light, resulting in greater tinting strength.

Transmission Method – Transmicell V2

The equipment used for measurements and control through the transmission of light in opaque and translucent materials is called TRANSMICELL V2, patent PCT/BR2019/050381, and is currently the only existing equipment for this purpose on the world market (Figure 2).

Figure 2 - Transmicell V2

In summary, the principle of the equipment involves identifying a specific analytical condition for each material, allowing a beam of light to radiate through a quantity of liquid sample and the spectrum generated from the transmitted light to be analyzed and compared with a standard. By quantifying the portion of light transmitted through the liquid sample film, it is possible to extract optical information that can be used to evaluate different properties of the product. These properties include tinting strength, hiding power, degree of dispersion, transparency, and color.

To achieve an ideal level of interaction between the incident light and the film of the material to be analyzed, the equipment uses a set of three degrees of freedom to define the analytical condition: the optical path (film thickness), light source power and the analytical dilution carried out automatically by the equipment at the time of reading.

High-precision syringes control the dilution, a chamber with mechanical agitation (micromixer) is responsible for homogenizing this mixture and, finally, a spectrophotometer measures the light transmitted through the sample in a reading cell composed of transmission windows where the material a being analyzed fills the space between them (Figure 3).

Analytical dilution is carried out using a transparent analytical vehicle with adequate compatibility with the products tested, ensuring that there are no instabilities or interferences in the measurement. Often, the base resin of the dispersion/paint formulation itself acts as an analytical vehicle, providing the stability and compatibility necessary for the test. In the case of water-based products, the vehicle used for dilution is water itself, in most cases.

Each sample interacts uniquely with light due to several factors, the main one being the differences between the types of pigments used in its formulation. Consequently, each sample has its ideal analytical condition to optimize sensitivity gains and guarantee product stability under established conditions.

The equipment automatically finds this ideal condition for each material, in order to achieve a %Transmission level at the peak of the spectrum of around 80%, where greater sensitivity can be achieved (low signal-to-noise ratio). In order to compare different batches of a given material, the same analytical condition must be used.

The result of the analysis, given by a transmission spectral curve, is the average of five consecutive readings carried out automatically by the equipment. With each reading, the entire dosing, dilution and mixing process is carried out quickly with a new portion of sample and vehicle, ensuring sampling homogeneity and avoiding possible destabilization of the sample generated by dilution.

During transmission analysis, unlike conventional reflection techniques, the value of interest is the

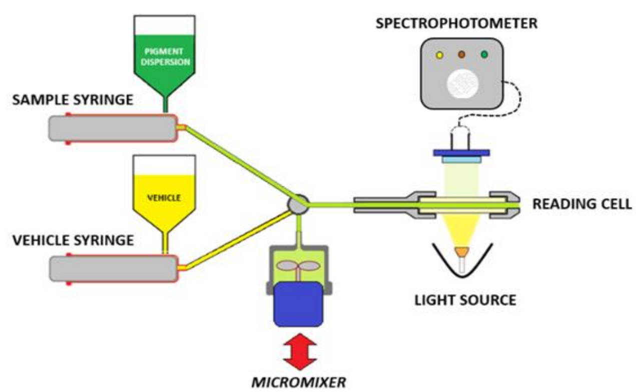

Figure 3 - Analysis at Transmicell V2

transmittance at the peak wavelength of the spectrum, where there is greater sensitivity and lower signal-to-noise interference.

The repeatability and reproducibility (GageR&R) of the Transmicell equipment was evaluated using specific statistical methods (AIAG, 2010), calculated using Minitab software (Figure 4). The result of 17.66% is considered very good for the application in question, being much higher than conventional methods. In addition to better R&R, the analysis time using this new technique is extremely shorter than the conventional method.

Gage Evaluation

Source	StdDev (SD)	Study Var (6 × SD)	%Study Var (%SV)
Total Gage R&R	0.60601	3.6360	17.66
Repeatability	0.46129	2.7678	13.44
Reproducibility	0.39301	2.3580	11.45
Operator	0.26114	1.5669	7.61
Operator*Sample	0.29370	1.7622	8.56
Part-To-Part	3.37734	20.2640	98.43
Total Variation	3.43128	20.5877	100.00

Figure 4 - Gage R&R Results – Transmicell V2

Reflection Methods

Analysis methods using dry reflection on charts, in general, have low repeatability and reproducibility mainly due to the various manual steps in which the product is subjected so that it can be analyzed, such as: weighing on a scale, mixing with a standard basis (in the case of TS evaluation), application speed and thickness, drying temperature, oven time, among others.

