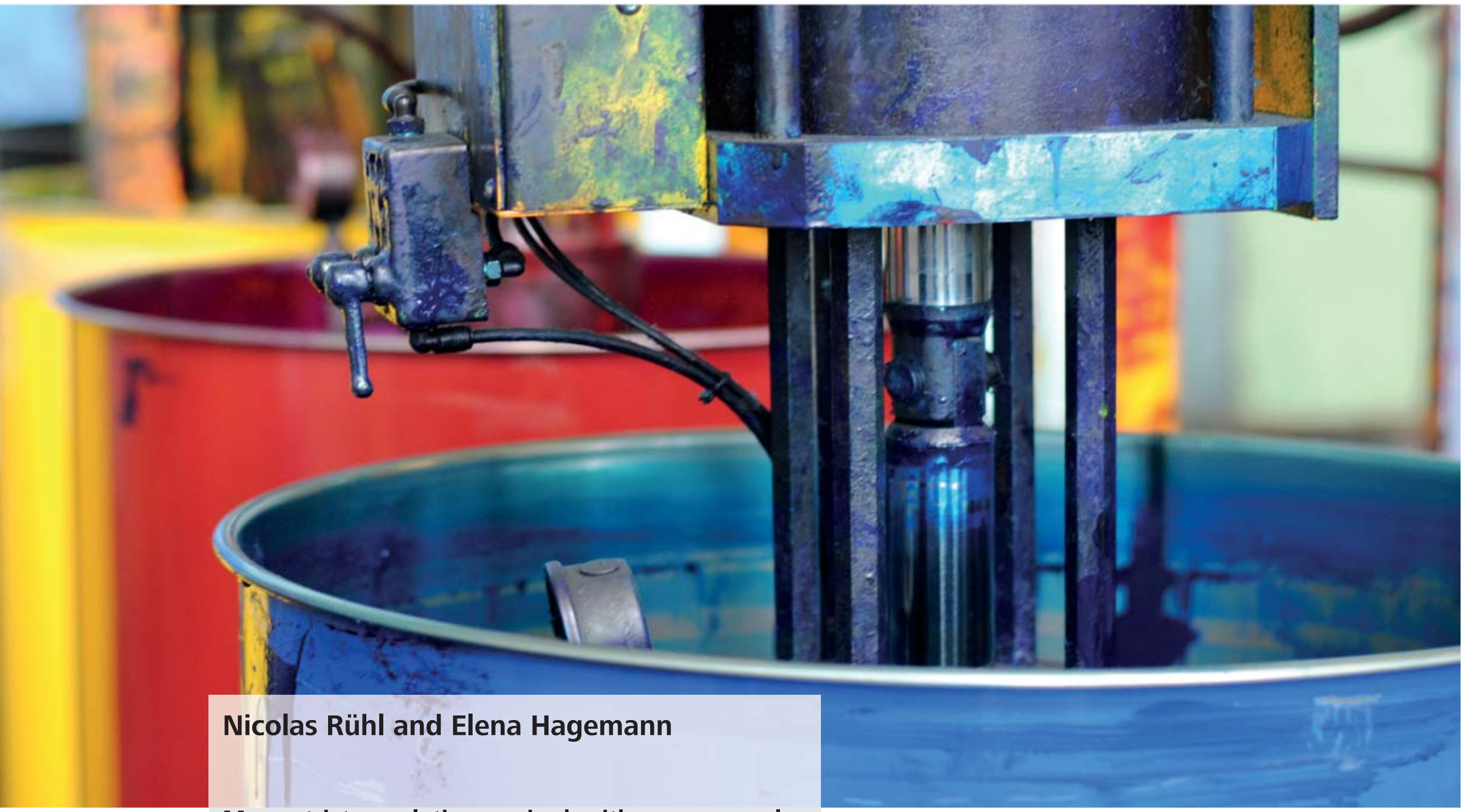
Metrohm White paper

Sustainable Testing of Paint and Coatings



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More strict regulations paired with more complex products have increased testing complexity in the paint and coating industry. Therefore, producers ask for more powerful, safe and sustainable analytical methods. Testing by Vis-NIR spectroscopy is a sustainable and cost efficient alternative to many wet chemical methods. This white paper describes how Vis-NIR spectroscopy improves testing procedures for various analyses during the formulation and production of paint and coatings in an economic and ecological way.

