



ANALYTICAL SERIES

Chemiluminescence for the Early Detection of Weathering Effects of Coatings

Part II: Experimental Set-Up and Examination

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In this two-part series, the analytical technique of chemiluminescence for early detection of weathering effects is presented. Part I (see April 2010 CoatingsTech, page 66) introduced the fundamentals of chemiluminescence. This concluding Part II presents the experimental set-up and examines chemiluminescence modes and combinations with other techniques.

EXPERIMENTAL

Set-Up

The chemiluminescence (CL) cell consists of an oven and a physical device sensitive enough to detect the weak emission of CL photons. Typically, either a photomultiplier or CCD detector is used for the latter. Sample and oven are placed in a gas-tight cell that allows exposure of the sample with gases and that incorporates a quartz window that allows the emission to leave the cell and enter the detector.

The principal set-up is represented in *Figure 8*. (Part I of this article contains *Figures 1–7*.) While oxygen is blown into the CL cell to start the auto-oxidation reaction to be detected as CL emission, alternatively nitrogen is used, especially during heat-up phases. This allows the detection of dissolved oxygen or the break-up of hydroperoxides (formed in the prior history of the sample) already in the sample. In those two special cases mentioned, a heat-up under nitrogen would generate CL emissions until this source of oxygen is used up. If no further hydro-

peroxides or dissolved oxygen is in the sample, the detected emissions should be only in the order of the background noise of the detection system.

In most cases, apart from initial heat-up, isothermal temperature curves are applied, while the alternative linear heat-up is used more rarely. Either way, it has to be taken into account that the CL emission observed is influenced by the temperature dependence of the reaction rate constant, the aging process, and transport properties of ambient gaseous oxygen into the sample.

Choice of Investigation Temperature

An important experimental factor of the CL investigation of weathered samples is the temperature up to which the sample is heated in the CL investigation. On one hand, a raise in temperature increases the reaction rate of the oxidation reaction and hence the CL emission (*Figure 9*). On the other hand, the investigation temperature should generally not exceed normal conditions of exposure. The latter demand is important even in the case when CL only is used to evaluate rankings of oxidative stabilities of different materials. Temperatures higher than those under normal exposure conditions might open degradation paths that do not occur under normal exposure conditions for one material. However, this may not occur for the others, thus relatively disfavoring the sensitive material in the evaluation, which might be completely irrelevant under actual exposure conditions.

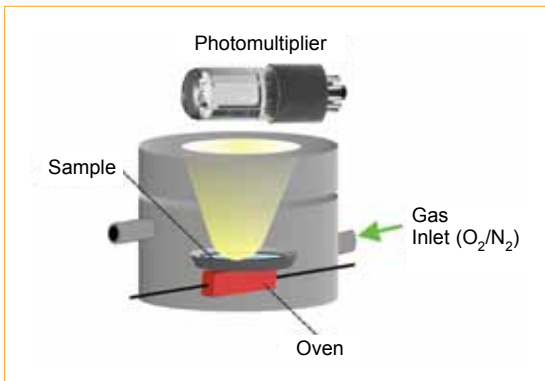


Figure 8—Principal set-up for CL measurement consisting of a gas-tight oven, a detector for the weak CL emission, and a gas inlet and outlet.

An example of this might be a different sensitivity to high temperature for different stabilizers used in various plastic materials in a CL evaluation.

Quantum Efficiency

As outlined in equation (1) (see Part I, April 2010 *CoatingsTech*, page 68), the quantum efficiency of the process influences the observed CL emission. This quantum efficiency is material specific and characterizes the probability that a photon actually is emitted after chemical excitation of a molecule into an electronic excited state. Its value can vary dramatically from one material to the next between the possible maximum of 1 (each excited molecule emits a photon) found for fluorophores down to a typical value for less ideal emitters, as found for most polymers, of 10^{-8} to 10^{-15} .

The quantum efficiency is difficult to determine but becomes important as soon as different materials are compared in terms of their absolute CL emission. As will be shown in the Applications section, one approximation to get around the dif-

ficult determination of the quantum efficiency consists of a normalization procedure of the CL emissions of the aged material to the CL emission of the unexposed one.

Usually, a real sample is not a single material but rather consists of a mixture of different materials, each of which will contribute to the overall CL emission according to its quantum efficiency and its reaction rate. The observed CL emission is the sum of these individual CL emissions of each component in the system. Apart from the polymer matrix, additives such as stabilizers, fillers, unreacted adducts, catalyst residues, and other contaminations can also contribute. Even if their relative concentration is low, a high quantum efficiency for these components can mean that the overall CL emission can be influenced by it in an over-concentration-proportional way.

