Use of specific equipment that uses the Transmission of Light technique to adjust the Tinting Strength in pigment dispersions and its influence on the variability of the final color through the measurement of CIELAB coordinates

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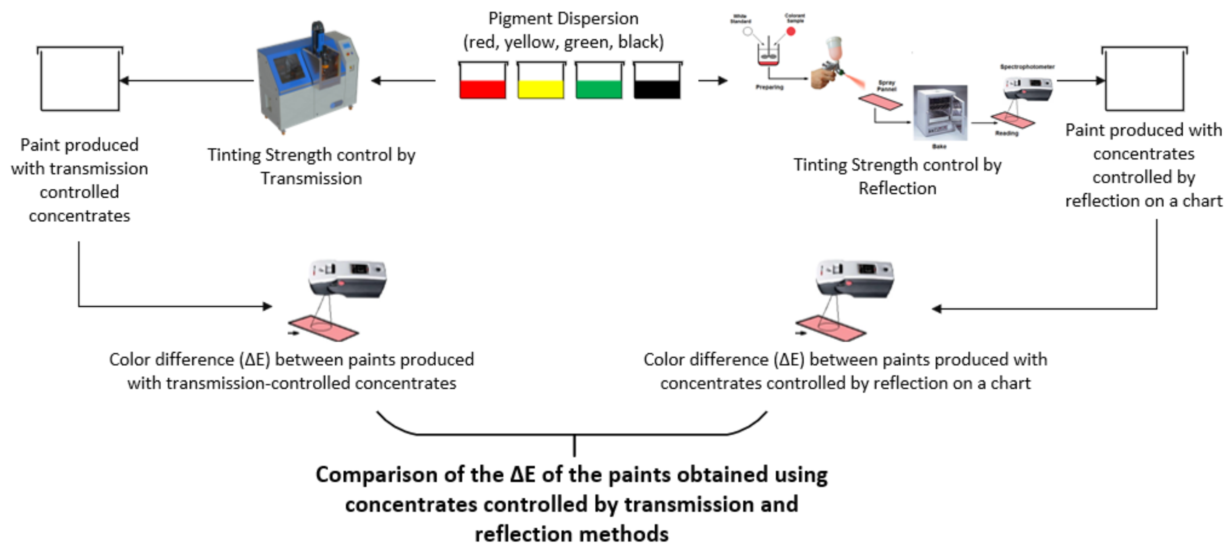
Introduction

This work consists of controlling the tinting strength in pigment dispersions through two different methods of analysis of this property and measuring the impact on the final color of paints produced from these dispersions. The tinting strength control methods used in this paper are the conventional method (blend with standard base, application in drawdown chart and measurement by reflection spectroscopy) and a new method for adjusting the tinting strength, which uses transmission spectroscopy on samples *in natura* using specific equipment called *Transmicell*. The following flowchart illustrates the procedures performed for the production of paints and the comparison of the final colors.



Key-words: pigment dispersion; tinting strength; paints; transmission; reflection; adjustment of color; new technologies; color difference ΔE; sensibility; pigment dispersions control.

Assumptions

The color measurement and evaluation process were carried out following current regulations and using a DATACOLOR Check 3 reflection spectrophotometer. Color differences were calculated using the CIEDE2000 system. The reflection measurements and the drawdown chart extensions performed were tested in triplicate and the transmission measurements correspond to an average of at least three consecutive readings. As the objective of the study was to evaluate only the influence of dispersions of colored pigments, the tinting strength of the bases used for the formulation of paints was kept constant.

Reflection Technique for Tinting Strength Control in Pigment Dispersions

The conventional measurement of the tinting strength of a pigment is normally carried out by measuring the light reflection spectrum of the material applied on a standardized drawdown chart, this material being a blend in specific proportions of the dispersion of that pigment with a standard base. The application of this blend must be carried out in standardized and low-absorption drawdown charts, allowing the reading of an equally thickness of the film. Currently, there are several standards that regulate this procedure, including ISO 787-16 and ASTM D4838-88.

