On-line measurement of silicone release coating on paper substrates using a scanning industrial spectrometer

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ABSTRACT

The on-line scanning measurement of silicone basis weight on release paper has been a great challenge as the coating basis weight typically is only in the range from 0.5 to 3 gsm (0.3 to 2 lbs/ream). Until recently, on-line sensors for silicone measurement have not been reliably accurate or have required prohibitively high levels of on-site technical support. A new sensor employs a high-resolution grating spectrometer in the near infrared (NIR) spectrum to measure silicone coatings down to 0.25 gsm (0.15 lbs/ream) as part of an industrial scanning, web-gauging system. This sensor does not require any intensive maintenance or specialized on-site expertise. Technical details of the sensor design, as well as long-term field results, are presented.

Introduction

A scanning measurement system (see Figure 1) is comprised of one or more sensors mounted to a motorized frame, which transports the sensors back and forth across the moving web while transmitting the cross-machine direction (CD) measurements to a computer console, where the data normally are presented graphically and logged for reporting and control.

FIGURE 1. *Typical on-line web-gauging system*

Silicone coatings are applied to paper substrates to modify the release characteristics of an adhesive label or transfer sheet. If too little silicone is applied or if there are areas of the web where the silicone coating is missing, the adhesive release properties will be adversely affected, creating rejection of the manufactured roll and disruption in manufacturing and other downstream processes. If too much silicone is applied, the cost of the manufactured roll increases, reducing profitability. Excessive silicone coating also can cause contamination to roll edges, excessive overspray and airborne volatiles. There is a very high and unsatisfied demand for an accurate and easy-to-use, on-line scanning, silicone-coating measurement system. The following discusses the past measurement methods that have been attempted and details the introduction of a new on-line silicone industrial measurement system that meets the silicone release-coated paper manufacturing requirements.

Historical attempts at on-line silicone release-coating measurement

Throughout the past 30-plus years, numerous methods of measuring a thin silicone release layer directly on the coating line have been attempted. These methods include total mass subtraction, typically with a beta transmission sensor, laboratory-style FTIR spectrometers, filter wheel IR sensors and X-ray fluorescence sensors. Following is a brief introduction to these methods with typical field experiences.

Total mass subtraction: The total mass subtraction method uses two basis-weight measurement devices, such as beta transmission sensors, to measure

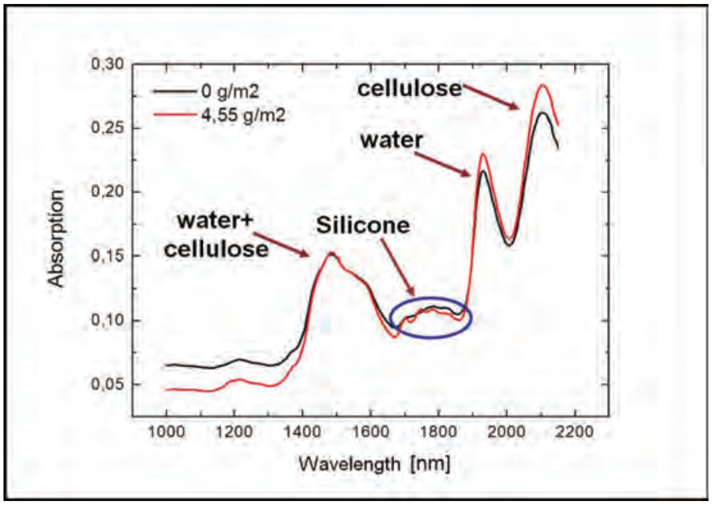

FIGURE 2. *Raw absorption spectra of silicone on paper*

the total web mass before and after the silicone coater and then coordinates the data from each scanner to provide a "same spot" subtracted measurement of just the silicone coating. Due to the relatively light silicone coating weight compared to the paper or polymer substrate, this total mass subtraction method requires unachievably high measurement repeatability from each sensor so as to obtain a useful subtracted net-silicone measurement. For example, a good basis weight measurement system uses a Krypton-85 beta-emitting source and has a measurement repeatability of 0.15 grams per square meter (gsm), 2 sigma, for the basis-weight range of interest. When considering the repeatability of measurement of the dual-measurement subtracted net coating, the measurement variability of each sensor statistically combines as the square root of the sum of the squares of each measurement (the first measurement is of the substrate paper or polymer film, and the second measurement is of the substrate plus silicone coating – both are quite massive compared to just the thin silicone layer), which then must be applied mathematically to the basis weight of the net coating:

$$[(0.15 \text{ gsm})^2 + (0.15 \text{ gsm})^2]^{1/2} = 0.21 \text{ gsm}$$

For a silicone release coating of 1.0 gsm, for example, a variability of 0.21 gsm equals a measurement system repeatability of 21%, barring any additional sources of error, which probably is not good enough. There are lower energy, beta-transmission sensors available that have a somewhat better measurement repeatability, but their purchase and maintenance costs become prohibitive. Also, the net-measurement precision of the very thin silicone coating still is no better than 10% and can be applied only to very lightweight substrates. X-ray transmission sensors also have been attempted for this subtractive measurement method, but are still at best a 10% repeatable measurement – and often much worse due to the high sensitivity of X-ray transmission interactions with the web to the composition of both the substrate and coating.

Filter wheel IR measurements also have been attempted in a dual mass subtraction configuration, but the low specific absorption of silicone and the broad spectral bandwidth and spread of the center wavelength of the discrete filters result in a low-resolution measurement with an ever-changing calibration. For this reason, the dual mass subtractive method usually is not attempted for thin silicone coatings.

Laboratory FTIR spectrometers: There have been a number of attempts to take FTIR spectrometers designed for laboratory use and mount them onto scanning frames for on-line use. Whereas these benchtop instruments are stable in a lab environment, they were never fundamentally designed for the vibration, temperature-extremes and continuous-use requirements of a factory environment, especially with their dependence on an internal scanning mirror. Field calibration techniques were never satisfactorily developed and required Ph.D.-level support. This technique has been abandoned.

Filter wheel IR sensors: There also have been attempts to measure the silicone coating with optical filter-wheel systems working in the Near Infrared (NIR) spectral range. In the NIR, the silicone absorption is quite low, and with the broad spectral resolution of the filter wheel, it is very difficult to separate the silicone absorption (see the red line in Figure 2) from the overlapping absorption of the base paper as shown in Figure 2. Any compositional changes of the paper due to grade changes or recycled content create continuous calibration shifts and measurement "noise" with the filter wheel IR method. Although this method still is available, its usefulness continues to be questioned by silicone-coating manufacturers.

X-ray fluorescence (XRF) instruments: XRF measurements historically have been the most accepted on-line method of measuring silicone release coatings, in part due to their large installed base as a laboratory standard. The XRF technique infers the amount of silicone in the target by measuring the amount of elemental Silicon in the coated paper sample. Because there also is a significant amount of Silicon in the substrate paper, a representative uncoated-paper sample must be measured first, and the Silicon contribution of the paper must be subtracted from the silicone coated-paper measurement. The accuracy of this method is dependent on how truly representative is the uncoated paper sample used to obtain the baseline Silicon measurement. Different grades, different paper suppliers and a variable amount of recycled content in the paper will affect adversely the silicone-coating calculation as the differing contribution from the paper will add a first-order error. XRF measurement of silicone coating on-line has been abandoned as the dominant supplier discontinued this type of measurement system in the late 1990s.

New on-line silicone-measurement method

A new on-line sensor for the measurement of silicone release coatings on paper substrates was developed in 2012 and

