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Handheld FTIR Spectroscopic Applications of Modern Coatings

A review of current coating applications with an in-depth study of a three-layer system using principal components analysis (PCA) and a discussion of wet paint to dry coating changes.

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Introduction

Industrial coatings are designed to protect a material or the underlying structure. Modern coatings are often multilayer systems in which each layer has a specific role. These layers are often two-part formulations, especially for higher performing grades containing a resin, binder, or film former (Part A) and the curative or hardener (Part B). Before these two parts are mixed and applied, the surface condition of the material must be devoid of contaminants and in a suitable condition to be coated. Handheld FTIR instruments are used to monitor, evaluate, and quantify a variety of factors throughout a coating's life cycle from the unused product to its end of useful life.

I. Handheld FTIR: Interface selection, Spectral results, and Overview of current applications

Here we report the degree of cure of three discrete coating types: a 2K epoxy primer, a 2K polyurethane intercoat, and a 2K polyurethane finish coat. These were all marine-grade ambient cure systems and were characterized with a handheld FTIR with a diffuse reflectance interface. This combination of instrument and interface enables us to analyze the sample nondestructively, force free, and independent of orientation. The characterization of the coating as applied to the metallic substrate was performed in-situ without the need for any sample preparation whatsoever.

Below are the types of interfaces available for the handheld FTIR system and below that are examples of typical spectra acquired from the same sample with the three main interface optical designs (ATR, 45°SR, and diffuse reflectance).
The latter two are external reflectance techniques which need no contact force during data collection and therefore will not damage the sample. The ATR, which does require contact, was found to deliver poor results on cured thin hard coatings such as shop primers and better on elastic coating such as silicone. The spectral details were highly dependent on the user's ability to maintain adequate contact during the data collection period. The clear choice for this study is diffuse reflectance.

Figure 1.

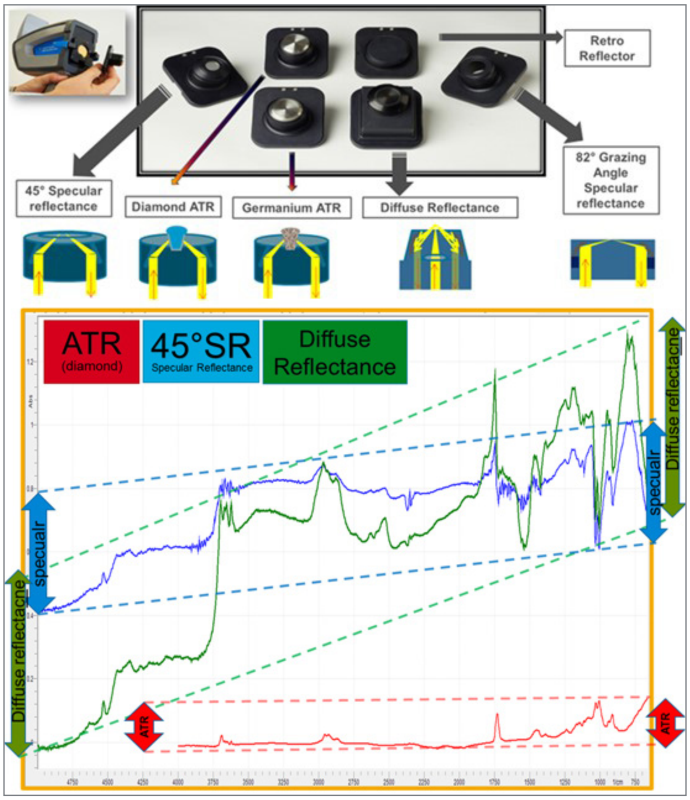


Table 1 provides an overview of the applications, including treatment, cleaning or conditioning the substrate, evaluating chemical and physical changes of the applied coating while still wet, preapplication during its cure, and long-term aging studies. All applications use handheld FTIR with practical in-field use where the selectivity and sensitivity of the instrument enable you to evaluate a diverse range of coatings applications. All the applications can be run in situ with the appropriate interface. However, it is noted that the in-situ degree of cure was rarely reported, and often discrete thin film curing was reported in the literature instead.

Table 1. Proven handheld FTIR coating applications and related information.