For the analysis of the tinting strength of chromatic pigments, the standard base is generally a dispersion of titanium dioxide, where this property has been previously adjusted. For the production and standardization of the white bases, preset bases of green, blue or black pigments are also used, which had other TiO_2 bases as a previous reference standard. Because the standard white base has been patterned with a green, blue or black base, which in turn has been patterned with another white base, there is a gradual degradation in the quality of these patterns. In this way, cumulative deviations are generated in the tinting strength adjustments over time This is due to the difficulty of producing a stable and unalterable primary standard that can be used to reference property.

The big problem with the method of controlling the intensity of tinting strength by reflection on the drawdown chart is the low sensitivity, associated with low repeatability and reproducibility. Given these circumstances, the specification range for product approval must be relatively wide to contain the variability of the measurement method itself, leading to false-positive and false-negative results if it is too narrow. It can be said that a wider range of properties leads to the use of more raw material than necessary and, in this way, ends up producing, on average, batches with an excessive amount of pigments, which, in addition to causing unnecessary color adjustments, add variable costs undesirable for the process.

Light Transmission Technique for Tinting Strength Control in Pigment Dispersions

The principle of the technique consists of quantifying the portion of light transmitted through a pigment dispersion film and thus extracting optical information that can be used to evaluate different dispersion properties, such as the tinting strength, hiding power, etc. Thus, the use of standard bases to measure the tinting strength becomes unnecessary, as the standardized light of the spectrophotometer, under specific and well-controlled conditions, is used for this purpose.

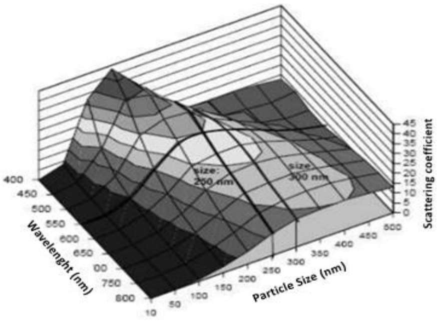
Usually, the tinting strength presents a behavior directly proportional to the opacity of the medium, in physical terms, is the measure of the occlusion to the passage of visible light. Thus, it is possible to state that a dispersion of pigments with high opacity will transmit a low amount of light, the rest being absorbed, reflected or scattered.

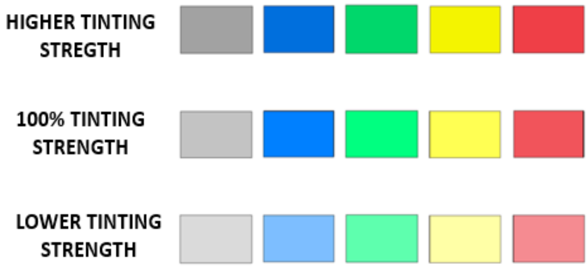
It is known that, in a dispersion of pigments, the smaller the particle size, the greater the sum of the surface areas and thus more light will be blocked by the dispersion film, which is totally consistent in physical terms. Therefore, a lower degree of dispersion transmission is directly related to a higher tinting strength. However, there are cases where the opposite behavior is observed, where the light transmission is inversely related to the tinting strength. This phenomenon is related to the particle size which, when less than about 200 nm, presents a reduction in interaction, behaving like a translucent pigment and conferring low opacity when analyzed by transmission. Pigments with this behavior will not be covered in this paper, but they can be controlled by transmission in a similar way.

When the particle has a very large size, as for example at the beginning of the pigment dispersion process, there is also a weak interaction of light with the available surface area. 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 the highest tinting strength.

The tinting strength directly interferes with the final color tone, which can be more intense when using products with greater strength and lighter when using products with lower tinting strength. This property turns out to be a systemic problem, as it concerns the ability of one medium to dye the other and to originate paints of different shades and intensities, thus demanding a long adjustment time to reach the ideal specifications.

The image on the left illustrates the particle size distribution and their behavior regarding interaction with light along the spectrum from 400 to 800 nm. The image on the right shows the variation caused by three pigment dispersions with different strengths.

