How Much Softener Is Enough?
Determining Silicone Add-on Level for Tissue Substrates

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About Dow Corning
Dow Corning was established in 1943 as a joint venture between Corning Glass Works (now Corning Incorporated) and The Dow Chemical Company to explore the potential of silicones.

Today, Dow Corning provides performance-enhancing solutions to serve the diverse needs of more than 25,000 customers worldwide. Dow Corning is a global leader in silicon-based technology and innovation, offering more than 7,000 products and services.

Dow Corning and the Tissue Industry
Dow Corning has resources specifically dedicated to the tissue industry, including a global team of experts who possess a unique understanding of factors that have the potential to impact tissue processing.

The company continually develops new materials for the tissue market and offers a range of material solutions with potential benefits for tissue manufacturing.
Introduction
When incorporating any chemical in the tissue-making process, knowing how much has been added is essential. This is also true when using topical treatments such as silicone softeners. Only when we know exactly how much has been added can we properly judge how different quantities and types of silicone softeners impact tissue properties, such as softness, absorbency, strength and cost. But before we can understand the impact, we need to understand how to accurately and reliably measure the amount of silicone softener added during treatment.

This paper offers basic information about silicone and the benefits it conveys to tissue. The focus, however, is on work done by Dow Corning to identify a test method that would verify the amount of silicone softener applied to tissue substrates in a variety of tissue development and production situations. This document defines the needs an appropriate test method would be required to meet and offers the results of Dow Corning’s comparative evaluation of four potential measurement solutions – gravimetric analysis, solvent extraction and atomic absorption, sample digestion and gas chromatography, and x-ray fluorescence. Results of laboratory and coating trials are provided to demonstrate the value of the chosen method in actual tissue development and manufacturing applications. Finally, information will be provided about analytical services and solutions available from Dow Corning.

Silicone Basics
“Silicone” is a generic term referring to a class of materials possessing the advantages of both silicon-based and organic chemistry. It typically refers to polymers of the following structure, where “R” is most commonly a methyl group.

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R \quad - (\text{Si} - \text{O})_n - \quad \text{Si} \quad \text{O} \quad \text{Si}
\]

In silicone polymers, two or more Si units are connected by an oxygen atom and the other two Si bonds are organic. Silicones vary by size from a few Si-O units to tens of thousands. They may include branching architectures and may contain a small to a large degree of organic character.

In testing add-on and performance benefits, we are looking for the amount of silicone polymer or emulsion added to the tissue. In analytical terms, we are looking for the silicon atom, a silane or a silicone polymer.

The Need to Determine Silicone Add-on Level
Dow Corning’s impetus for studying various options for determining silicone softener add-on level came from the need to understand the impact of different quantities and types of silicone on tissue properties, such as softness, absorbency, strength and cost.

To accomplish this, we first had to understand how to accurately and reliably measure the amount of silicone softener added during treatment.

Silicone Benefits for Tissue
Silicones provide performance benefits to many industries that require surface modification for improved softness, smoothness and liquid absorbency modification. This is also true for tissue substrates, where both tissue softness and hydrophilicity (absorbency) can be modified by topical treatment with a silicone polymer.

One of the properties that enable silicones to provide these benefits is their low surface tension. This gives silicones the tendency to migrate to the air interface and orient at surfaces. Additionally, silicones can be substituted with almost any organofunctional group to yield specific performance characteristics. Finally, silicone polymers can be delivered at either high or low viscosities. For coating purposes, viscosity can be kept to less than 100 cPs either by using a low-molecular-weight silicone fluid or by emulsifying or dispersing a higher-molecular-weight silicone polymer in water or other diluent.
capable of measuring silicone softener level in a wide variety of situations, including

- To evaluate application methods, treatments and base sheets in short-duration coating trials
- To identify process and production trouble spots, such as machine-direction (the direction the tissue paper is moving down-line during processing) or cross-direction variation, aging rolls and plugged nozzles
- To appraise modified assemblies, such as surface vs. penetrating treatments
- To accurately relate tissue properties, such as softness, absorbency and strength, to add-on level
- To quickly and accurately determine the cost:benefit ratio

**Test Method Requirements**

To be viable for situations ranging from product development to production, the test method would require:

- Fast turnaround time – ideally less than 10 minutes from the time the sample was coated to the time it was analyzed
- Reasonable sample preparation costs, in terms of materials, tools and labor
- Reasonable capital investment in analytical equipment
- Reliable, robust, accurate and reproducible results (within +/-10%)

**Potential Measurement Solutions**

To identify such a method, Dow Corning evaluated four potential measurement solutions in terms of turnaround time, sample preparation costs, capital investment and the accuracy and reliability of the data. The test methods analyzed included gravimetric; solvent extraction and atomic absorption (AA); sample digestion and gas chromatography (GC); and x-ray fluorescence (XRF).