PRE-COATING APPLICATIONS
• Aluminum oxide thickness and anion inclusion – precoating check of correct oxide thickness and type • Metal surface cleanliness prior to coating – nondestructive, direct measurement of cleanliness to µg/cm2 • Surface cleanliness of CFRP – spectroscopic changes due to surface contamination • Release agent quantification of release agent on CFRP – Direct nondestructive release agent quantification • Plasma treatment evaluation of release agent + CFRP – results of the treatment of the mold release agent • Onsite portable wet mix ratio quantification of the 2K PU clearcoat in a multiplex paint system – coating uncured and enables both paint spray gun adjustment and prevention of poor coating performance IN-SITU COATING CURE • Three layers (primer, intercoat, and finishing coat) of 2K types were characterized with handheld FTIR
POST-COATING APPLICATIONS (SHORT TO MEDIUM TERM)
• Coatings discrimination of 14 acrylic based paints – positive material identification to either ensure that the correct coating is applied or for warranty claims • Postcure dry coating mix ratio quantification of a 2K EP primer and a 2K PU coating – quality assurance of the dry coating mix ratio to ensure maximum coating performance • Coatings ID and evaluation – nondestructive and portable characterization of coatings • Epoxy primer thickness – direct nondestructive quantification of the coating thickness and condition • Residual solvent inclusion post-curing correlated to the cure state and degree of cure
POST-COATING APPLICATION (LONG TERM)
• 2K industrial epoxy finish weatherometer study (accelerated aging) – nondestructive analysis and modeling of the aging stages enabling prediction of end of life as well as benchmarking for alternate formulations • Polyester film aging study: 1. UV and 2. Hydrolysis – characterization of the spectroscopic changes of PET with two major degradation pathways
GENERAL
• Paints, minerals, and concrete analyzed by a variety of interfaces – most fit for purpose interface selection based on ease of use, sample representation, and information depth • Diffuse interface details and example spectra for a variety of materials, including paints and soils

You can view the above application notes in the Coatings Insights eHandbook http://www.agilent.com/cs/library/brochures/5991-8223EN-Coatings-eBook.pdf

II. Muliplex coating system: Cure and physical changes study

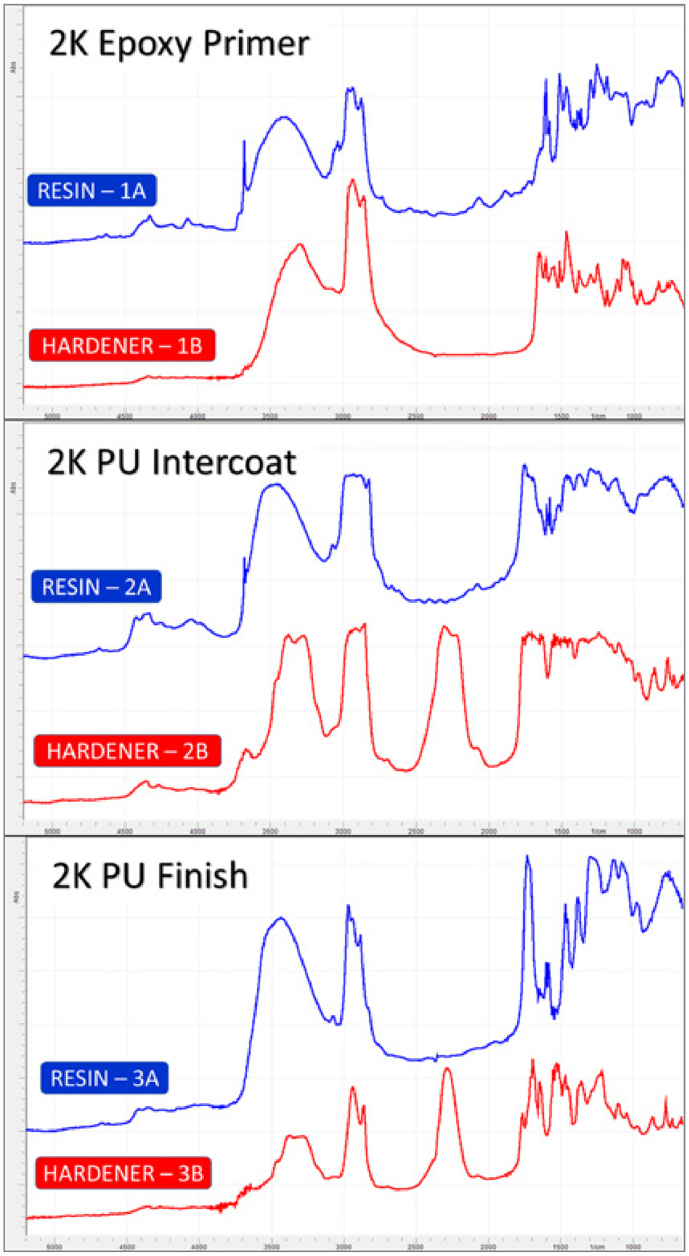
The use of multicoat systems (typically two to four layers) is common where higher coating performance is required. To ascertain the abilities of handheld FTIR for evaluating cured coatings, a 2K epoxy primer, a 2K PU intercoat, and a 2K PU finish marine-grade coating system were characterized individually throughout the recommended cure conditions. This specific multiplex coating system was designed for high-end marine pleasure craft. Each layer was cured under ambient conditions and required thorough mixing of the resin (Part A by convention) and the curative (Part B) followed by chronological FTIR data collection with an Agilent 4300 handheld FTIR spectrometer coupled with a diffuse reflectance interface. The details of each paint are shown below.