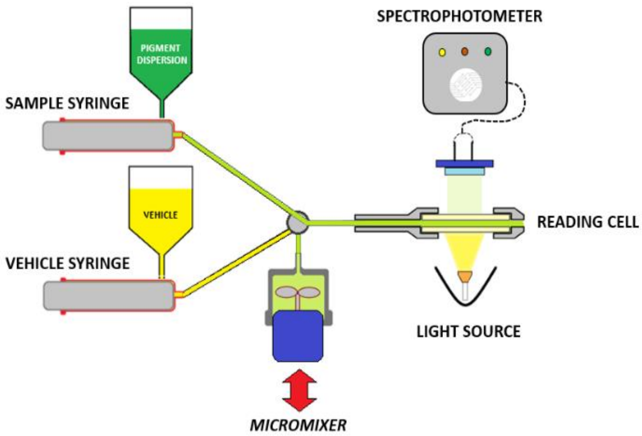




Transmicell

The equipment used to carry out measurements and control of pigment dispersions by transmission is disruptive in the world, and is called *Transmicell.* The equipment is patented *PCT/BR2019/050381* with all rights reserved to *RMA Industrial Technology Ltd*. In short, the principle of the equipment consists of seeking a specific analytical condition for each product in order to allow a beam of light to radiate on a sample film and the generated spectrum of the transmitted light to be analyzed and compared with a standard, providing parameters for the comparative determination of tinting strength and also other properties.

The figures below correspond to the *Transmicell* equipment, used in the transmission analyses, and the illustration of the tinting strength reading process.

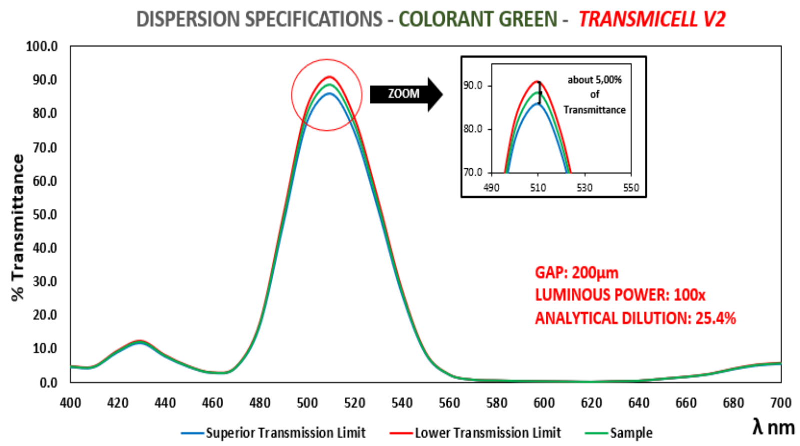


In order to obtain an optimal level of interaction between the incident light and the film of the material to be analyzed, the equipment uses three degrees of freedom, namely: optical path length, light power and analytical dilution, performed automatically by the equipment at the time of reading. High-precision syringes are responsible for controlling the dilution, a chamber with mechanical agitation (micromixer) is responsible for homogenizing the mixture and, finally, a spectrophotometer measures the light transmitted from the sample.

The analytical dilution is carried out using an analytical vehicle completely compatible with the dispersions used, so that it does not produce instabilities or interferences in the measurement, thus guaranteeing that any interactions captured by the spectrophotometer come only from the interaction between the pigment particle and the incident light. Most of the time, the base resin of the dispersion formulation itself acts as an analytical vehicle, as it guarantees the constancy and compatibility with the dispersion that are necessary for the analysis. At the end, the machine performs an automatic cleaning in order to decontaminate the entire reading system so that it does not interfere with the subsequent measurement.

The sample is analyzed in liquid form, *in natura*, through sapphire windows, automatically and without the need for previous treatments, which leads to excellent reproducibility and repeatability values, proven through a Gage R&R study resulting in a value close to 15% with the help of statistical software. This is an excellent result, considering the robustness and sensitivity of the equipment, thus indicating that it is suitable for evaluating the tinting strength and much more accurate than the conventional methodology.

During transmission analysis, unlike the conventional technique, the value of interest is the transmittance at the peak wavelength, where there is greater sensitivity and less signal-to-noise interference. Below are presented three transmission curves of green pigment dispersion and their respective analysis parameters. The lower and upper curves correspond to the transmittance control limits on the *Transmicell* for this pigment dispersion that will be used in this work.



