Improvements in oil and grease resistance (OGR) test methodology for waterborne barrier coatings

ALLYSON MARIANELLI, BRIAN EINSLA, ELIZABETH SHOW, SAMANTHA WOODFIN, BO SHUANG, KEVIN HENDERSON, MIKE LINSEN, JONATHAN DEROCHER, AND SHAWN OLIVER

ABSTRACT: Paper-based food packaging is becoming more popular due to consumer demands for sustainable packaging options. Waterborne paper coatings that provide performance properties (i.e., resistance to oil and grease) not inherent to paper and board substrates offer improved sustainability profiles over earlier paper treatment options, including fluorocarbon treatment and coating with extruded plastics. The continued development of new paper coating technologies requires re-evaluation of current test methods and development of new methods to ensure lab evaluations can serve as accurate predictors of real-world performance.

This paper provides an overview of commonly used oil and grease resistance (OGR) test methods within the paper coatings industry, and then describes improvements and developments made to two key methods: the 3M Kit test and an internally developed oil breakthrough test. The combined use of these adapted methods provides a more efficient testing workflow and a more complete understanding of the OGR performance of barrier coatings.

Application: The development of new barrier coatings for paper packaging requires robust and quantitative methods for performance evaluation. This paper reviews industry standard oil and grease resistance (OGR) test methods and describes improvements to two key methods: the 3M Kit test (TAPPI Standard Test Method T 559) and an internally developed oil breakthrough test.

As the demand for more sustainable food packaging continues to grow, focus has shifted towards paper-based packaging. However, paper by itself has poor barrier performance against many of the substances food packaging is in contact with, including oil/grease, water, moisture vapor, and oxygen. This lack of barrier performance highlights the need for paper coatings that impart resistance to substrates and enables them to be used in applications such as quick service restaurant containers, sandwich and bakery wraps, and cups.

Paper-based oil and grease resistant (OGR) packaging has traditionally been achieved through either wet-end treatment with perfluoroalkyl substances (PFAS) or coating paper with extruded plastics. The PFAS are currently facing regulatory and consumer pressure due to increasing environmental and health concerns [1], while extrusion-coated paper products often require thick coatings that can impact product cost and recyclability. Waterborne paper coatings offer a more environmentally friendly alternative without the use of fluorochemicals or the need for thick films.

Robust, quantitative, and rapid performance testing is critical to ensure that new product candidates meet expectations both in a laboratory setting when compared with competitive offerings, but more importantly in the real-world application where they will be employed.

A traditional method for evaluating the oil and grease resistance (OGR) of paper food wraps is the 3M Kit test (TAPPI Standard Test Method T 559 "Grease resistance test for paper and paperboard"), which was developed to test the degree of repellency and/or the anti-wicking properties of fluorocarbon-treated paper or paperboard. Because it was not designed to evaluate film-based barrier performance, its practicality is decreasing as PFAS-treated materials are being phased out of the market. Additionally, the test method suffers from limitations including short evaluation time (15 s), inherent subjectiveness of the operator, and the use of solutions (blends of castor oil, toluene, and heptane) that the final product will not likely be exposed to (**Table I**). While paper suppliers still request Kit data when evaluating new barrier coatings, many admit the test does not predict real-world performance in their targeted application area.

Another well-known method, the RP2 test developed by Ralston Purina to predict performance of pet food packaging, evaluates performance over longer periods of time at elevated temperatures [2-4], but is much more time consuming from a data collection/analysis standpoint and relies on manual counting of grid squares with oil breakthrough.

The ASTM F119-82 "Standard method for rate of grease penetration of flexible barrier materials" describes a comparable method for evaluating longer-term resistance to oils and similarly requires a significant time commitment for testing and analysis.

Kit #	% Castor Oil	% Toluene	% Heptane
1	100.0	0.0	0.0
2	91.9	4.6	3.5
3	83.5	9.3	7.2
4	74.6	14.3	11.0
5	65.4	19.5	15.0
6	55.8	25.0	19.2
7	45.7	30.7	23.6
8	35.1	36.7	28.2
9	24.0	43.0	33.1
10	12.3	49.6	38.1
11	0.0	56.5	43.5
12	0.0	51.5	48.5

3M Kit Test Solution Compositions

I. Compositions of Kit solutions (in weight/weight%).

Other relevant OGR standardized test methods include: TAPPI T 454 "Turpentine test for grease resistance of paper," TAPPI T 507 "Grease resistance of flexible packaging materials," and the Solvay fatty acid test. **Table II** describes several OGR test methodologies that could be evaluated and compared in the future to expand on this work.