Table 2. Primer, intercoat/undercoat, and finishing coat details

	PRIMER	UNDERCOAT	FINISHING COAT
TYPE	Solvent 2K EP	Solvent 2K PU	Solvent 2K PU
DENSITY OF RESIN (A)	1.54769	1.49492	1.38703
DENSITY OF CURATIVE (B)	0.87095	1.06207	1.05206
VOLUME SOLIDS (%)	45	50	49
MIX RATIO (VOLUME)	3:1	3:1	2:1
FINISH TYPE	Matte	Semigloss	High-gloss
CURE DATA	0–1045 mins	0–1045 mins	0–895 mins
COLLECTION INTERVAL	5 mins	5 mins	5 mins
NOMENCLATURE	1A, 1B and 1AB	2A, 2B and 2AB	3A, 3B and 3AB

The primer, undercoat, and finish coats have different functions, and as such are chemically and physically engineered to suit those functions. A single spectrum for each component is shown in Figure 2 paired according to their two-part formulation. In all three cases, the curatives (hardeners) were completely transparent. In addition, all three resins contained white pigment and were visually difficult to discriminate. FTIR spectral features however, clearly distinguish the compounds as related to their chemical formulation and main ingredients. As shown in Table 2 many replicate spectra that were collected separately to create and validate the model. All the data were analyzed in Microlab Expert software, which was also used to collect the chronological cure/phase change/cross linking/densification/solvent loss stages spectra of each of the paint systems.

Figure 2. 2K epoxy primer, 2K undercoat and 2K finish coat. Part A (resin) and Part B (hardener/curative) for each of the three paint types.



III. PCA of the 1A, 1B, 2A, 2B, 3A, and 3B for pre-application positive material ID

As noted earlier, the chemical similarity of 2B and 3B would cause the ATR technique to struggle to discriminate. However, the reflectance spectra contain more information that when combined with multivariate analysis techniques, further reduces identification errors in situations where there could be any doubt. Higher-order PCA discrimination, when used correctly, separates the individual parts of each layer better than library search-based algorithms. This is evident when you look at the PCA of replicate diffuse reflectance spectra using only three factors that explain 90.6% of the variance. Their 3-D score plots show clear demarcation of all six formulations in Figure 3.

Figure 3. This plot of the PC1, PC2. and PC3 (representing the first three principal components are shown below as Factor 1, 2 & 3) three-dimensional scores shows the well resolved clustering of each white pigmented resin (1A, 2A, and 3A) and the three clear hardeners (1B, 2B and 3B). A test set shows that all spectra were correctly identified by the PCA model. The Al blank or Al plate refers to the substrate that the resin or hardener was applied to. A number of reflectance spectra were then tested to ascertain if the PCA model could identify the correct individual component. These results are all tabulated below.