Methodology and experiment

The pigment dispersions used in this paper can be divided into two groups: the first corresponds to dispersions that were approved through conventional control method within their 95% - 105% tinting strength limits, widely used by industries, and the second by the limits of the method of transmission, specified by the authors and in use in the market by the manufacturers that adopted the technology.

It must be realized that the approval limits should contain, in addition to the acceptable variation in product quality, the measurement variation of the method. In the case of analysis by reflection, repeatability and reproducibility are low due to the excess of manual operations and variables involved in the analysis, which requires a wide range for product approval, in this case 10 percentage points.

In transmission analysis, the sample is analyzed in liquid form, quickly and automatically, not requiring previous treatments, which, in addition to the greater sensitivity of the method, produces much greater repeatability and reproducibility, as previously mentioned. In this way, it is possible to work within a much narrower approval range, as the measurement variability of this new method is extremely small.

The transmission presents different behaviors depending on the optics and morphology of each pigment in question, and for white color dispersions, the approval limits correspond to ± 1.5% of transmittance at the peak. When dealing with chromatic pigments, the specification limit is ± 2.5% in transmission and for black pigments, which have a high response in optical terms, they have a specification range of ± 3.0% in transmission.

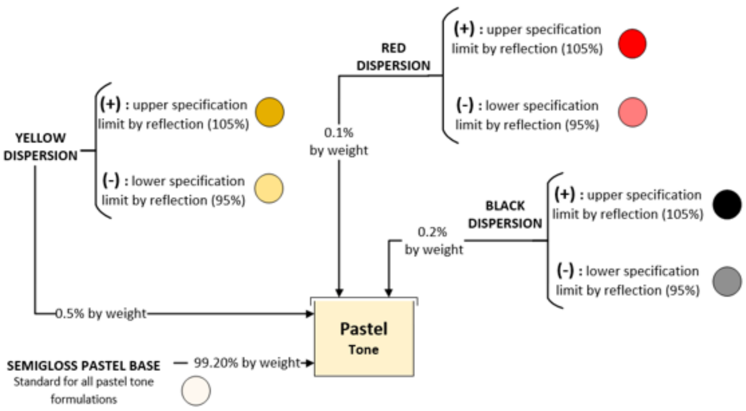
It should be noted that the variations observed in the different methods are not proportional and also do not have a direct relationship. For example, a variation of one point in the tinting strength by reflection on the drawdown chart can generate a response of four points in transmission, due to the high sensitivity of the wet method, which allows the narrowing of the approval range of pigment concentrates and consequent reduction of over-quality and gains in variable costs.

The colors formulated from the dispersions were chosen in order to contemplate three colors of different intensities, one pastel, one medium and the other intense, thus making the colors produced have representativeness in relation to the colors used by the industry, in addition to having distinct hue in the visible spectrum. In addition, a specific white base was used for each tone, keeping their tinting strength constant as a standard. Each of these bases was perfectly homogenized and stored under controlled conditions so as not to produce any variation in the tests carried out.

The composition of each final color is represented in the table below, as well as the application of the three tones evaluated in the drawdown chart.

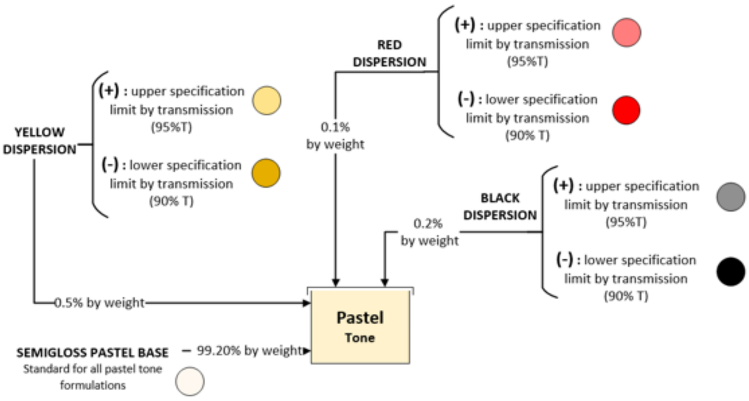
Paint Composition	Oxide Yellow (%)	Oxide Red (%)	Black (%)	Green (%)	Semigloss Pastel Base	Semigloss Mid Base	Intense Base
Mix pastel tone	0.50	0.10	0.20	-	99.20	-	-
Mix mid tone	5.00	-	1.60	3.00	-	90.40	-
Intense tone	5.00	8.00	1.50	-	-	-	85.50