The hiding power can be analyzed via reflection from the chart, in accordance with ASTM D2805-11 using the contrast ratio method. In this method, a paint film is applied with controlled thickness to a substrate that has half of the surface black and the other half white. The assessment of hiding power is related to the black and white reflectance index caused by coverage with the paint under analysis. The result of the contrast ratio is a value between 0 and 100. The higher the value, the greater the hiding power of the material.

Controlling the tinting strength in pigment dispersions is essential, as the reproduction of formulas in paints directly depends on the dyeing performance of the pigment (YOSHIDA et al., 2009), where paints produced from pigment concentrates with variations in tinting strength will differ from its final color, requiring long and expensive corrections.

To determine the tinting strength of colored pigments using the reflection method, a mixture is normally made between the pigment paste to be analyzed and a standard white base of titanium dioxide (which in this case also presents variations in its properties and adds errors to the method). The homogenized mixture is applied to a chart under standardized conditions in accordance with ISO 787 and ASTM D4838 – 88 and then the tinting strength is measured using a reflection spectrophotometer. Tinting strength is a relative measurement given in percentage terms, based on the relationship between the maximum absorption (minimum reflection point) of the sample and a reference standard.

In the reflection method, the minimum specification limit for approval for sale in the Brazilian market is 90% of contrast ratio for Premium class water-based decorative paints, according to the ABNT NBR 14943 standard. Most manufacturers choose to deliver paints with coverage above specification, given the difficulty of making a precise adjustment due to the lack of repeatability of the method, which ends up resulting in excessive quality without remuneration and inconsistency of the product delivered to the market.

The approval limits for the tinting strength of pigment pastes vary depending on the manufacturer, with 100% ± 5% being normally used (MARTINELLO, 2020). In this case, there is no specific standard for these limits, as pigment pastes are intermediate products in the industry. In practice, this specification range is too wide to contain the errors of the reflection reading method and, therefore, even within the specification, they lead to subsequent color corrections in the paints produced by these pigments.

Methodology

The tinting strength of the pigment dispersions was measured and adjusted in the dry method (reflection) and also in the wet method (Transmicell), so that a comparison could be made. Likewise, the measurement and adjustment of the wet hiding power of paints from the Super Premium decorative line were carried out using the conventional contrast ratio method (reflection) and Transmicell.

To carry out the tests, it was ensured that the samples were stable in their own analytical condition, with the transmission curve representing the average result of at least five consecutive readings, varying a maximum of 0.8% in transmission between them.

The calculation of the adjustment of properties (tinting strength and hiding power) is based on the response curve obtained through concentration variations caused in the standard sample of a given material. The transmission variation caused by small dilutions can be described by a linear or exponential correlation equation, resulting in the ideal amount of resin to adjust the property (tinting power or hiding power) to the % transmission value chosen as standard.

In this study, the reference value of %Transmission for adjusting the properties was chosen based on the variation observed between the different samples. Among them, the sample/batch with the highest peak transmission was used as a reference value for adjustment.

The first stage of the tests consisted of determining the ideal analytical condition for the type of product in question. This set of parameters was followed for all analyzes of the same type of product so that comparisons between results were possible. Subsequently, the products were analyzed and variations in the %Transmission were verified between the different batches, which translates into differences in tinting strength or wet hiding power.

Once the differences between the samples were verified, a kind of database was created, formed by a gradient of dilutions in one of the batches, leading to the material's response curve. The last step of the process was to perform the adjustment calculated from the response curve and analyze it again in both methods (dry and wet) to verify the efficiency of each method.

In this paper, the tinting strength of a blue pigment paste (opaque) was evaluated and adjusted, and, in the same way, the wet hiding power was adjusted on a super-premium class decorative paint sample.