The oil breakthrough test described in this paper (**Fig. 1**) reflects an internally developed method designed to address key gaps and challenges associated with the previously described tests. The test evaluates resistance to breakthrough of a test oil (typically vegetable oil) onto underlying graph paper over a period of 24 h at elevated temperature (60°C). The test provides additional flexibility of test conditions, with the ability to use customer-specific test liquids in the place of vegetable oil, change the length and temperature of the test, and fold the coated substrate prior to evaluation to probe film flexibility.

Although the PFAS-treated materials that the Kit test was designed to evaluate are being phased out of the market, the short duration of the test could be beneficial for screening studies if a correlation was established between Kit scores and longer-term OGR performance. Some of the work in this paper was completed to determine whether the Kit test can still provide relevant performance information to aid in down-selection of high performing candidates for additional testing.

This paper describes improvements to the internally developed oil breakthrough test and the Kit test. First, more aggressive Kit solutions were added to enhance differentiation between high-performing samples. Second, an image analysis program was developed to reduce human error in measurement and increase experimental efficiency for the oil breakthrough test. The combination of these adapted methods provides a more complete understanding of the OGR performance of barrier coatings.

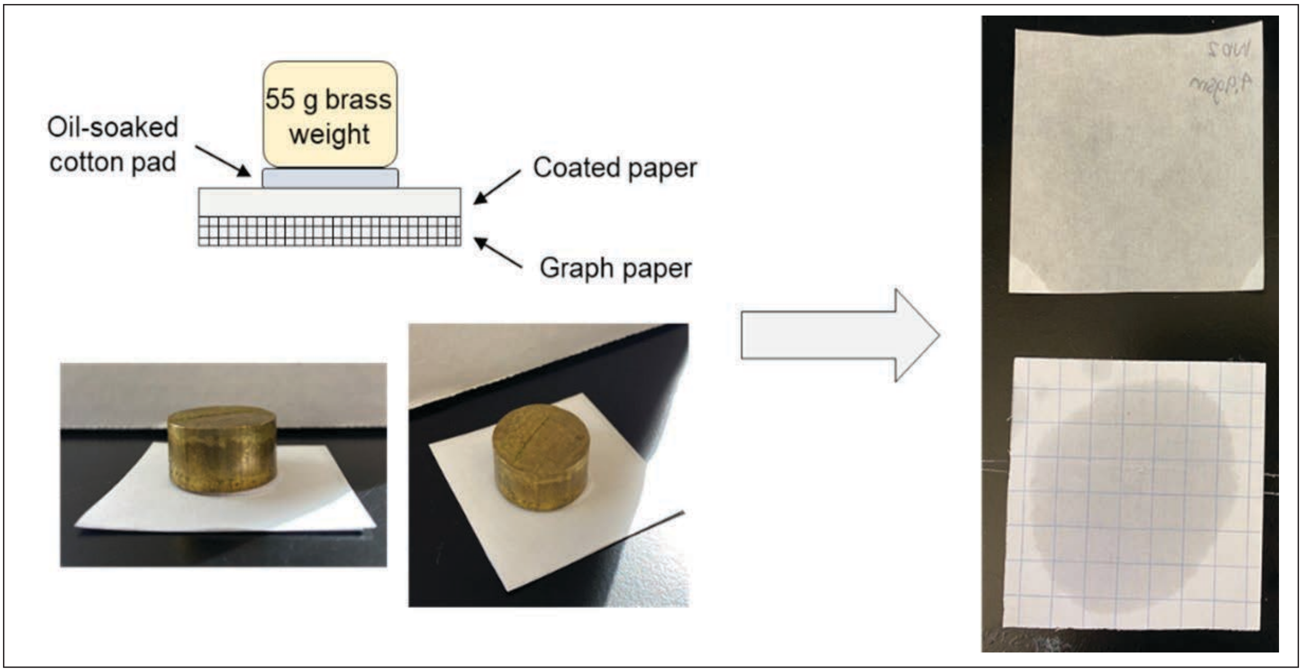
EXPERIMENTAL METHODS

Coating preparation

Coating formulations were prepared targeting the maximum solids content possible for each coating based on solids content of binders, additives, and thickeners (between 39%–50% solids) and a Brookfield viscosity of 600 cP at 100