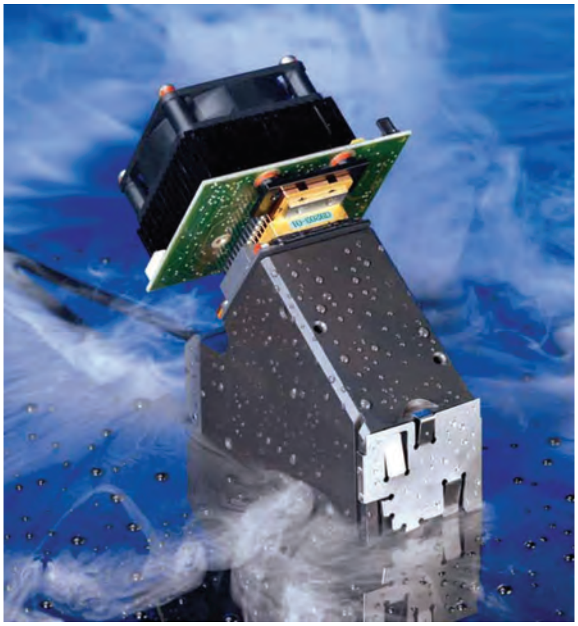

FIGURE 3. *On-line PGS NIR spectrometer. ©Carl Zeiss AG*

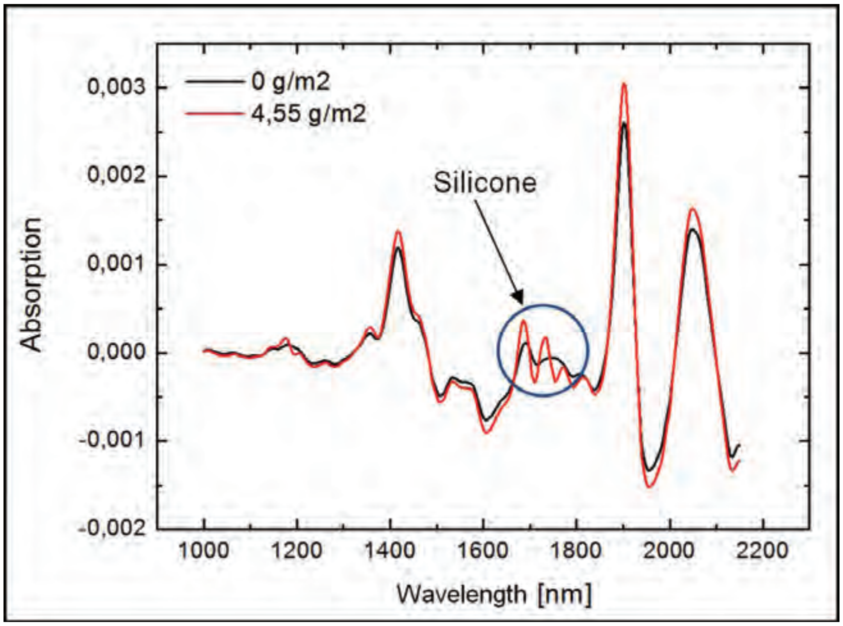

FIGURE 4. *Post-processed absorption spectrum of silicone on paper*

incorporates a solid-state grating spectrometer to obtain high-resolution spectra in NIR between the wavelengths of 1,000 and 2,200 nanometers (nm). It employs active temperature control and advanced signal processing to provide a very selective and stable measure of silicone release coatings with little influence from the substrate paper (see Figure 3).

The heart of this new on-line sensor is an NIR-grating spectrometer using an InGaAs detector with a combination of aspheric collimator and focusing lens allowing the use of plane gratings optimized for the NIR, while maintaining good flat-field correction of the spectral imaging. This solid-state spectrometer was designed anew specifically as an on-line instrument appropriate for the environmental conditions present in a manufacturing plant. A version of this spectrometer in the visible spectrum has been in use in 100+ installations over more than 15 years as an on-line textile color sensor as part of an industrial scanning system in very hot and dusty conditions.

New method operating principle

The sample is illuminated with a stable source of broad spectrum infrared light (1-3 µm). The new on-line sensor scans the infrared spectrum every 5 to 10 milliseconds depending on the reflectivity of the target surface. The acquired spectrum is mathematically manipulated calculating the first derivative to accentuate the silicone response. One of the key features of the grating spectrometer, which allows it to resolve the small absorption peaks of silicone is its ability to achieve 1-nm resolution (compared to ~50 nm for filter wheel IR systems). This high spectral resolution enables the differentiation of silicone absorption and facilitates the use of very selective post-processing analysis (see Figure 4).

Further manipulation of the spectra then is performed by multivariate analysis to provide very high-resolution absorption peaks for the measurement of interest (see Figure 5). In the case of silicone, this is the wavelength range between 1,700 and 1,800 nm.