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Paint and coating industry – A growing field

Paints and coatings make our life more colorful, safer, and easier. The importance of this industry is reflected by the steady growth of its annual production. From 2007 to 2012, the worldwide compound annual growth rate of the coating industry in GDP was 4.3% with a revenue of 110 billion USD for 2012.[1] As a result of a strong demand especially from Asia Pacific, Eastern Europe, and Latin America, a worldwide increase in growth to 6% by 2019 is predicted.[2]

The main reason for the importance of paints and coatings is the diversity of application possibilities. Paints and coatings are not only used to beautify substrates but also for protection, as anti-skid surfaces, for insulation, or as electrical conductors, to name just some examples. To cover this variety, complex formulations are created, which consist of four main components: solvents, binders, pigments, and additives. The individual amounts of these can vary significantly. For the group of powder coatings, for example, solvents are not needed (see figure 1).

Only after the smart combination of these main components, a product with specific functions according to the user needs is formulated and produced. To guarantee best results, a reliable and fast-performing quality control is essential. This, hoewever, becomes more and more challenging as product complexity increases.

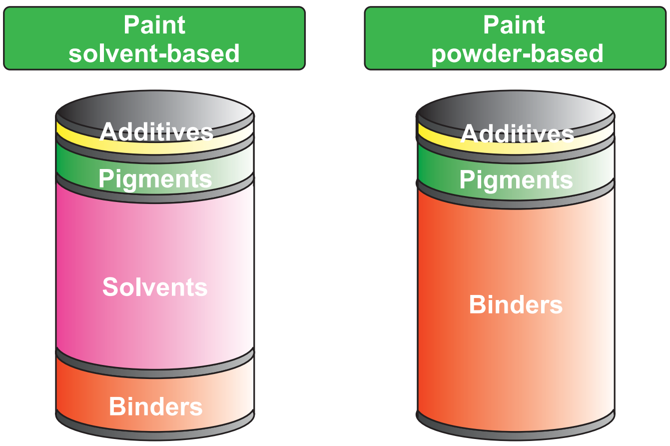

Figure 1. Overview of ingredients and possible amounts of sovent-based and powder-based coatings.

Quality control – Essential at every step

To ensure an optimal end product, quality control has to take place throughout the entire manufacturing process. The individual production steps have different requirements regarding analysis. Three main production steps with different analysis requirements can be defined:

High throughput is key in the warehouse

In the warehouse, the incoming raw materials for the production of the paints and inks have to be identified and validated with respect to quality and purity. Analytical methods that help to substitute time-consuming wet chemical procedures should be used preferably in order to fulfill the demand for high throughput.

Precision and accuracy for successful production

During the steps of formulation and production, the quantity of several characteristic values is set and the identity of the intermediates is tested. These control mechanisms are performed atline (next to the process) as well as online (in a process bypass). Precision and accuracy are key parameters in these steps. An analytical method should be selected accordingly.

Complex matrices demand powerful methods

Prior to delivery, the last but nevertheless very important step in quality control is the final testing. To assure best product performance at the customer site, all relevant properties and the general quality have to be confirmed. As the multiple components of the end products give rise to complex matrices, final testing can turn out to be a very ambitious task. Therefore, a combination of different analytical instruments is necessary to obtain reliable results.

Many parameters – A challenging task

Producers have the possibility to use instrumental as well as wet chemical methods, which are both used throughout the complete production process. As a reference, the standard operating procedures described in the ASTM methods can be used (see table 1).[3] This small section alone shows that many different analytical instruments and methods are required, resulting in major training effort for employees.

Wet chemical analysis – A long tradition

Typical wet chemical analysis methods include, e.g., titration, ion chromatography, and colorimetry. All of them are highly precise and accurate. Because of their long-standing importance as analytical tools, they are also well studied and abundantly described in the literature. However, these techniques are generally restriced to certain parameters. Furthermore, additional costs arise for auxiliary chemicals needed for sample preparation and the analysis itself. The implementation of the strict safety regulations and the regular training of employees further add to the bill. Therefore, the search for alternative instrumental methods has been trending. Instrumental methods can be carried out with only minor training while also being fast and requiring less auxiliary chemicals. These advantages are especially true for Vis-NIR spectroscopy.