Method	Test Liquid	Time	Temperature	Weight	Results
TAPPI T 559 "Grease resistance test for paper and paperboard" (3M Kit)	Solutions containing castor oil, toluene, and heptane	15 s	Room temperature (23°C)	None	Most aggressive solution without breakthrough
RP2	Proprietary synthetic oil	24 h	40°C	5 g sand	Percent of stain on grid paper
ASTM F119-82 "Standard method for rate of grease penetration of flexible barrier materials"	Animal oil, mineral oil, vegetable oil, and other reagents	Until sample failure	40°C or 60°C	50 g weight	Time at which sample failure/penetration occurs
TAPPI T 454 "Turpentine test for grease resistance of paper"	Dyed turpentine	Up to 30 min	Room temperature (23°C)	5 g sand	Time at which sample failure/penetration occurs
TAPPI T 507 "Grease resistance of flexible packaging materials"	Oleic acid, vegetable oil, mineral oil, and other fats/oils	4 h	60°C	408 g block	Number and area of stained spots
Fatty acid test	Solutions containing castor oil, oleic acid, and octanoic acid	5 min	60°C	None	Most aggressive solution without breakthrough/ discoloration

II. Summary of various oil and grease resistance (OGR) test methods.



1. Illustration of oil breakthrough test procedure for oil and grease resistance.

rpm. Latex binders were mixed with each other, additives, deionized water, and an alkali-swellable emulsion thickener under constant stirring for approximately 20 min using an overhead benchtop mixer.

Preparation of coated paper samples

Hand drawdowns

Formulated coatings were applied to NewPage (Miamisburg, OH, USA) freesheet paper (basis weight: 58 g/m², roughness: 4.00 µm, Gurley porosity: 24.6 s) in the machine direction using an automated coater (K Control Coater, RK Print Coat Instruments; Royston, UK) equipped with various wire wound rods to achieve coat weights ranging from 4–10 g/m². Samples were dried at 80°C for 2 min. Coat weights were determined by calculating the difference between the basis weight of the substrate and the average weight of at least six 2 in. x 3.5 in. punched out coated samples. Coated paper was conditioned in a temperature-controlled room for at least 1 h in accordance with TAPPI T 402 "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products."

Performance testing

3M Kit testing

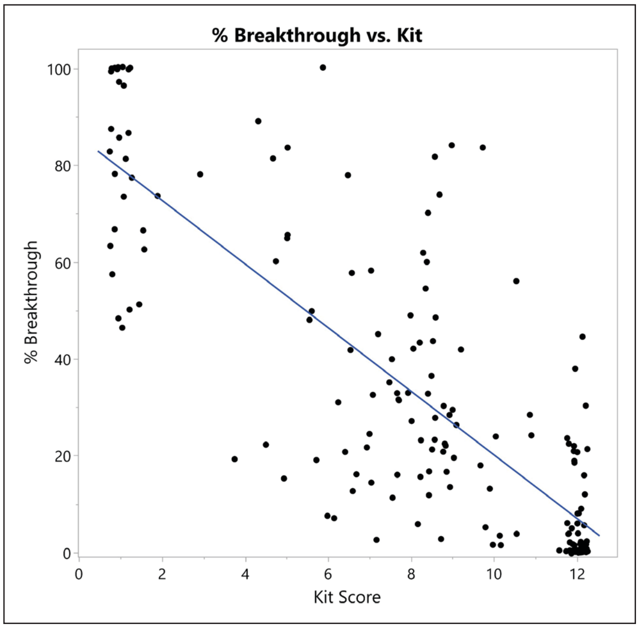
Coated paper samples were tested for oil and grease resistance using TAPPI T 559. Kit solutions composed of castor oil, toluene, and heptane in varying ratios were applied dropwise to the coated substrate, allowed to sit for 15 s, and then wiped away. Any occurrence of solvent breakthrough or substrate discoloration was classified as a failure for that Kit solution. The Kit score for a given sample was assigned using the number of the highest (most aggressive) Kit solution that passed on that coated substrate. Higher Kit scores indicate better performance. Kit tests were performed in replicates of six.