Below is a visual explanation of all the procedures carried out for the production of paints, where an experiment plan was applied to schedule the test batteries for controlling the intensity of tinting strength by reflection and transmission, respecting the operational control ranges for each methodology. Thus, paints were produced containing all possible combinations of dispersions within the lower (-) and upper (+) limits of the specification, totaling 16 samples of each tone, with 8 combinatorial experiments having been designed for each control method.



Mixture A - Pastel Tone - Reflection Control

Sample	Red	Yellow	Black
Sample 1AR	+	-	+
Sample 2AR	+	+	+
Sample 3AR	-	+	+
Sample 4AR	-	-	+
Sample 5AR	+	-	-
Sample 6AR	+	+	-
Sample 7AR	-	+	-
Sample 8AR	-	-	-



Mixture A - Pastel Tone - Transmission Control

Sample	Red	Yellow	Black
Sample 1AT	+	-	+
Sample 2AT	+	+	+
Sample 3AT	-	+	+
Sample 4AT	-	-	+
Sample 5AT	+	-	-
Sample 6AT	+	+	-
Sample 7AT	-	+	-
Sample 8AT	-	-	-

The experiments for the mid and intense color paints followed the same procedures as the pastel color, also generating 16 samples for each tone, as already presented previously.

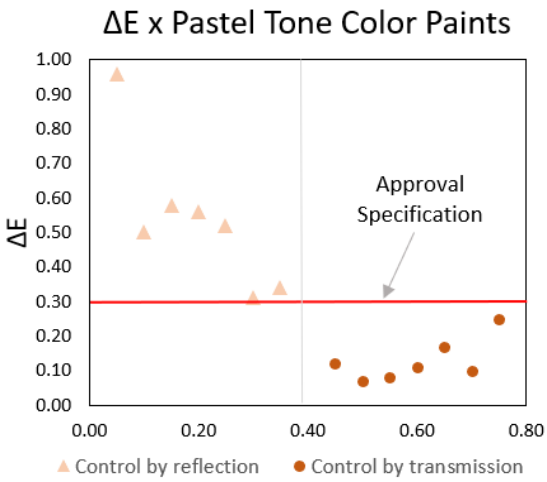
Results

The following tables present all the results of colorimetric measurements of the paints produced from the dispersions controlled by the two methods.

Mixture A - Pastel Tone

Sample	ΔE[1] reflect.	ΔE[2] reflect.
Sample 1A	0.96	0.12
Sample 2A	0.50	0.25
Sample 3A	0.58	0.07
Sample 4A	0.56	0.08
Sample 5A	0.52	0.11
Sample 6A	0.31	0.17
Sample 7A	0.34	0.10
Sample 8A	reference	reference
Average	0.54	0.13
Standard Deviation	0.21	0.06

ΔE[1]: Samples produced by pigment dispersions controlled by reflection and final color measured by reflection.
ΔE[2]: Samples producted by pigment dispersions controlled by transmission and final color measured by reflection.



Analyzing the pastel tone, it is observed that in the control by reflection the biggest difference found in the ΔE was 0.96 while in the control by transmission the major difference was only 0.25. The samples used as reference have the same formulation, differing only in the strength control method of the formula dispersions.

Observing the average of the results, it is possible to observe that the ΔE average difference values were reduced about four times in the samples where the transmission control was used. The standard deviation indicates that the variation around the mean also reduced significantly, thus ensuring paints with less variability when using transmission control.

It is possible to verify that all samples that were produced from the transmission control remained within the acceptable value for approval, thus completely eliminating color adjustments for tints possible through this control technology. The distribution of transmission samples was also much more observed and consistent when it came to reflection.