APPLICATIONS

Comparison of Specific Points in the CL Curve

As already mentioned in the Principles of Chemiluminescence section, two possible specific points (*Figure 3* in Part 1) could be used to characterize a CL curve:

- the duration of the induction time of oxidation (after which the propagation period starts)
- the time to reach a maximum of the CL emission

In many cases, a comparison of the oxidative stability based on the evaluation as induction time will lead to very similar or the same rankings as an evaluation on the basis of the CL maxima. An evaluation on the basis of induction time, however, at times can be difficult as the system may

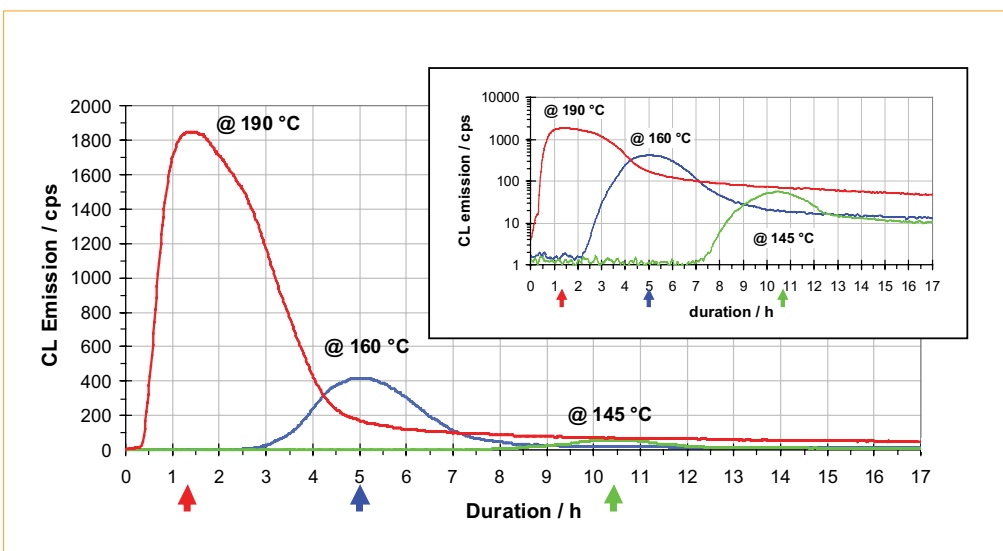


Figure 9—CL emission of an LDPE at three different CL investigation temperatures (isothermally). Linear CL emission scale for big diagram and logarithmic emission scale for smaller inset.

not show a quasi constant CL emission prior to the end of the induction time and/or a nonlinear rise after the end of the induction period. This then makes a construction of the induction period as the intersection of two tangents more difficult (Figure 10).

A possible reason for this non-ideal behavior could be the superimposition of the oxidation reaction with diffusion of oxygen into the polymeric sample, which is altered drastically near the glass transition temperature (T_g) of amorphous or semi-crystalline polymers (where many related properties can change by orders of magnitudes).

A major advantage of the evaluation of the CL emission curve at specific points compared to the evaluation of absolute emissions is the independence of the quantum efficiency of the respective CL emitting system. The main disadvantage is the need to pursue the CL experiment until the induction time has been overcome and the CL emission rises to the maximum. This duration can be prohibitively long for stabilized systems.

The first example for model LDPE agricultural films stabilized with a low concentration of HAS (hindered amine [UV] stabilizer) of 0.2% (Figure 11) shows the systematic influence of a variation in the duration of a weathering exposure from unexposed to 42 days artificial ADF test on the subsequent CL emission curves.

The example shows a systematic decrease in the duration to reach the CL maximum with increasing weathering exposure. In absolute CL emissions there also is a systematic increase with increasing exposure duration up to 21 days. However, there is a decrease in emissions for 42 days again, which is thought to be caused by a

change in quantum efficiency due to the weathering exposure-caused degradation process.