Oil breakthrough test

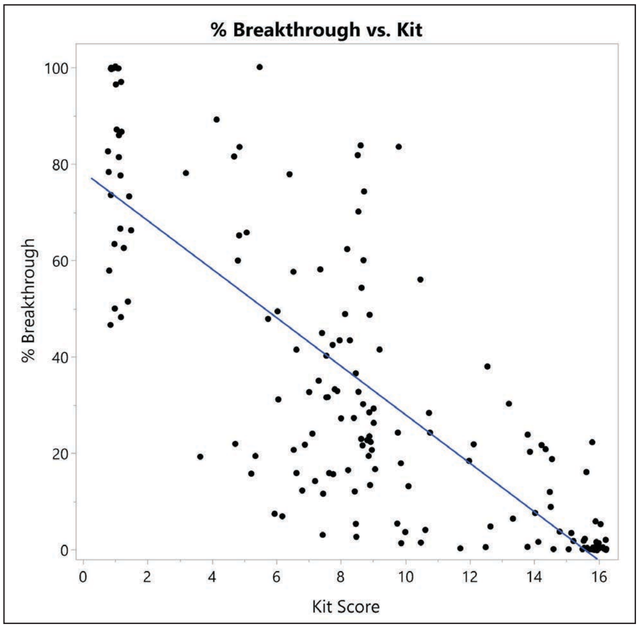
Coated paper samples were also evaluated for oil and grease resistance using an internally developed oil breakthrough test. Coated paper substrates were cut to 2 in. x 2 in. squares and weighed, before being placed coated side facing up atop graph paper squares (also cut to 2 in. x 2 in. and weighed). A 1-in. diameter cotton pad was placed on top of the coated substrate and then saturated with 600 µL of vegetable oil via pipette addition (Crisco pure vegetable oil, B&G Foods; Parsippany-Troy Hills, NJ, USA). Immediately after saturating cotton pad with oil (within 5 min), a 55 g brass weight was placed on the cotton pad, and the samples were placed in the oven at 60°C for 24 h. After cooling samples for 5 min at room temperature (23°C), the weight and cotton pad were removed, and any remaining oil was wiped from the substrate. The coated substrate and graph paper were both weighed to calculate the amount of oil absorbed by each substrate, and the number of squares on the graph paper with visible oil breakthrough was counted. Lower breakthrough percentages indicate better performance. Each sample was tested in replicates of nine. A step-by-step protocol for this test method is included in the Appendix.

RESULTS AND DISCUSSION

Multiple waterborne latex dispersions were applied at varying coat weights and evaluated using both the Kit and oil breakthrough tests (**Fig. 2**). A weak correlation between



2. Percentage of oil breakthrough from oil breakthrough test as a function of Kit score (1-12) for waterborne latex dispersions at various coat weights. Data points have been jittered to aid visibility of densely populated graph areas. The coefficient of determination (R^2 = 0.65) between Kit and oil breakthrough test performance demonstrates a weak correlation between the two data sets.



3. Percentage of oil breakthrough from the oil breakthrough test as a function of Kit score (1-16) for waterborne latex dispersions at various coat weights. Data points have been jittered to aid visibility of densely populated graph areas. The coefficient of determination (R^2 = 0.64) between Kit and oil breakthrough resistance demonstrates a weak correlation between the two data sets.

the two types of data was identified, although there is significant spread in the data that makes it challenging to predict performance of one test based on the performance of another. Samples with low Kit scores (<6) consistently resulted in poor oil breakthrough resistance as well, with breakthrough percentages >40%. This finding enabled the use of Kit testing as a screening method to identify and eliminate coatings with poor performance, which improved experimental efficiency, as the oil breakthrough test is much more time-consuming than the Kit test. Unfortunately, coated samples with the maximum Kit score (12) had oil breakthrough ranging from 0–45%, suggesting the Kit scores cannot always be used to predict high performance in the oil breakthrough test.