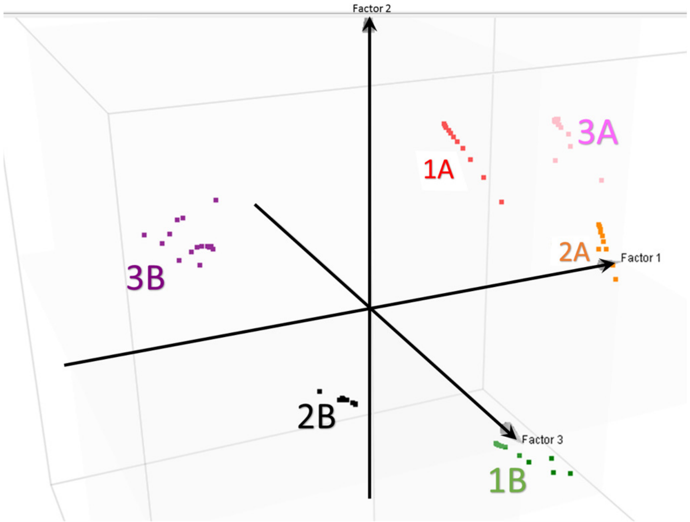


Table 3. Validation spectra tests of the discriminatory power of PCA

SPECTRA	PCA ID	SPECTRA	PCA ID	SPECTRA	PCA ID	SPECTRA	PCA ID
3A_val_1	3A	3B_Val_1	3B	1A_Val_1	1A	1B_Val_1	1B
3A_val_2	3A	3B_Val_2	3B	1A_Val_2	1A	1B_Val_2	1B
3A_Val_3	3A	3B_Val_3	3B	1A_Val_3	1A	1B_Val_3	1B
3A_Val_4	3A	3B_Val_4	3B	1A_Val_4	1A	1B_Val_4	1B
3A_Val_5	3A	3B_Val_5	3B	1A_Val_5	1A	1B_Val_5	1B
3A_Val_6	3A	3B_Val_6	3B	1A_Val_6	1A	1B_Val_6	1B
3A_Val_7	3A	3B_Val_7	3B	1A_Val_7	1A	1B_Val_7	1B
3A_Val_8	3A	3B_Val_8	3B	1A_Val_8	1A	1B_Val_8	1B
3A_Val_9	3A	3B_Val_9	3B	1A_Val_9	1A	1B_Val_9	1B
3A_Val_10	3A			1A_Val_10	1A	1B_Val_10	1B
3A_Val_11	3A			1A_Val_11	1A		

Validation spectra for the discrimination of wet paint

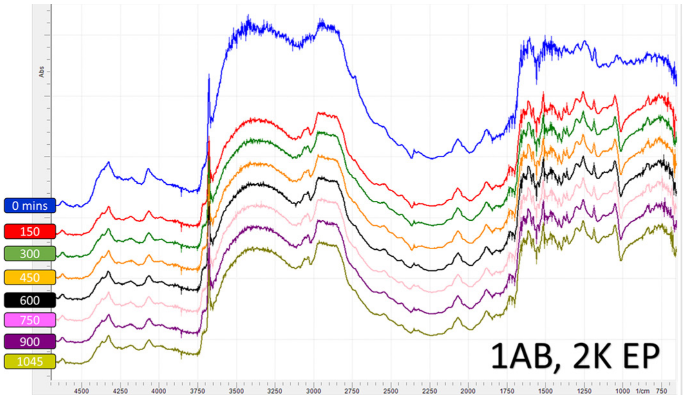
SPECTRA	PCA ID	SPECTRA	PCA ID	SPECTRA	PCA ID	SPECTRA	PCA ID
2A_Val_1	2A	2A_Val_1	2A	2B_Val_1	2B	2B_Val_1	2B
2A_Val_2	2A	2A_Val_2	2A	2B_Val_2	2B	2B_Val_2	2B
2A_Val_3	2A	2A_Val_3	2A	2B_Val_3	2B	2B_Val_3	2B
2A_Val_4	2A	2A_Val_4	2A	2B_Val_4	2B	2B_Val_4	2B
2A_Val_5	2A	2A_Val_5	2A	2B_Val_5	2B	2B_Val_5	2B

IV. PCA of the chronologically collected data for all three systems

The material for each layer was prepared and mixed to the manufacturer's volume ratio, which was re-calculated as mass ratio to reduce errors. It was then applied directly to cleaned aluminum substrate, and measurements were taken every five minutes with a data collection time of ~30 sec. The coating was measured in-situ, resulting in no damage to the coatings or marking of the coating. The temperature in the lab was 21°C. The data collection time exceeded the cure rate by a significant margin to ensure that the cure stage was included in the kinetic measurements. The spectral measurements are of the same exact spot during the chemical and physical changes.