**Gravimetric**

Gravimetric testing, which uses a 0.0001-gram capability scale to check for weight change from untreated to treated samples, is the simplest of all the tests evaluated. It meets the first three criteria very well. Turnaround time is very quick – approximately 3 minutes off-coater. There is no added sample preparation cost or labor involved. Plus, the only capital cost is the cost of the scale, which is a relatively low $3,000 to $8,000. However, this test method provides only a very rough estimate of silicone add-on level. Variability is +/-100%. If we add on 0.2 g/m² of silicone softener, we find the results for a 20 g/m² tissue basis weight sample can vary by +/-0.2 g/m². It is difficult to know if this variability is caused by the tissue stretching during the coating process or by the actual amount of the silicone being added on. Because most silicone softeners are applied as emulsions, water is evaporating at the same time the gravimetric analysis is being performed. This is another point of variability that makes determining the exact amount of silicone add-on very difficult. Accuracy suffers even more when base sheets, softener water content and softener coat weight vary during experimentation. Consequently, the accuracy of gravimetric data is simply not consistent enough to be useful.

**Solvent Extraction and Atomic Absorption (AA)**

In solvent extraction and atomic absorption, a non-polar solvent is used to separate the silicone polymer from the tissue fiber. The extracted polymer solution is then run through a lab-top AA instrument.

This method has a very slow turnaround time. Sample preparation is not that difficult, and it requires only about 30 minutes to dissolve the silicone into the solvent. However, it takes an entire day to complete the analytical phase. Additionally, capital costs are high – from $30,000 to $100,000 or more for a lab-top AA unit. These units are quite accurate. Unfortunately the accuracy of the results is limited by the poor efficiency of the solvent extraction process. A variety of non-polar solvents was tested, but in every case, a significant amount of the silicone polymer could not be pulled away from the tissue fibers. Because the solvent extraction process was only 70-90% efficient, the accuracy of the atomic absorption suffered, yielding only a rough estimate of silicone add-on level.
Sample Digestion and Gas Chromatography (GC)

With sample digestion and GC, the silicone softener is broken down via a digestion process to its monomer units and run through a GC device.

The turnaround time for this method is prohibitively slow – approximately one week, with 8 hours required to prepare each sample. Sample preparation is also expensive on a per-sample basis due to the cost of the specialized reagents required and the labor-intensive preparation procedure.

Capital costs are moderate, however, (approximately $30,000) and the data generated from this test is quite accurate, yielding a very precise estimate of silicone add-on level that can serve as a standard. Unlike solvent extraction, the digestion process is virtually 100% efficient, and GC has the added benefit of being able to differentiate the functionality on the silicone. So, if different organic groups are present, this can be determined through the GC testing.

This method also offers a high degree of flexibility and can also be used to test mill process water, felts and pulps.

X-ray Fluorescence (XRF)

XRF uses a lab-top XRF device to perform a topical analysis of the amount of silicone present on the treated sample. This method offers very fast turnaround – 10 minutes off-coater – enabling quick determination of coater performance and the implementation of necessary adjustments to keep the run going.

There is no added cost or labor required for sample preparation. There are no reagents or special equipment required, other than a hammer and a punch. Capital costs are moderate – approximately $30,000 for an XRF lab-top unit – and, more importantly, this method delivers a good estimate of silicone add-on level. Accuracy is +/-10% at 0.2 g/m² silicone add-on.

The XRF method meets all the criteria – it is very quick, accurate and inexpensive. This method can be used in both troubleshooting and product validation when the silicone add-on is unknown.

However, it cannot be used as a stand-alone test. A calibration curve referencing a known quantity from another analytical method must be created as a standard. At Dow Corning, the chosen method for creating this curve is digestion and GC functionality.

As long as a calibration curve can be defined, XRF has proven very accurate and reliable. Additionally, there is the potential to use silicon as a marker to assist in the evaluation of non-silicone treatments.

### Practical Applications

X-ray fluorescence generates reliable data that has been correlated during previous lab experiments and random trials. Figures 2 through 4 show how XRF is able to validate silicone add-on in controlled lab experiments where a known add-on quantity has been determined. In these figures XRF is compared to digestion and gas chromatography and controlled gravimetric data.