Different amounts of silicone result in a large change in measurement signal (see Figure 6). Specifically, absorption at the following three wavelengths is of most interest for the silicone molecule:

1,703 nm	CH_3 Group Vibration
1,746 nm	CH_3 Group Vibration
1,760 nm	C-H Methyl Group Vibration

New sensor assembly

The embodiment of the new on-line sensor includes power supplies, communications module and a temperature controller to maintain a constant internal temperature through a wide range of ambient factory conditions. The entire sensor housing is insulated and includes an embedded air wipe to keep the external surface of the optics clean.

The new sensor functions as a single-sided measurement mounted onto a motorized scanning frame. The output of the sensor is transmitted to a control and display station where CD profiles and machine-direction (MD) trends are presented, logged for reporting and used for silicone coatweight automatic control.

Calibration and spectral analysis tools are built into the control and display station and, because the IR-absorption spectrum of pure silicone is known, the

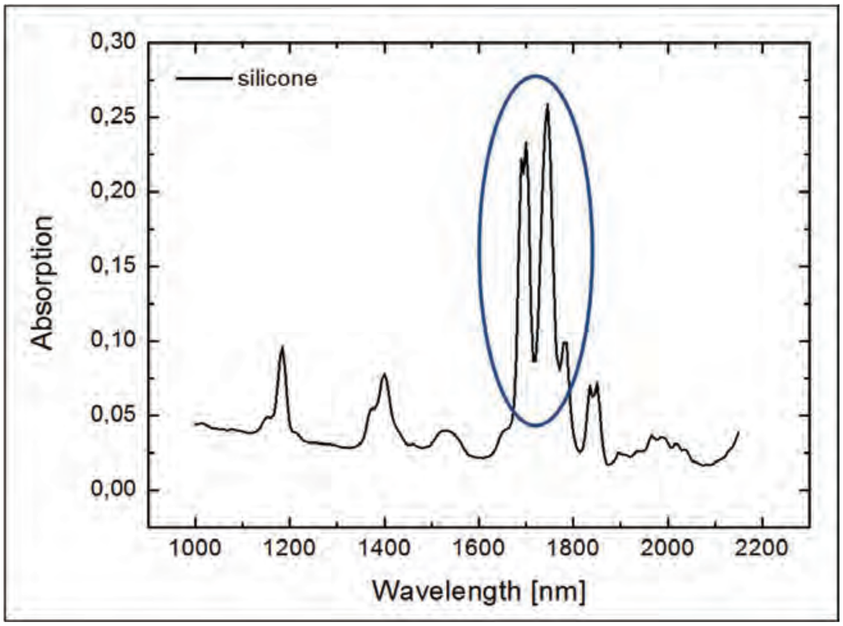

FIGURE 5. *Silicone spectrum after multivariate analysis*

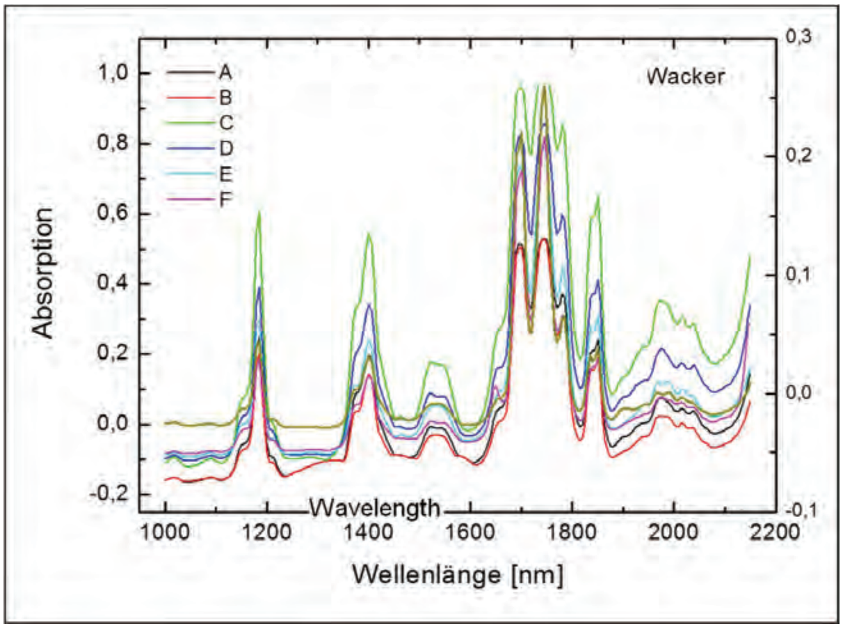

FIGURE 6. *Different basis weights (A-F) of silicone release coatings*

system can be pre-linearized before it is installed on the silicone-coating line (see Figure 7).