Table 1. Overview of ASTM Methods for different key parameters and the corresponding methods and instruments.

Parameter	Instrument/method	ASTM Method
Density of liquids	Pycnometer	ASTM D1475
Water in paint	Titration	ASTM D4017
Particle size	Oil adsorption of a pigment	ASTM D1483
VOC content	Chromatography	ASTM D6886
Powder Coating	Colorimetry	ASTM D3451
Viscosity	Rotational viscometers	ASTM D2196

Vis-NIR spectroscopy – A simple solution

The visible-near-infrared (Vis-NIR) technology is an established analytical method in the chemical, pharmaceutical, and food and feed industries. Its high precision and reliability have led to a continuous expansion to many different application fields. The high flexibility of Vis-NIR spectroscopy, which is reflected by its versatile uses in process analysis as an inline, online, at-line, and offline tool, has also contributed to this expansion.

Functionality of Vis-NIR spectroscopy

The measurement principle underlying Vis-NIR spectroscopy is based on a nondestructive interaction between light and matter. This interaction is used to determine various physical and chemical parameters within one measurement, which typically takes only a few seconds. The combination of visible and near-infrared light allows to determine information related to the color of the sample as well as information linked its chemical side groups.

Economical and ecological

Vis-NIR spectroscopy achieves a high throughput by detecting multiple parameters in a single measurement. In addition, it fulfills economical as well as ecological criteria. As sample preparation is required for neither liquid nor solid samples and analyses are nondestructive, the need for expensive auxiliary chemicals is eliminated while, at the same time, safety is improved and costs are reduced. Especially for the emerging field of powder coatings that are in better compliance with volatile organic compounds (VOC) regulations, Vis-NIR spectroscopy as a nondestructive, ready-to-use technique shows great promise.

Pigments

The process of beautification is the most obvious application of paints and coatings. Present in a concentration range of 0–30%, pigments are among the central ingredients in the majority of paints and coatings. In addition to the color effect and intensity, pigments are also responsible for the opacity, coating thickness, and the gloss of the coating.

It is not only the chemical, but also the physical structure of the pigments that determines their properties. These are the crystallinity, the particle size, and the particle distribution. DIN 5943 groups pigments according to their chemical structures and their optical effects: The first level of classification groups pigments into inorganic and organic pigments. At the second level, they are further grouped into white pigments, colored pigments, effect pigments, and luminous pigments.

To obtain the desired properties in the end product, it is not only important to select the appropriate pigments, but also to get the pigment concentration right. Coating layer thickness and color intensity are both influenced by the total pigment volume concentration (PVC), which relates the volume of pigments to the volume of all solids.[3] In addition to the PVC, the relationship between binder and pigment concentration is crucial. This parameter known as CPVC (critical pigment volume concentration) is critical to determine, as a shortfall results in a loss of paint stability and strength.[3]

Therefore, determination of the pigment concentration is crucial. The analysis by Vis-NIR spectroscopy is presented in the following section.

Quantification of dye content in inks

Triphenylmethanphenazin and azo dyes are typically used for ball pen inks. Besides the dye itself, such inks consist of multiple ingredients which are, for example, solvents to prevent clogging and surfactants to avoid foaming. This complex matrix can make the evaluation of the absolute dye content a challenging task.

In application note AN-NIR-026, 20 ink samples where investigated with respect to the concentration of blue ink dye in ball pens.[4] The examined concentration range was between 0.56% and 4.56%. Figure 2a) displays a selection of the spectra. The information extracted from these were associated with the values from the primary method, which resulted in a high correlation as displayed in figure 2b).