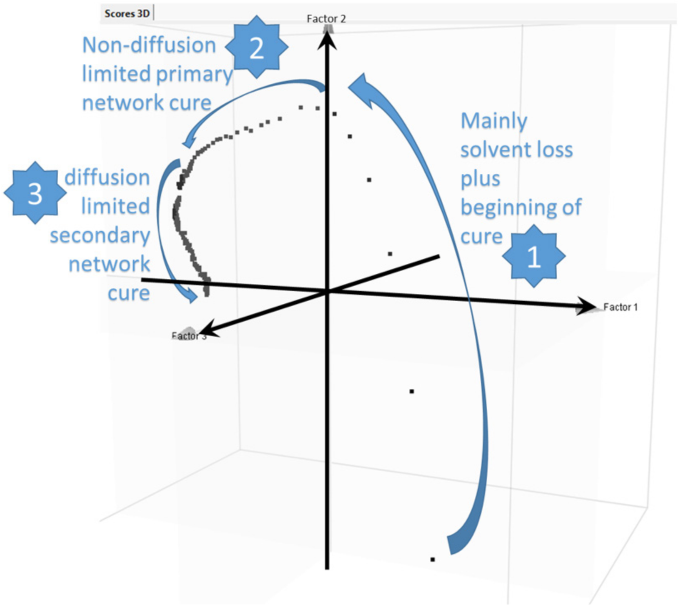
All three of the two-part paints cure in a complex manner with distinctive phases resulting in detailed spectra that are particular to each system with complex chemical changes to match. The changes are numerous, requiring multivariate analysis to highlight the details for each system's principal components. A partial least squares analysis was also performed. The former was used to elucidate phase changes, and the latter was used to evaluate the possibility of a cure state model.

Figure 4. Selected diffuse spectra of the ambient cure of the 2K epoxy primer, spectra stacked for clarity. Ratio 3:1 (<0.01% error, gravimetrically extrapolated volume).



The PCA model reveals some distinctive phase changes as the two-part paint mixture cures into a cross-linked and reacted dry coating. The main changes have been marked onto Figure 4, where these three factors explain 99.2% of the variance in the cure data of 1AB.

Figure 5. PCA score plot of the first three factors of the PCA model for all the spectra of the 2K epoxy primer system. In total, 210 spectra.



The successful qualitative PCA model with the reflectance spectra was subsequently re-analysed and re-worked into a quantitative cure model using the cure progression time as the measured Y-value.

The spectra were re-modelled using the multivariate partial least squares algorithm and Savitsky-Golay 1st order derivative with 9 point smoothing. The actual vs. predicted values table for some of the chronological predictions based on a six-factor model are presented below.

Table 4. PLS1 partial least squares quantification model, predicted cure times vs. vs the actual cure time, note the predicted results are based on spectrometer spectral results

ACTUAL (MINUTES)	PREDICTED (MINUTES)	ACTUAL (MINUTES)	PREDICTED (MINUTES)
0	-23	**600**	618
100	66.3	**700**	757
200	222	**800**	776
300	326	**900**	910
400	391	**1000**	1011
500	499	**PLS1 predicted results for 1AB**	

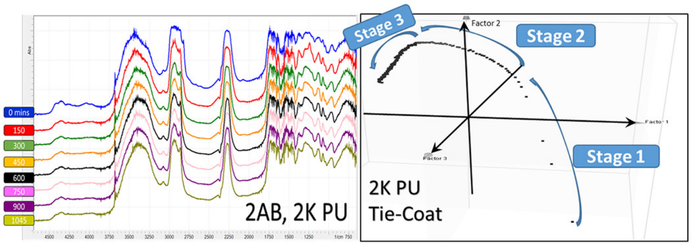
The reflectance spectra of the 2K PU intercoat or tie coat was also examined using a multivariate PCA, the statistical factors are presented below.