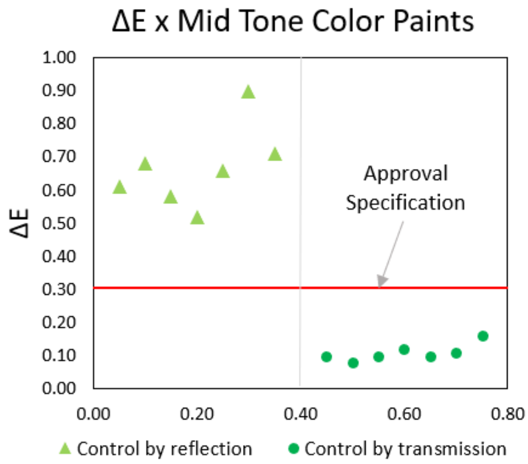
The tinting strength controlled by reflection, for the same series of samples, showed all the results of ΔE above the tolerable value of the specification and a high heterogeneity regarding the distribution of the samples. Thus, it can be stated that in all samples of the pastel tone color adjustments would be necessary for the specification to be achieved.

The results of mid tone color results are shown in the following figures.

Mixture B - Mid Tone

Sample	ΔE¹ reflect.	ΔE² reflect.
Sample 1B	0.61	0.10
Sample 2B	0.68	0.16
Sample 3B	0.58	0.08
Sample 4B	0.52	0.10
Sample 5B	0.66	0.12
Sample 6B	0.90	0.10
Sample 7B	0.71	0.11
Sample 8B	reference	reference
Average	0.67	0.11
Standard Deviation	0.12	0.03

ΔE¹: Samples produced by pigment dispersions controlled by reflection and final color measured by reflection.
ΔE²: Samples produced by pigment dispersions controlled by transmission and final color measured by reflection.



The mid tone presented a maximum value of ΔE of 0.90 for the control via reflection and 0.16 for transmission, both from the same reference sample. According to the average values obtained, the difference in color was reduced about six times when control by transmission was used. The standard deviation shows that the variation range has been narrowed by about four times, thus ensuring excellent color homogeneity in paints produced through transmission-controlled dispersions.

It is possible to observe that all samples presented ΔE values much lower than the maximum tolerable value. In addition, there was great homogeneity between the recorded values, representing a great technical gain.

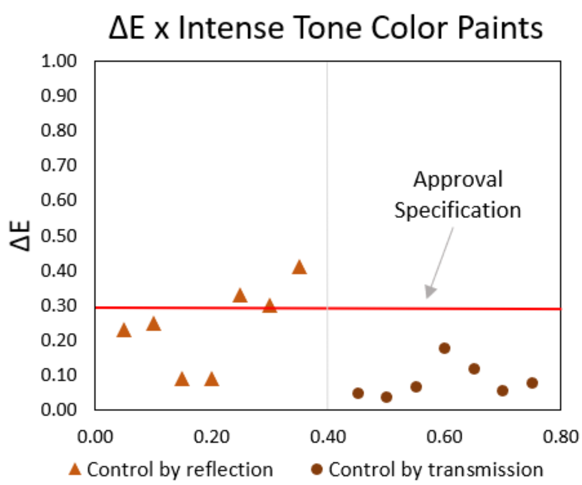
The reflection control showed unsatisfactory results, since all ΔE values are far above the acceptable limit and therefore failed, indicating the need for adjustments in all samples.

A similar behavior was obtained for the intense tone, presenting a ΔE about three times smaller in the samples controlled from the transmission when compared to the reflection.

Mixture C - Intense Tone

Sample	ΔE¹ reflect.	ΔE² reflect.
Sample 1C	0.23	0.05
Sample 2C	0.25	0.08
Sample 3C	0.09	0.04
Sample 4C	0.09	0.07
Sample 5C	0.33	0.18
Sample 6C	0.30	0.12
Sample 7C	0.41	0.06
Sample 8C	reference	reference
Average	0.24	0.09
Standard Deviation	0.12	0.05

ΔE¹: Samples produced by pigment dispersions controlled by reflection and final color measured by reflection.
ΔE²: Samples produced by pigment dispersions controlled by transmission and final color measured by reflection.