It should be noted that a very high temperature of 172 °C was used for this CL investigation (while the artificial ADF test was conducted at temperatures up to 60 °C). The main reason to do so was the reduction of resulting time to reach the CL maximum compared to lower CL investigation temperatures. However, it should be pointed out that the HAS used in the samples can migrate out of the sample and be rendered inefficient at a much higher extent than at actual application temperatures. If different stabilizers had been compared, different rates for migration and thermal deactivation could be different at those higher temperatures, and, as such, unproportionally affect some stabilizers over others as compared to maximum application conditions.

Comparisons of Absolute CL Emissions

The advantage of this approach is the fact that, especially for stabilized samples, it is not necessary to wait the long exposure time until the end of induction time. Instead, in many cases, it is only necessary to wait for the absolute emissions to exceed the noise level. Given that the sensitivity of the CL instrumentation is sufficiently high, this often allows one to compare different samples at much shorter exposure durations. The disadvantage results from the comparison of absolute emissions, which for different samples means that the respective quantum efficiency has to be taken into account.

An approach that avoids the cumbersome determination of the respective quantum efficiencies of all sample materials to be compared^{10, 16, 17}

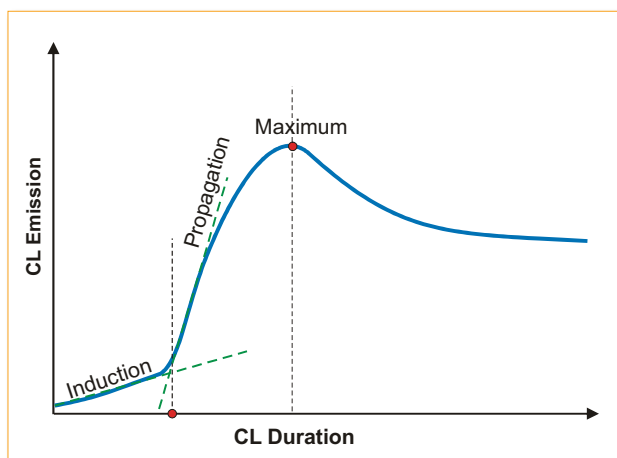


Figure 10—Construction of the induction time in the case of a non-ideal course of a CL emission curve.

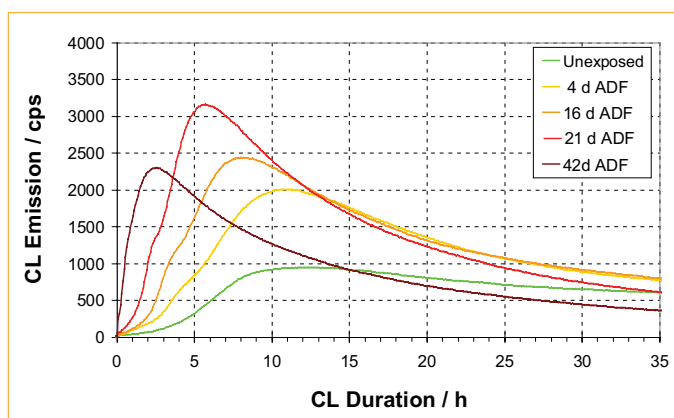


Figure 11—CL investigation of the influence of artificial weathering duration (BAM developed Acid Dew and Fog test ADF-J 1,5) for a model LDPE stabilized with 0.2% Hostavin N30 HALS under air, isotherm at 172°C. (BAM is the acronym for German translation of Federal Institute for Materials Research and Testing.)

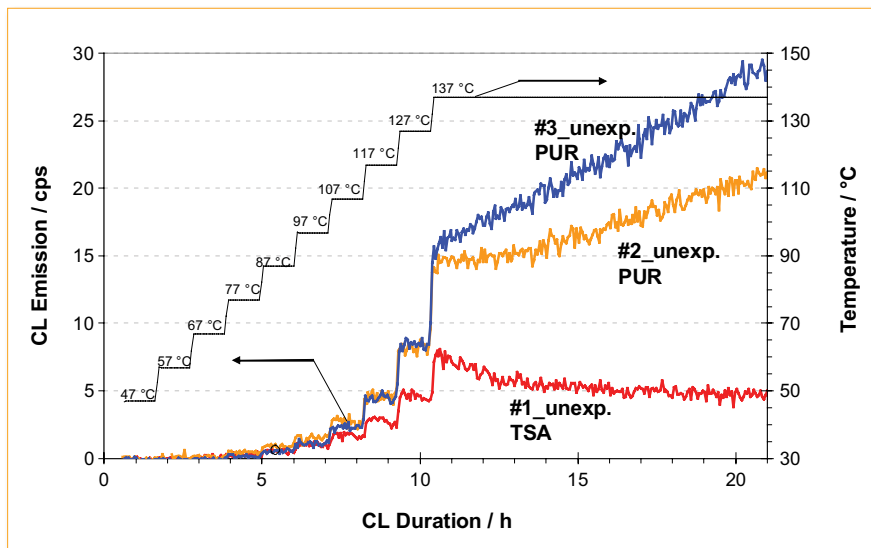


Figure 12—CL emission of unexposed automotive coatings (#1: TSA; #2 and #3: PUR).