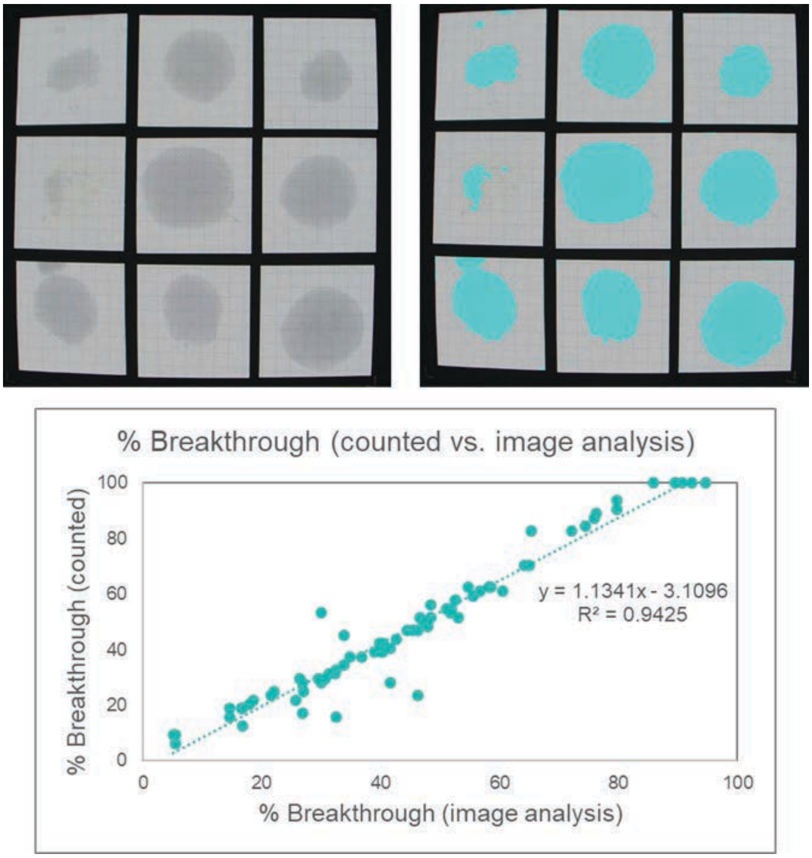
A recently published patent by Taniguchi [5] describes the use of additional, more aggressive Kit solutions (13-16) to achieve further differentiation between samples with high Kit performance. Following the trends identified in original Kit solution compositions, solutions 13-16 were prepared using increasing proportions of heptane to toluene (**Table III**).

Kit #	Castor Oil, %	Toluene, %	Heptane, %
13	0	46.4	53.6
14	0	41.2	58.8
15	0	35.8	64.2
16	0	30.2	69.8

III. Compositions of additional Kit solutions, Kit 13 – Kit 16 (in weight/weight%).

When Kit testing was conducted using the expanded set of 16 solutions, the correlation between Kit and oil breakthrough resistance remained similar (**Fig. 3**). However, coated samples with the new maximum Kit score (16) now had oil breakthrough ranging from 0–25%, suggesting an increase in the likelihood that a sample that had excellent Kit performance will also have good oil breakthrough resistance. Figures 2 and 3 are comprised of the same data set representing the same samples, with the only difference being the range of Kit solutions used. In Fig. 2, many samples achieved the maximum Kit score of 12, while in Fig. 3, those same samples had a range of Kit scores between 12 and 16, highlighting the improved ability to differentiate between samples with high Kit performance. Internal testing procedures were updated to include the four additional Kit solutions in future testing to aid in the screening and down-selection of large sample sets.

The combination of Kit and oil breakthrough testing provided a broader understanding of the OGR performance of current products and new candidates. However, the oil breakthrough test required a significant time commitment not only for the procedure itself but also for data analysis. The initial method for analysis of oil breakthrough test data included measuring the amount of oil absorbed into the coated substrate and the underlying