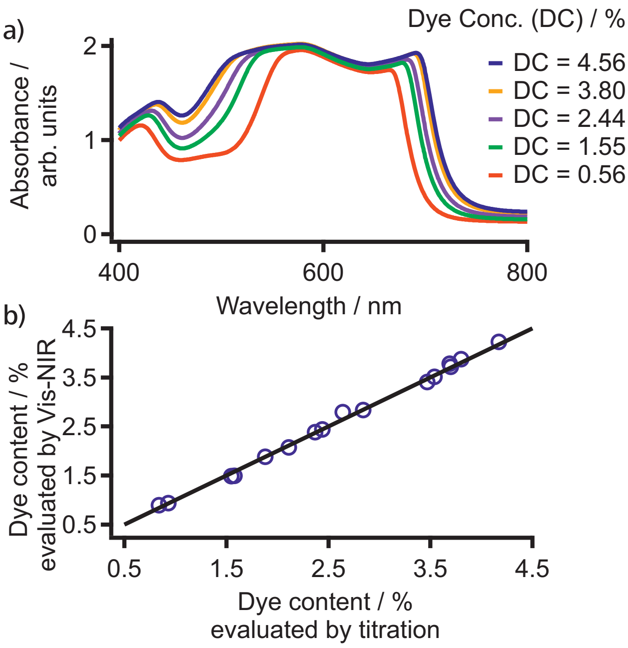

Figure 2. a) Exemplary spectra for five different dye concentrations which are typically used for ball pen inks. The visible region 400–800 nm displays a high correlation between the dye quantitity and the absorbance of the sample.
b) Correlation plot of dye content determined by Vis-NIR spectroscopy and titration. Beside the high correlation of $R^2 = 0.99$, the standard error of validation was < 0.1% with two factors used.

Additives

Though the total amount of additives in paint and coating formulations is only minor, additives are the key means to modify notably properties of paints and coatings for specific applications.

Besides these product-specific additives, which are only present in small concentrations, three main additives are almost always part of paint and ink formulations: paint driers, surfactants, antioxidants. These control important product properties such as drying time, durability, processability, sprayability, and brushability.

As minor changes in the amount of additives used can substantially change the behavior of the final product, multiple chemical and physical properties of every additive underlie high quality standards. Table 2 presents a summary of typical parameters of paint driers and their limits defined by ASTM.

Table 2. Overview of relevant parameters and respective limits for quality control of paint driers according to ASTM.[3]

Parameter	Specification	ASTM Method
Specific gravity / -	±0.05	ASTM D1289-85
Solid content / %	±5.00	ASTM D1644
Metal content / %	±0.30	ASTM D2373-85
Dynamic viscosity / mPas	±1.00	ASTM D2196

As a method that can be used to determine multiple parameters within one measurement, Vis-NIR spectroscopy is a valuable tool to support quality control. The following section describes the use of Vis-NIR spectroscopy for additive analysis. The important additive class of paint driers is used for this demonstration.

Multiple parameter analysis of paint driers

Paint driers are an essential part of nearly every paint or coating product because they are able to modify the drying process of paints and coatings.

The drying process can be divided into two steps: The first step is the physical process where the solvent evaporates. The second step is the chemical process where the binder undergoes an oxidative crosslinking reaction. Paint driers, which are metal ligand complexes, accelerate significantly the second step and reduce the coating time from multiple hours to minutes. However, the catalytic function depends strongly on the total metal amount, where even slight shifts to higher or lower concentrations change the behavior considerably.[5] As a result, it is of high importance to quantify precisely the concentration during production. The most commonly used paint driers are cobalt octoate complexes. Formulations made with these additives are examined with respect to the metal content, viscosity, and specific gravity, which can be evaluated within one measurement with Vis-NIR spectroscopy as shown in AN-NIR-033 (see figure 3).[6]

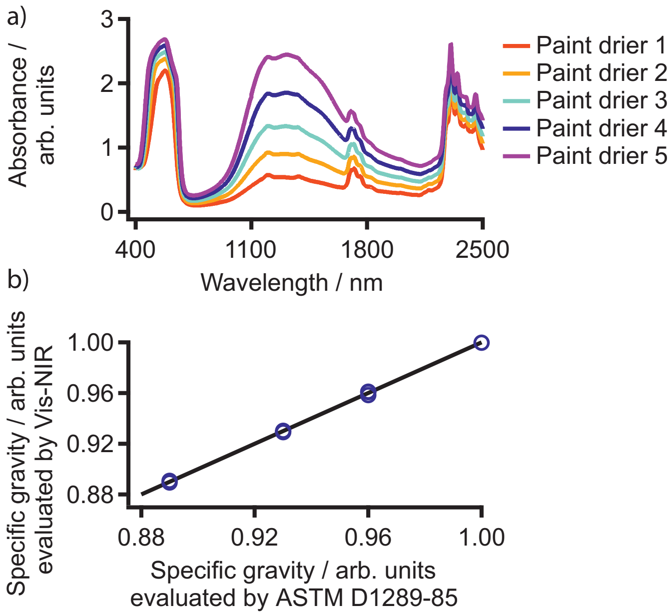

Figure 3. a) Exemplary spectra for different cobalt octoate paint driers. b) Correlation plot of values for the physical parameter viscosity obtained according to ASTM D1289-85 and measured by Vis-NIR spectroscopy.