More importantly, Figures 5 through 8 show how XRF can be used in troubleshooting or product validation when the add-on level is unknown.

Figure 2 shows a correlation between XRF and GC digestion on three separate base sheet trials.
three separate base sheet trials conducted in different mill locations using different coating equipment. In spite of the variability, the correlation coefficient on these samples was quite good – 0.94.

Figure 3 shows the results of a laboratory experiment to determine whether XRF could detect differences in how a silicone emulsion penetrates into the plies of tissue. An eye dropper was used to drip the silicone onto 8 plies. As you can see, the less silicone was applied, the less deeply it penetrated into the tissue, which is rather intuitive. What this experiment does show is that XRF can be used to investigate the interaction between the tissue and the treatment.

Figure 4 shows the correlation between the XRF data obtained in the Figure 3 experiment and the known add-on level, which was determined gravimetrically, in advance. The correlation coefficient was 0.94.

Figure 5 illustrates the results of a trial conducted, where a high and low coat weight were targeted, to observe the affect the amount of silicone had on the base sheet. Seven XRF samples were run per data point to ensure the variation came from the processing. Even though there is quite a bit of variation in the machine direction, the average coat weight between Sets A and B within a coating group actually agrees quite well. The variability we see is not caused by the XRF or by the sample preparation, but rather by the coating process.

Another point of interest on this graph is the teal line (--) at the bottom with only five data points. This shows a hank of coated tissue where the inconsistency of the coating applied ranged from zero up to about 0.2 g/m². This data is further explored in Figure 6.

Here we see not only the inconsistency of the coating, but also the difference in the degree of penetration from the top to the bottom of this one-sided coating process. In one-sided coating, it is beneficial, both for performance and financially, to keep as much coating on the surface of the tissue as possible.

Figure 7 illustrates a coating trial conducted on a one-sided roll coater. As can be seen, from the left to the right, there was quite a bit of inconsistency in the coat weight. In this situation, there were some production problems and process issues. It was believed that the coating was going on properly, but this

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**Figure 3. XRF analysis of coat weight on tissue plies.**

**Figure 4. XRF vs. known gravimetric add-on.**

**Figure 5. Trial A – Total silicone content on tissue plies measured via XRF – one-sided coater.**

**Figure 6. Facial tissue silicone content per ply.**

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**Conclusions:**
1. Coat Weight varies much in machine direction.
2. There is some amount of transfer to the Middle and Bottom ply, but the majority of the silicone remains on the top ply.
showed quite a bit of silicone was being added to one side vs. the other. Additionally, the sample labeled “For Sure Coated Sample,” sent by an observer who was certain it came from the coated section of the tissue, had no coating at all according to both the XRF and GC digestion testing.

The trial in Figure 8 shows fairly consistent silicone add-on at various points throughout the trial and on different runs. What this reveals is that the actual silicone add-on was far below the target of 0.6 g/m², resulting in softness that failed to meet the performance expectation.

**Conclusion**

Through a series of trials Dow Corning determined that gravimetric testing, while quick and easy to use, does not deliver the degree of accuracy required to determine silicone add-on level. Solvent extraction and atomic absorption test methods are slow, inaccurate and have high capital costs. Sample digestion and GC methods also are slow, requiring one week to receive the results.

With sample digestion and GC, sample preparation is expensive, but the results are precise estimates. XRF testing has a quick turnaround with no cost to prepare the sample and medium capital costs. This method gives a good estimate of the amount of silicone in the tissue.

From the evaluated methods, Dow Corning found the XRF test method to be the best to produce quick, reliable, cost-effective data to detect the amount of silicone softener on a tissue substrate. However, XRF cannot be used as a stand-alone test. Established standards are needed to create a calibration curve. The chosen method for producing the calibration curve is by using GC with sample digestion or standards from past experiments.

**Analytical Services and Solutions from Dow Corning**

The work reported in this paper was completed with the assistance of the Dow Corning Analytical group.

In addition to silicone softeners for tissue, Dow Corning offers a full range of analytical solutions for the pulp and paper industry, including:

- Material analysis and characterizations
- Problem solving
- Contaminant determination
- Analytical method development
- Contract research
- Product deformation
- Training and consultation

Dow Corning’s analytical laboratory is ISO 17025 accredited.

For more information about analytical services from Dow Corning or to request assistance,

- E-mail [analytical.solutions@dowcorning.com](mailto:analytical.solutions@dowcorning.com).
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