Results and Discussion

a) Opaque Pigment Paste Tinging Strength

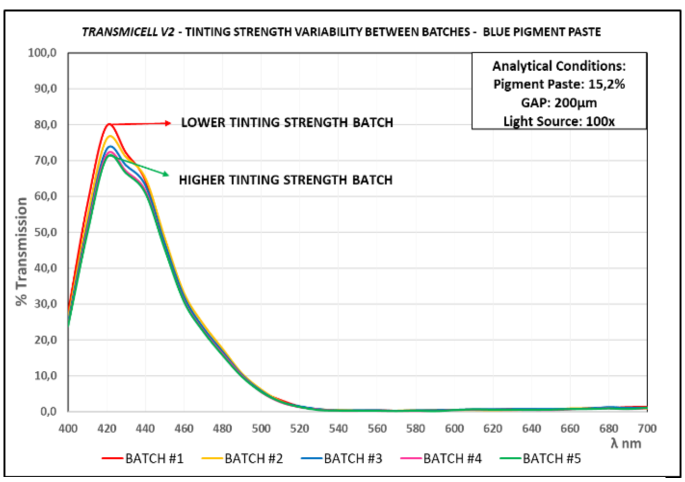

Figure 5 - Blue Pigment Paste Transmission Curves

Five different batches of an inorganic blue pigment paste had their tinting strength evaluated by transmission, so that the possibility of an adjustment was identified (Figure 5). These batches are real samples of industrial production, all of which have been tested and approved by the quality control sector.

The batch with the highest transmission was considered as a reference for adjusting the tinting strength, that is, it was considered as the lower limit of the specification. This consideration makes it possible to maximize gains as long as precise adjustments are possible.

Batch #1 presented 79.64% peak transmission and was the reference for adjustment. Batch #5 presented 70.76%Transmission at peak and had its tinting strength subsequently adjusted to the reference. This variation of 8.88%Transmission corresponded to a difference of 2.52%TS in the chart reflection method – the method with the lowest sensitivity (Figure 6). Given this difference in TS by the reflection method, the batches would be approved, while by the transmission method an adjustment would be suggested.

Once the differences between the batches were known using the transmission methodology, a response curve was generated based on the resin additions so that an adjustment could then be calculated (Figure 7).

Figure 6 – TS Analysis by Chart Reflection

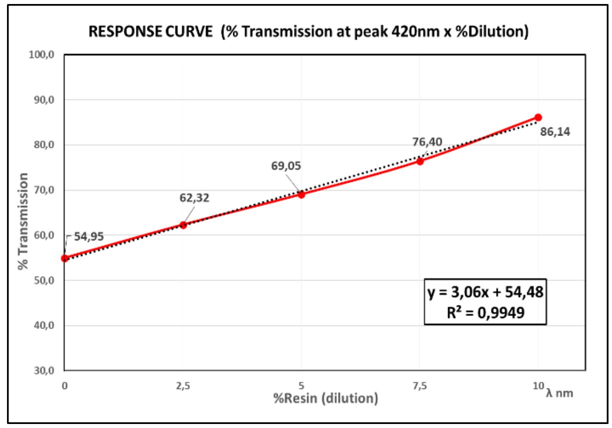

Figure 7 – Blue Pigment Paste Response Curve

Based on the response curve obtained, the adjustment made was 2.90% resin addition. Adjusted batch #5 was evaluated again using Transmicell and the chart reflection method to verify the effectiveness of the correction.

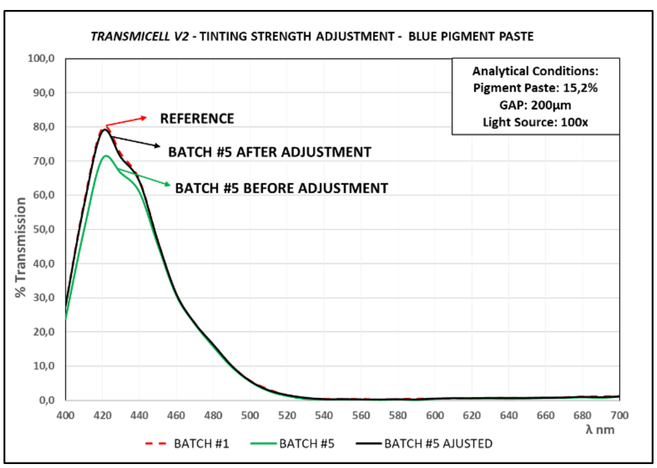

Figure 7 – TS Adjustment by Transmission

Sample	%Transmission (peak)	%TS Reflection
Batch #1	79,64	100,00
Batch #5	70,76	102,52
Batch #5 Adjusted	78,76	100,25