Then, the only recipe-dependent adjustment that may be required is a small scalar (gain) adjustment to correct for any small effects of the substrate paper. This is an easy task and is conceptually the same as that required for a common beta or gamma gauge that is performed by a line operator or QC technician. No in-depth chemistry or spectroscopy knowledge is required.

Testing results

Testing has included stationary laboratory samples with varying basis weights and manufacturers of silicone, coated onto a large variety of papers, including kraft, clay-coated, white and colored stock. Early field testing in paper converting plants has been ongoing in Europe for three years. Discussed in detail in this paper are the field testing results acquired through the second half of 2015 on a production silicone-coating line at Green Bay Packaging's (GBP) Coated Products Operations in Green Bay, WI.

Laboratory test results: The test setup in the lab included the new on-line spectrometer sensor with a ceramic reflector positioned 30 mm from the sensor face. Lab tests were performed on nine different paper qualities (three different base papers coated with three different amounts of silicone). Twenty samples of each paper quality were provided. The lab samples were supported in the center of the measurement gap (15 mm from the sensor and the ceramic reflector). Measurement data were recorded in Excel. Samples of various basis weights of silicone coating on three different paper substrates were cut into precise 100-cm^2 area samples, which subsequently were measured with a laboratory XRF and then weighed.

The new on-line sensor data were compared to tests of the same samples using a laboratory XRF sensor (see Table 1).

Maintaining accuracy and long-term stability

The new sensor has been shown to measure correctly in the presence of silicone contamination of the external lens as this is not within the focal length of the sensor. Therefore, excessive window cleaning is not required. Web pass-line changes, such as flutter or edge curl, also do not noticeably affect the silicone basis-weight measurement, nor does a small change in distance between the sensor and the ceramic reflector beneath the web as would occur over time and temperature change. Varying moisture in the web, if uncorrected, would show a small change in silicone measurement, so moisture is measured concurrently with silicone and used by the system software to eliminate its effect on the silicone-coating measurement. The sensor can re-zero itself automatically off-sheet using the clean ceramic reflector as a target, but this tool was not employed during any of the GBP field testing to better evaluate long-term stability.

Field testing results: The new sensor was installed on one of Green Bay Packaging's silicone- and adhesive-coating lines where silicone release coating is applied to paper substrates with silicone basis-weight targets ranging from 0.7 to 1.2 lbs/ream (1.10-2.0 gsm).

The sensor, initially calibrated using the laboratory testing results described above, was used to scan continuously the silicone-coated paper during normal production runs of the coating line. Data were reported on a per-roll basis and compared to three laboratory XRF samples across one CD sample of the end of each roll. For the first 100 rolls, different silicone coating weights applied to two different paper substrates identified as “Roll Label” and “Layflat” were tested to determine final calibration factors. It was concluded that these calibration factors did not depend on the silicone basis weight or its composition (dilution ratio or release value) and depended only somewhat on the type of substrate paper. Roll Label paper can be white or kraft with low clay content, and Layflat is a high clay-component paper.