The reduction in standard deviation also shows a substantial reduction in deviations from the mean, thus ensuring a much narrower range when evaluating color difference values. Control by transmission in the intense tone also showed satisfactory results, and all samples would be approved within the specification limit of ΔE, so that color adjustments were not necessary.

As expected, in the reflection control, half of the samples were within the color specifications and the rest would require color correction.

Once the analyzes were completed, it was found that the control of pigment dispersions using the transmission technique resulted in paints with a substantially smaller final color variation.

Conclusions

Based on the results of the experiments carried out and the results obtained, we can conclude the following:

The control of the tinting strength in pigment dispersions, through the transmission technique in specific equipment, has a direct impact on the color results in terms of CIE2000 colorimetric coordinates, thus drastically reducing the color differences (ΔE) for paints produced from pigment dispersions that were controlled with this new technology.

The control of the dispersions carried out by the chart method within the specification ranges used by the market (95% - 105%), demonstrated a great operational inefficiency, since the great part of the paints obtained from these dispersions of pigments and approved through this method, ended up significantly exceeding the approval limit for the color evaluated via ΔE, requiring further adjustments to reach the color specification. This fact is observed in practical terms in the day-to-day of the paint industry and its main cause is the low sensitivity and poor R&R of the reflection technique to control the tinting strength in the drawdown chart, currently used by manufacturers, according to ASTM D4838-88.

All paint samples produced from controlled dispersions via transmission obtained ΔE values lower than 0.3 in their entirety, having been approved without the need for corrections. There was a reduction in the average value of the color difference for the pastel tone of four times, six times for the medium tone and about three times for the intense tone, and the significant reduction in the standard deviation in all tones demonstrated that the homogeneity and constancy of the measured color difference values were exceptionally better when compared to the conventional technique.

Bearing in mind that this study analyzed the effectiveness of two different techniques for controlling the tinting strength of colored pigment dispersions, keeping the white bases constant during all tests, it is to be expected even greater amplitudes in the color variability caused by variations in the tinting strength controls these white bases. This additional factor, not explored in this study, corroborates the thesis that a more accurate and reproducible adjustment of the tinting strength through the transmission technique, not only directed to the pigment dispersions, but also to the white bases, can promote the elimination almost total stage of color adjustments in paint factories.

It is also mentioned that, with the reduction or even elimination of adjustments in the colors of paints produced through bases and pigment dispersions controlled through the tinting strength control technique by transmission, in addition to the improvement of quality consistency batch by batch and its reflexes in reducing fixed control costs, one can easily predict a significant reduction in variable manufacturing costs resulting from possible narrowing of the tinting strength specification ranges, since in the current scenario the activities of color adjustments by adding pigment dispersions, when end result in additional hiding power that normally is not adjusted and it is not paid by the customers.

In addition, the transmission technique uses in natura analysis material, making it possible to reduce the tinting strength measurement and adjustment time by around 90%, resulting in productivity gains, lead time reduction and the elimination of a series of operations units associated with the conventional technique by the reflection method, such as weighing, flash-off, film extension, curing time, etc., all operations that contribute to the bad gage R&R of this methodology.

The color adjustments elimination resulting from the narrowing of tinting strength approval ranges also impacts on the systemic reduction in the consumption of raw materials, mainly in the amount of pigments needed for the production of paints, consistently reducing the environmental footprint resulting from manufacturing of these inputs that have a high contribution in the chain of pollutants and contaminants generated by the industries that produce these materials. Mention is also made of the high reproducibility of colors in in-store tinting systems (mixing machines) when using transmission-controlled products, thus ensuring a high quality in terms of color reproduction for the manufacturer.

The development of technology for adjusting properties through the Transmission technique, enabling the measurement of complex properties such as tinting strength and hiding power, with superior sensitivity and reproducibility, for materials in their liquid form and still in natura, opens a new moment for paint manufacturers, allowing them to enter in the Industry 4.0 era, as these analyzers can be incorporated and integrated directly into production lines, controlling processes with a high level of automation in real time.

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