Binders

As mentioned in the previous section, the concentration ratio of binders and pigments (CPVC) can strongly affect the stability of the final coating. Binders are responsible for making a coating solid and enduring. Binders undergo a chemical cross-linking reaction during the drying process. As this fixation of the coating on its substrate is absolutely essential, binders are the most important ingredient of every paint and coating product and are present in every coating and paint formulation, in contrast to pigments and solvents.

The most prominent representatives of binders are polymeric substances such as polyurethanes, polyamides, polyester, or epoxy resins (see figure 4). These synthetic resins have replaced the formerly used natural resins completely.

The binder affects not only the CPVC, which controls the hardness and the adhesion of the final product, but also the viscosity.[5] In addition to these direct influences, free amines in qualitatively poor polyurethane binders can negatively affect certain coating procedures. The example in the following section shows how Vis-NIR spectroscopy can support the process of quality control by detecting free amines in paints and coatings reliably.

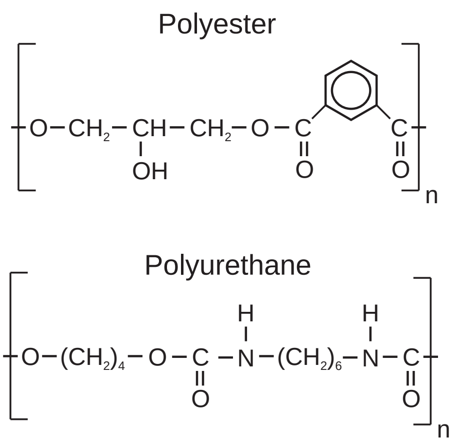

Figure 4. Chemical structures of two typical binders used in paints and coatings.

Quantification of amine value in dipping paints

A commonly used method to apply uniform coatings is the elctrodeposition process (EPC) for dipping paints. The main advantage of this process is that the thickness of the coating can be controlled with high precision even for difficult structures.

Because EPC is an electrochemical process, interfering redox-active molecules can negatively affect the coating result. These interfering molecules can occur as residuals from other coating constituents, e.g., free nitrogen as a residual impurity of the used binder.

Application Note AN-NIR-030 describes the use of Vis-NIR spectroscopy for the quantification of the amine number as an indicator for free nitrogen in dipping paints.[7] In the concentration range of 33.82–48.31 mmol/kg, a correlation of $R^2 = 0.97$ with five PLS factors was found (see figure 5).

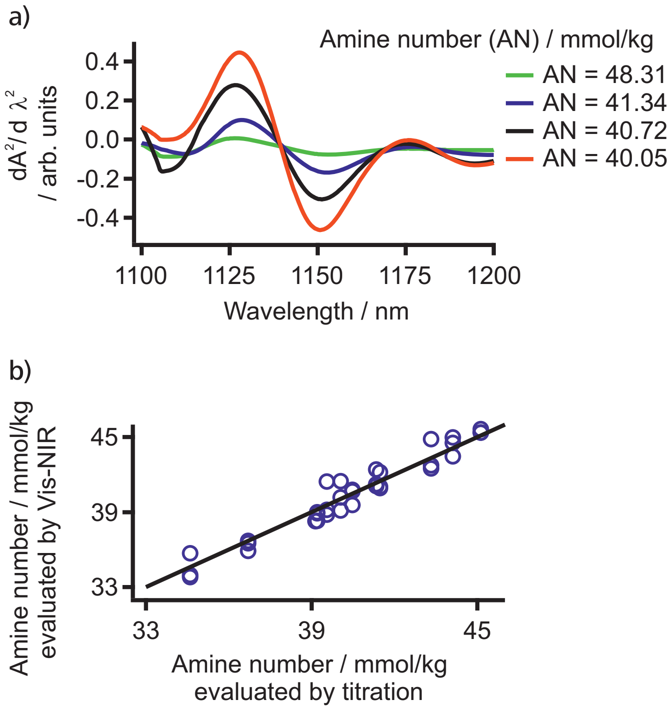

Figure 5. a) Exemplary spectra of the amine number analysis in dipping paints. b) Correlation plot of amine number values determined by Vis-NIR spectroscopy and titration.