Table 5. 2K PU intercoat five-factor PCA model explaining ~99% of model variance

2K PU INTERCOAT QUALITATIVE FACTOR ANALYSIS						
FACTOR	F-RATIO	F-TEST	REMAINING VARIANCE (%)	EXPLAINED VARIANCE (%)	EIGENVALUE	MALINOWSKI INDICATOR
1	348.7	1	15.4851	84.5149	292.0142	0.00E+00
2	49.56	1	3.5377	96.4623	41.2804	0.00E+00
3	7.163	0.9926	1.8199	98.1801	5.9356	2.54E-07
4	1.740	0.8129	1.4046	98.5954	1.4348	1.23E-07
5	1.579	0.7911	1.0299	98.9701	1.2946	8.92E-08

Figure 6 shows the selected spectra as well as the score plot of the first three principal components for the two-pack polyurethane paint during ambient cure. The spectra were stacked for clarity. The three main stages are again apparent and have not been superimposed. The first measurement began at the bottom right of the 3-D score plot. The complex curing and other physical changes are only evident from the PCA since classical direct spectral analysis is unable to elucidate these changes.

Figure 6. Selected stacked spectra collected during ambient cure (left), 3-D score plot for PC1, PC1, and PC3 of the five-factor model. Ratio 3:1 (<0.01% error, gravimetrically extrapolated volume). Arrows indicate the spectral order and major event changes.



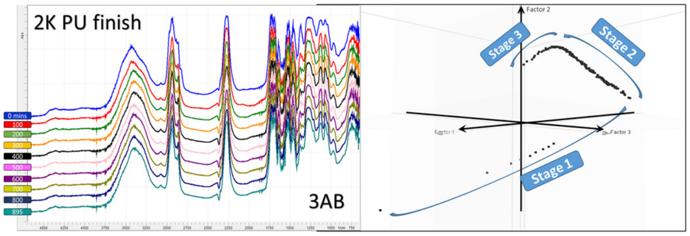
In Figure 6, the complexity of the cure is apparent where a number of processes were occurring to different degrees depending on the stage to which the cure had reached. The degree of cure can be modeled but would have required cross referencing with DSC or intimate knowledge of the chemistry involved.

The 2K PU finishing coat was also evaluated by PCA and the results of the qualitative factor analysis are tabulated below.

Table 6. 2K PU intercoat five-factor PCA model explaining ~99% of model variance

2K PU FINISHING COAT QUALITATIVE FACTOR ANALYSIS						
FACTOR	F-RATIO	F-TEST	REMAINING VARIANCE (%)	EXPLAINED VARIANCE (%)	EIGENVALUE	MALINOWSKI INDICATOR
1	113.9498	1	37.1372	62.8628	100.0892	0
2	54.7757	1	7.0997	92.9003	47.8251	0
3	4.6291	0.9686	4.5765	95.4235	4.0174	3.95E-07

Figure 7. 2K PU finish gloss white, selected spectra during the 895 minute spectral collection period (left). 3-D score plot includes all 180 spectra. The arrows indicate the direction the variance changes with chronological spectra.



Both PU paints behaved spectrally in a highly complex manner. More work would be required to create a quantitative model that compensates for the following factors throughout the reaction time: the reduction in chemical potential, film thickness, changes in density, increase in the extent of cure (polymerization and cross-linking), solvent loss, crystallinity changes, diffusion effects. Useful information from the in-situ characterization can be used to ascertain a layer reaction state.

Conclusion

Handheld FTIR has been used extensively for coatings analysis for a number of years. However, it is often seen as a "single issue" technique. We hope to have shown here that FTIR, when used with a proven interface, enables a single system analysis to address and provide answers to many of the issues that can lead to either improper application or to early coating failure. Coatings are highly evolved, chemically and physically engineered systems. In this study, we have shown that robust spatial discrimination of similar curatives is possible in PCA k-space analysis that would be highly dubious in traditional library algorithms using individual spectra-matching techniques rather than variance-matching techniques. The chronological ambient cure study reveals many interesting results in the PCA, which can be matched to spectral changes that are impossible to see visually, either in the coating or in the collected spectra. All spectra used in this study were collected with standard handheld equipment and a diffuse external reflectance interface in a non-destructive and force-free manner. The ease of data collection also means that a higher number of scans is attainable without affecting the number of acceptable spectra.

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