Table 1 – Blue Paste Pigment General Results

The adjustment carried out in batch #5 demonstrated great efficiency. It is observed that the transmission peak coincides with that of batch #1, considered a target for tinting strength.

In the %Reflection analysis on the chart, the tinting strength remained within the approval limit, with little change after the adjustment. This indicates the low sensitivity of this method of controlling this property and the possibility of sensitive adjustments using wet technology, generating savings and greater quality.

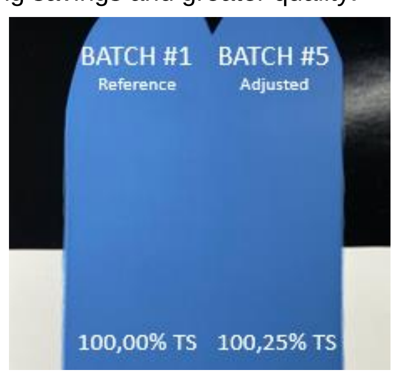

Figure 8 – TS Adjustment by Transmission read by Reflection

b) Hiding Power of Super Premium Class Decorative Paints

Following the same methodology used to adjust the TS, five different batches of Super Premium class architectural acrylic paint were evaluated by transmission (Figure 9). All samples tested were purchased commercially and therefore passed the manufacturer's quality control. The differences observed between the transmission peaks of the batches indicate a difference in the wet coverage of these paints and, consequently, point to the possibility of an adjustment.

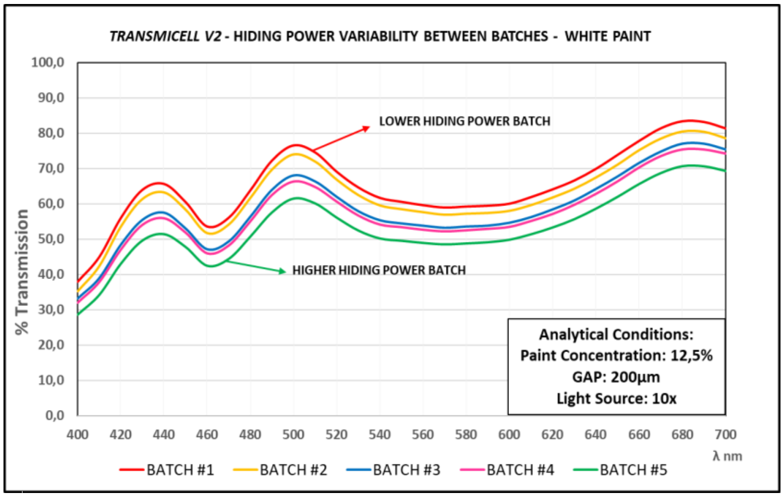

Figure 9 – White Decorative Paint Transmission Curves

A dilution gradient was used to determine the equation for the response curve of this product, which is the basis for calculating the adjustment necessary to achieve the %Transmission of the batch with the lowest coverage.

Batch #5, with the highest coverage, presented 70.73%Transmission at the peak, while batch #1, with the lowest coverage, presented 83.37%Transmission. This variation of 12.64%Transmission corresponded to a difference of 3.26%CR in the contrast ratio (CR) method.

The adjustment calculated for batch #5 was an increase in resin mass of 7.70%. Figure 10 illustrates the adjustment result of batch #5 using the transmission method. The peak transmission of the adjusted batch was 82.76%, indicating that the adjustment was carried out successfully.

To validate the adjustment also in the conventional contrast ratio method, the samples in question were applied to a chart for evaluation through reflection analysis.