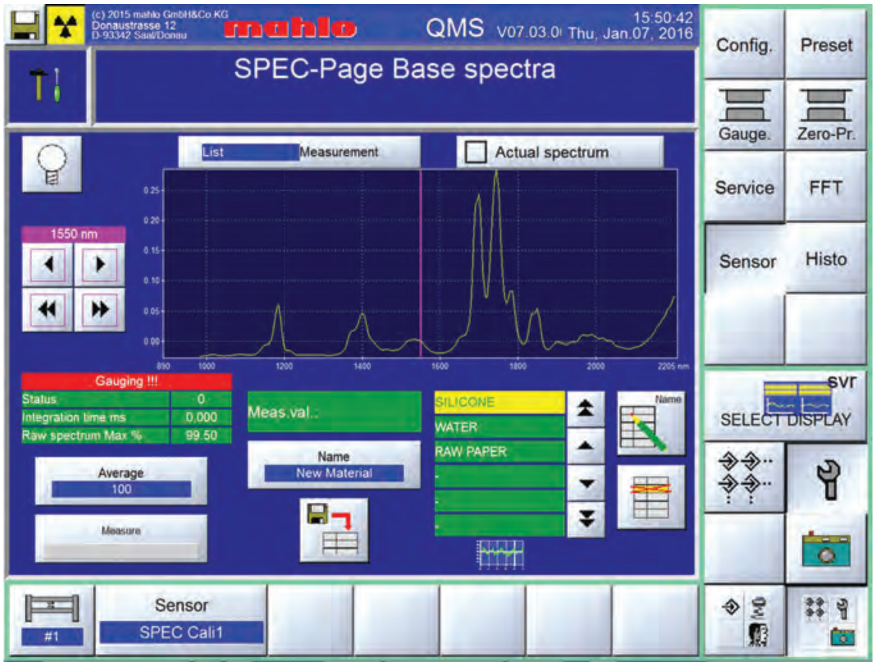

FIGURE 7. *Spectral calibration page for new on-line sensor*

TABLE 1. *Single-point correlation of new on-line sensor and XRF*

Paper	Lab value XRF (lb/3000ft^2)	InfraScope (Average of 20 Sheets) (lb/3000ft^2)	standard deviation (lb/3000ft^2)
T1964-3	0.860	0.873	0.032
T1964-2	1.047	1.022	0.019
T1964-1	1.175	1.187	0.028
T1965-3	0.990	0.992	0.006
T1965-2	1.077	1.074	0.007
T1965-1	1.157	1.159	0.012
T1972-3	0.802	0.797	0.030
T1972-2	0.957	0.969	0.021
T1972-1	1.130	1.124	0.033

The number of rolls used to perform the field calibrations was chosen to mitigate any sampling discrepancies as the new sensor data were an average of the entire roll, and the Lab XRF data were three points across a strip at the tail end of each roll. The correlation based on sampling-location differences is averaged out to a large degree with a larger data set.

Once a number of representative rolls of each silicone coating weight on each type of paper substrate were obtained, it was concluded that only two calibrations were required to satisfy the full range of manufactured products. These were implemented and used for the subsequent 600 rolls used for the field trial (see Figure 8).

The correlation calculates to 0.94 for the runs after calibration and is considered quite good given the different sampling methods for the new on-line sensor vs. the Lab XRF. The details in Figures 9 and 10 show the new sensor roll averages are smoother from roll to roll than the fewer samples per roll used by the Lab XRF, which is intuitive, but which also acts to artificially reduce the correlation calculation.

Dynamic specifications

Based on laboratory data and field testing performed at GBP and also in Europe, the new on-line sensor will meet the specifications shown in Table 2.

Discussion

The goal of the new sensor development was to provide a reliable, on-line scanning measurement of very lightweight silicone coatings on paper substrates. Further, the resultant gauging system was required to be easy-to-calibrate, maintain and understand by machine operators whose previous experience were with traditional basis-weight measuring systems, such as beta gauges. In addition, real-time display of moisture is provided as it is measured concurrently by the new sensor and used to maintain silicone-measurement accuracy. No spectroscopy knowledge is required, and calibrations are handled within recipes as a simple scalar adjustment only when the paper substrate differs significantly.

Conclusion

This firm’s new on-line spectrometer is proving to remain stable and repeatable in industrial manufacturing environments without requiring frequent cleaning of the window and is unaffected