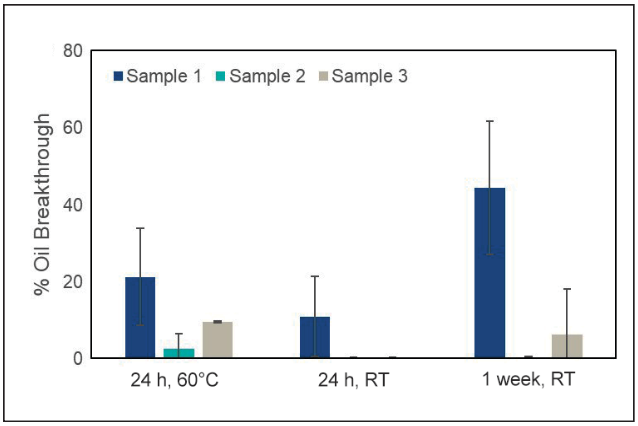
4. Raw (left) and analyzed (right) images of nine replicates of oil breakthrough testing. The analyzed images are highlighted to indicate areas identified as having oil saturation. A plot of the percentage of breakthrough collected via manual counting by the percentage of breakthrough collected via image analysis shows a strong linear correlation, with R^2 = 0.9425.

graph paper, along with estimating the amount of oil breakthrough by counting the number of saturated squares within the graph paper. This method proved to be time consuming and thus limited both the number of coatings evaluated and the number of replicates completed per sample, decreasing the usefulness of the test and the statistical strength of the data.

Through collaboration with an internal digitalization team, an image analysis program (and associated image capture station) was developed to measure the amount of oil breakthrough on the underlying graph paper to eliminate the need for manual counting. Up to nine replicates per sample can be imaged and analyzed at once, and the measured area of breakthrough is highlighted in the resultant images, allowing for manual confirmation of results (**Fig. 4**). The correlation between data collected using image analysis and data collected via manual counting was strong, with R^2 = 0.9452 (Fig. 4). Adoption of the image analysis program increased the efficiency of oil breakthrough test data analysis by 80% (i.e., from 8 h to 2 h for a set of 12 samples evaluated at 2 coat weights each).

The oil breakthrough test can be modified to evaluate performance over a range of conditions (time, temperature, pressure) against different test liquids to more closely mimic customer testing and real-world use cases. Because the end applications for OGR paper can vary significantly, some packaging may need to withstand heated oil/grease (hamburger wrappers or microwavable containers), while others only need to perform at room temperature (bakery wraps). Similarly, some applications require performance for a longer period of time (snack packaging), while others only require OGR for short windows of time (sandwich wrap).

To better understand how performance varies with test conditions, three coating samples were evaluated using the oil resistance test with vegetable oil as the test solution at three different conditions: 24 h at 60°C, 24 h at room temperature, and 1 week at room temperature (**Fig. 5**). The three samples exhibited different levels of sensitivity to the changing test conditions, with Sample 1 being most impacted and Sample 2 being least impacted. Unsurprisingly, samples generally performed better when evaluated at room temperature for 24 h than at 60°C for 24 h or room temperature for 1 week. In the case of Samples 2 and 3, a student's t-test revealed no statistical difference between the performance at 60°C for 24 h and room temperature for 1 week, suggesting that in some cases the added stress from elevated temperature may be able to mimic the effect of longer test periods.



5. Oil breakthrough results for three different coating samples at moderate coat weights (6–8 g/m²) at three different test conditions: 24 h at 60°C, 24 h at room temperature, and 1 week at room temperature (RT). Error bars represent the standard deviation of nine replicates.

While these findings should be further probed with a broader range of coating samples and test periods to better understand the correlation between increased temperature and increased evaluation time, the ability to evaluate the impact of longer exposure times without having to increase testing time would be useful for increasing workflow efficiency.

RECOMMENDATIONS/FUTURE WORK

This research paper investigated the relationship between two OGR test methods. As the market space continues to grow, the number of test methods, both standardized and customer-specific, is also likely to expand.

- A larger comparison study that evaluates the same coatings and substrates across a broader range of test methods would be beneficial to allow researchers to identify correlations between test methods and more easily predict performance for specific customers/application spaces.
- The identification or development of test methods that can differentiate between barrier failure mechanisms would allow a more targeted approach to product development.
  - Low quality of barrier film, including pinholes and inflexibility, could be resolved through addition of film formation aids.
  - Poor oil resistance properties of the barrier material itself would need to be addressed through material composition.
  - Due to the long evaluation time of the oil breakthrough test, poor performance could be caused by film defects, inherent material properties, or a combination of both.

CONCLUSIONS

Modifications were made to both the 3M Kit test and the oil resistance test to improve performance testing capabilities and achieve a broader understanding of oil and grease resistance of waterborne latex paper coatings.