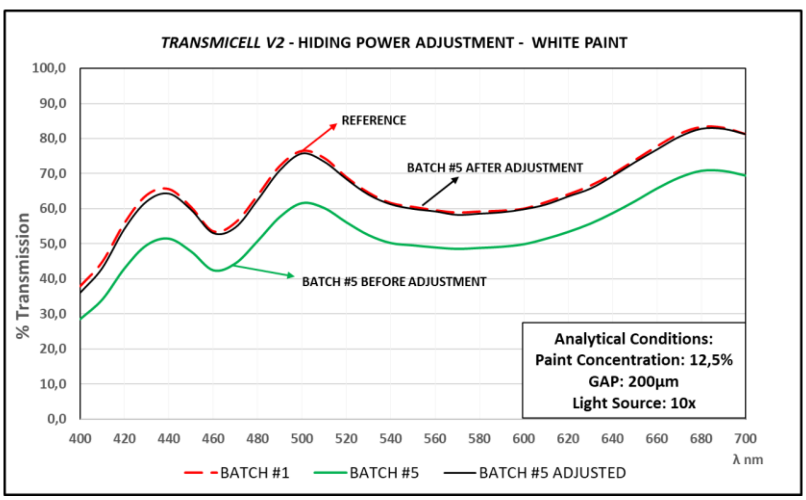

Figure 10 – Hiding Power Adjustment by Transmission

It can be seen in Figure 11 that the adjustment met expectations, remaining within the approval limit of the conventional method even after the correction. This demonstrates the sensitivity of the Transmission method, which allowed a precise adjustment and, in the same way, demonstrates that the contrast ratio method does not have inferior sensitivity compared to the new method.

Sample	%Transmission (peak)	%Contrast Ratio
Batch #1	83.37	90.35
Batch #5	70.73	93.61
Batch #5 Adjusted	82.76	90.22

Table 2 – White Decorative Paint General Results

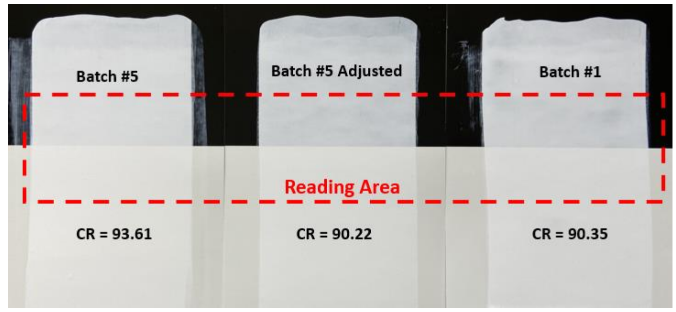

Figure 11 – Hiding Power Adjustment by Transmission read by Reflection

Practical Results of Using Wet Technology

The wet control technology using Transmicell equipment is already commercial and is in use by some industries in the Brazilian paint market. The data relating to the use of the wet methodology to adjust tinting strength were released (with identification confidentiality) by one of the companies using the new technology, where the benefits can be compared in relation to the conventional dry technique (Table 3).

Method	Total Analysis Time	Number of Coretions	Total Factory Adjustment Time	Analysis Accuracy
Dry	25 minutes	3	395 minutes	33,2%
Wet	10 minutes	1	40 minutes	92,2%

Table 3 – Results from a manufacturer using wet technology

Lead-time (total factory approval time) reduced approximately 10 times using wet technology. In the new method, just one TS adjustment is enough to release the product within a specification even narrower than the conventional one, with an assertiveness of 92.2%.

Stand-alone dispersion process control system and automated TS adjustment

The practical application project of the tinting strength wet measurement system consists of a dispersion control skid directly at the exit of the mills, using a process Transmicell, analyzing and processing the TS data from all mills sequentially. In this system, the dispersion of pigments is carried out by the mills and periodically a sample is sent through recirculating pipes to the Transmicell to check the level of dispersion (Figure 11).

The pigments continue to be dispersed in the mill until the %Transmission level of subsequent passes is observed to stabilize, which marks the ideal point of grinding and indicates that the maximum tinting strength of the pigment has been extracted.

Once the ideal level of dispersion has been reached, the tinting strength is automatically adjusted by adding the percentage of resin calculated by the equipment in order to reach the value stipulated as a

%Transmission standard, with the calculation being based on the response curve specific to each type of material in process.