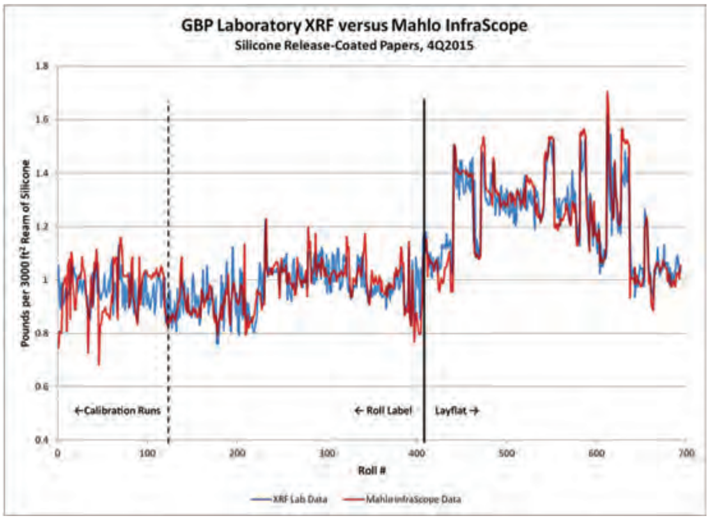

FIGURE 8. *New on-line sensor vs. Lab XRF data for 700 rolls*

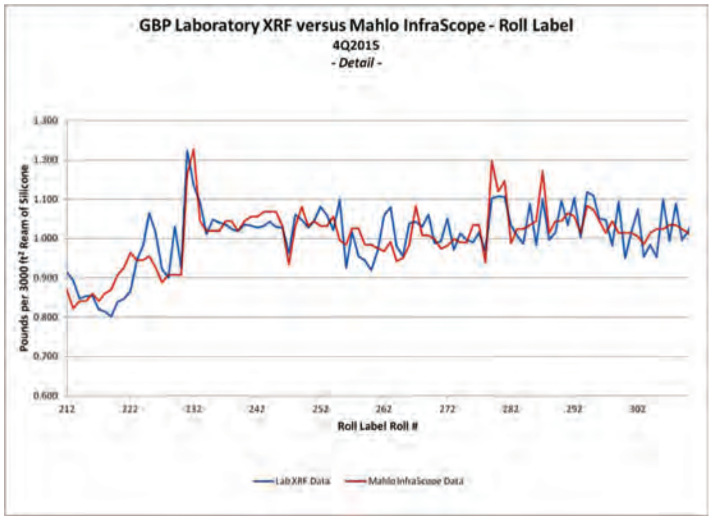

FIGURE 10. *Detail of new on-line sensor vs. Lab XRF data for Roll Label paper substrate*

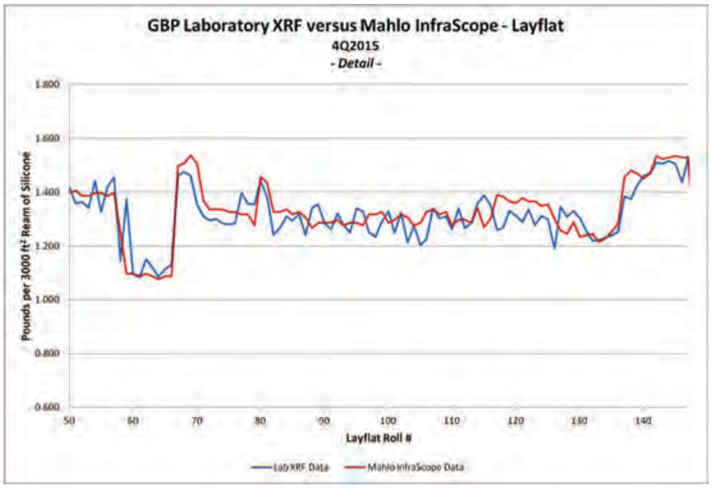

FIGURE 9. *Detail of new on-line sensor vs. Lab XRF data for Layflat paper substrate*

TABLE 2. *New sensor on-line specifications*

Specifications	
Sensor	INFRASCOPE NIR
Measurement principle	Absorption of infrared energy
Spectral range	1000 nm – 2170 nm
Measurement Range	Silicone: 0.25 g/m² – 150 g/m² Additional ranges upon request
Measurement Accuracy	0.03 g/m²
Measurement Spot Size	25 mm
Measurement Gap	10, 15, 30 mm
Measurement Mode	Reflection Mode
Power Supply	24 V DC
Max. ambient temperature	60 °C without additional cooling

by web pass-line, flutter or edge curl. The 1-nm spectral resolution and the sub-10 millisecond sampling rate are keys to measuring accurately the very low basis weights of silicone required for the release coating industry. It is important to note that, at this time, the new sensor is specified for silicone coatings on paper substrates, not on polymer film substrates. ■

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