- The inclusion of four additional Kit solutions of increasing severity (13-16) afforded the opportunity to achieve better differentiation among high performing coatings and enhanced our ability to use the Kit test as a screening method when evaluating a large volume of coatings.
- The oil breakthrough test provided coating breakthrough data with a more directly applicable test liquid over longer periods of time, but the original protocol was incredibly time consuming. The use of an internally developed image analysis program reduced data analysis time by 80%.
- These advancements have resulted in a broader and more robust oil and grease resistance testing protocol that can be easily modified to suit customer-specific evaluations. **TJ**

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APPENDIX

Standard operating procedure for oil breakthrough test

1. Heat oven to 60°C (or desired temperature).
2. Cut nine samples of each coated substrate to be evaluated to 2 in. x 2 in. squares.
3. Cut nine 2 in. x 2 in. squares of underlying test paper (grid paper if using grid squares to count approximate breakthrough area or white copy paper if using image analysis software).
4. Place each sample of coated substrate coated side up on top of a square of test paper. It is best practice to prepare the samples on a tray so they can be quickly placed into the oven after preparation.
5. Place a 1-in. diameter round cotton pad on top of each coated substrate.
6. Using a pipette, dispense 600 µL of vegetable oil (or desired test liquid) onto the cotton pad.
7. Place a 55 g circular brass weight (1-in. diameter) on top of the saturated cotton pad.
8. Place the prepared samples in the oven for 24 h (or desired evaluation time).
9. Upon removal of the samples from the oven, allow them to cool at room temperature (23°C) for 5 min.

10. Remove the brass weights, cotton pad, and coated substrate.
11. If using graph paper as the underlying substrate, capture photographs of each square of graph paper, then use the grid squares to measure the percentage of the square with oil breakthrough. If using image analysis software, capture photographs of each square of copy paper to import into analysis software.
12. Results are reported in percentage of the underlying test square with oil breakthrough present. Lower percentages represent better oil resistance of the coated substrate.

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About this journal

ABOUT THE AUTHORS

Test method improvement is critical to evaluation of experimental candidates for product development. The improved test methods in this research paper provide a broader understanding of the oil and grease resistance (OGR) of experimental candidates.

The most challenging aspect of this research was the variability in data points, due in part to the roughness/porosity of paper substrates and local variability in coating thickness. This was addressed by conducting statistical analyses on experimental data to ensure an appropriate amount of replicates were evaluated and that observed impacts were supported by data.

We reviewed new oil and grease resistance (OGR) test methods as part of this research. We found that though there is a broad range of oil and grease resistant (OGR) test methods, overall the methods have more similarities than differences.

The additional, more aggressive Kit solutions described here can be utilized immediately in mills with minimal modifications to their current workflow. The correlation between Kit performance and oil breakthrough performance can provide additional confidence that the Kit-screened materials can perform as expected during real-world evaluations.

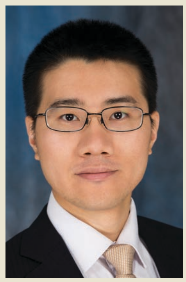
An ideal next step would be a broader study comparing performance of multiple coatings across a larger number of test methods to identify trends and correlations between methods. An additional follow-up project would be the development of a test method that can distinguish between mechanisms of failure (i.e., poor film formation vs. poor inherent grease resistance of coating).

Marianelli

Einsla

Show

Woodfin



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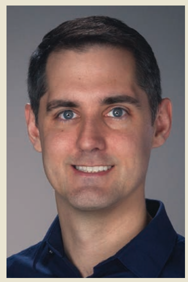
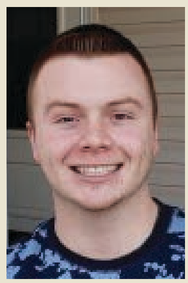


Henderson

Linsen

DeRocher



Oliver

Marianelli is associate research scientist, Einsla is senior research scientist, Snow is R&D/TS&D technologist, Woodfin is senior R&D/TS&D technician, Henderson is senior TS&D scientist, Linsen is senior TS&D specialist, DeRocher is senior TS&D scientist, and Oliver was a senior R&D/TS&D technician for Dow Coating Materials in Collegeville, PA, USA. Shuang was a research scientist at Dow Polyurethanes in Freeport, TX, USA. Email Marianelli at amarianelli@dow.com.