Solvents

Solvent-based coatings, whose main constituent is the solvent, are the most common class of coatings. The two key parameters of the solvent are the evaporation rate and the solvating power, which both affect the viscosity and the wetting behavior of the end product. The solvent furthermore influences many aspects of the product-specific behavior. Therefore, it needs to be chosen carefully while considering the intended application.

Solvents are generally grouped according to their chemical properties. Three classes of solvents can be distinguished: hydrocarbon solvents, oxygenated solvents, and other solvents, e.g., water.[3] The latter form the basis of all waterbased coatings, whose importance has strongly increased in the last years because they contain lower levels of volatile organic compounds (VOCs). The use of VOCs is restricted in some countries and states.

Water-based products are therefore becoming more dominant in the market. Vis-NIR spectroscopy as a precise technique can support the essential quality control of solvents, especially for water-based coatings.

Anaylsis of cosolvents in water-based paints

As presented in the previous sections, binders, pigments, and additives are essential ingredients of paints. To be able to also use these compounds in water-based coatings, so-called cosolvents have to be added. Cosolvents such as butyl glycol and propylheptyl alcohol do not only help to solubilize binders, but are used for rheology control and as plasticizers, respectively. Plasticizers determine several coating properties such as dry film appearance or substrate adhesion.[8]

Metrohm Application Note AN-NIR-029 demonstrates the use of Vis-NIR spectroscopy for the quantification of butyl glycol and propylheptyl alcohol content in different water-based paints.[9] Prediction models based on spectral data and reference values for each solvent resulted in a high accuracy of prediction by Vis-NIR spectroscopy with a standard error of validation < 1% (see figure 6).

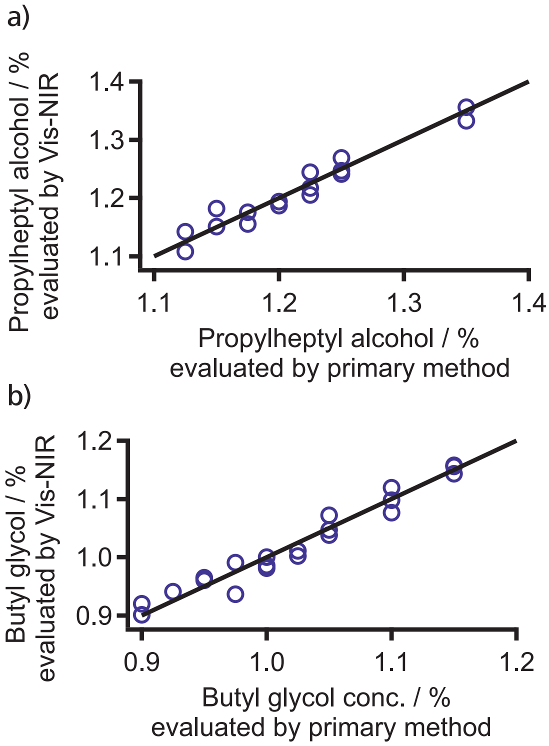

Figure 6. Correlation plots of a) propylheptyl alcohol and b) butyl glycol.

Summary and conclusion

Paints and coatings are used for multiple purposes and need to fulfill high requirements. As a result, these complex products require extensive quality control, which demands the use of sophisticated technologies to ensure reliable and accurate analysis. This need is met by Vis-NIR spectroscopy which fulfills economical as well as ecological requirements.

The combined analysis of the visible spectral range and the near-infrared spectral range by Vis-NIR spectroscopy allows to determine chemical parameters, e.g., the amine number and concentrations of individual constituents, as well as physical parameters such as the specific density and the dynamic viscosity. Compared to conventional methods, Vis-NIR spectroscopy offers the advantage that multiple parameters are evaluated simultaneously within one measurement in less than one minute, without damaging the sample.

The applications presented in this white paper provide but a glimpse of the possibilities that Vis-NIR spectroscopy offers. Because of its many benefits, Vis-NIR spectroscopy can complete and in part replace the conventional methods used in the quality control of paints and coatings and is therefore expected to gain importance over the next years.

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