The adjustment is carried out through a resin tank positioned next to the mills, in which the resin is transported to the mills through lines suspended from the skid. A recirculation system guarantees the homogeneity of the analyzed samples. Finally, a portion of the adjusted sample is read again in the Transmicell to confirm the adjustment and is then released for use.

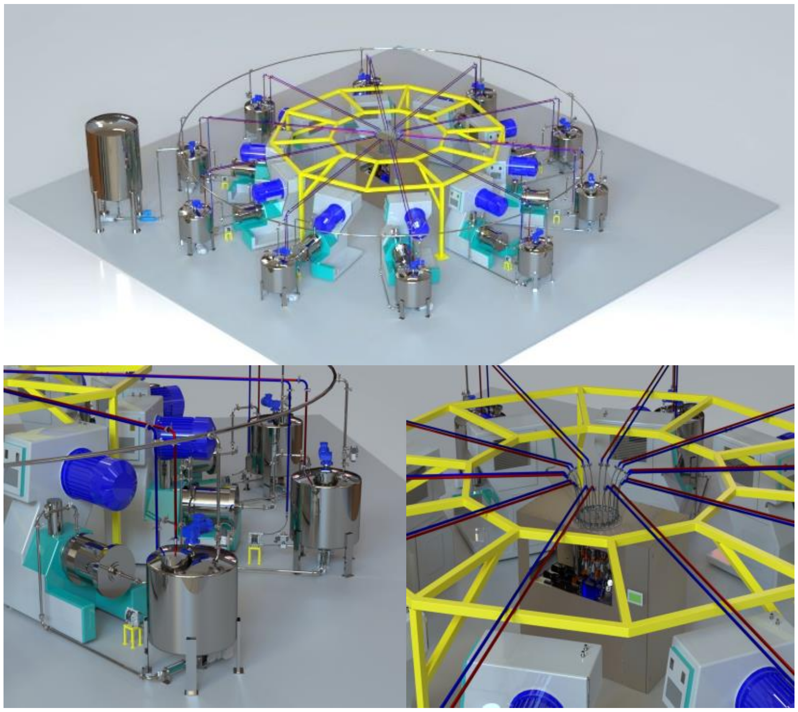

Figure 11 – Tinting Strength Automated Control and Adjustment Skid

Conclusions

In summary, the results of this study indicate that the tinting strength and hiding power adjustment methodology using transmission spectroscopy provided highly satisfactory results. In this way, the application of wet control technologies emerges as the key to the effective implementation of Industry 4.0 in the paint sector.

The reliability of this innovative technology, corroborated by repeatability and reproducibility studies of the equipment, offers substantial advantages, including reducing process lead time, minimizing rework and operational costs, increasing productivity, reducing variable costs and guaranteeing batch to batch quality, according to the data presented.

The use of transmission spectroscopy also opens the possibility of narrowing the approval range for pigment pastes, proving to be the most sensitive method for discriminating TS differences. In this case, such narrowing promotes a reduction in the variability of tinting strength between batches, allowing the production of paints without the need for major adjustments to the final color and, consequently, enabling the reduction of consumption of valuable raw materials, also contributing to environmental sustainability.

In the case of decorative paints, the possibility of sensitive control at the minimum limit of the coverage specification leads to lower variable costs, pigment savings and guaranteed quality constancy.

By using transmission spectroscopy to adjust the tinting strength, the paint industry can focus its efforts on quality control at the source, preventing rework by effectively adjusting tinting strength before formulating the final color. This approach not only saves resources and time, but ensures consistent quality over time, making it an essential tool for companies seeking to optimize their production processes and ensure customer satisfaction.

Given the results presented, it is possible to glimpse the transition of the paint industry to the 4.0 era, enabling access to full automation of the production process given the possibility of controlling properties in liquid form. In this case, it is possible to integrate data with intelligent systems (AI) and machine learning, creating a connected production environment, where machines can learn and adapt automatically, in order to continuously optimize the process.

The adoption of transmission spectroscopy represents a significant advance, placing paint manufacturing on a new level of competitiveness and productivity, while also being aligned with cleaner and more sustainable production principles. The implementation of the method proposed in this study therefore represents a significant step towards these objectives, signaling a promising future for the paint industry.

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