uses a normalization to the emission of the respective unexposed samples and will be highlighted in the following on the basis of a comparison of the stability of three clearcoat / basecoat coating systems on aluminum. The exposure duration of a few hundred hours of artificial weathering still left the materials within the induction time; the actual main loss in properties like gloss and haze retention only occurs at about 3000 hr of artificial weathering. That means that the end of the induction time is not expected to be earlier than at least 2000–2500 hr of artificial weathering.

While a complete coating system was studied, the CL evaluation was predominantly sensitive to the uppermost clearcoat layer. This is mostly due to absorption of emission in deeper layers of the material and could be demonstrated by a comparison of the CL of the whole coating system to the CL of free films of the clearcoat.

As the temperature dependence of the CL emissions for the three systems was not known, CL was not only the measure for one temperature level but for 10 levels between 47 °C and 137 °C.

For the three unexposed coating systems (Figure 12) the two polyurethane systems (#2 and #3) not only show higher CL emission on all temperature levels but also show a different behavior within the highest temperature level of 137 °C. The decrease with increasing duration on this temperature level for the thermosetting acrylic #3 contrasts with the increase for the two polyurethanes, which is likely due to different oxygen diffusion behavior.

The CL evaluation of artificially exposed systems (Figure 13) shows emissions that are about six-fold higher than for the unexposed systems. For a comparison in terms of stability, however, the different quantum efficiencies have to be considered.

Normalization of the CL emission maximum at 137 °C of the respective unexposed system results in a change of rankings for system #3 (Figure 14).

To allow a better comparison of quantum efficiency corrected CL emissions, the respective initial CL emissions upon reaching a new temperature level are plotted versus this temperature (Figure 15). The evaluation shows that for a temperature range between 60 °C and 115 °C, a stability sequence #3>#2>#1 is valid, whereas

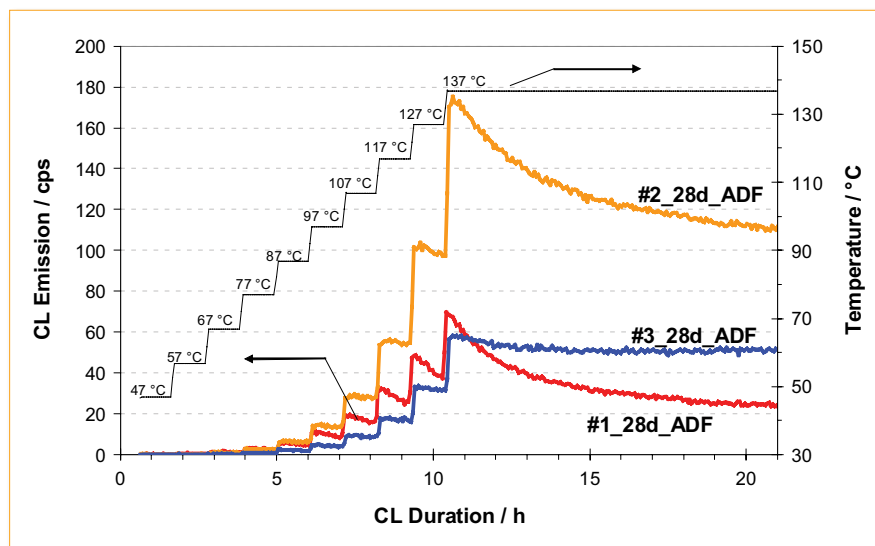


Figure 13—CL emission of automotive coatings that had been exposed for 28 days in the artificial ADF weathering test. For a comparison in terms of stability, the respective quantum efficiencies still have to be considered (#1: TSA; #2 and #3: PUR). Note the different ordinate scaling compared to Figure 12.

Figure 14—CL emission that was corrected to different quantum efficiency by normalizing to emission of respective unexposed systems at 137°C. (#1: TSA; #2 and #3: PUR).

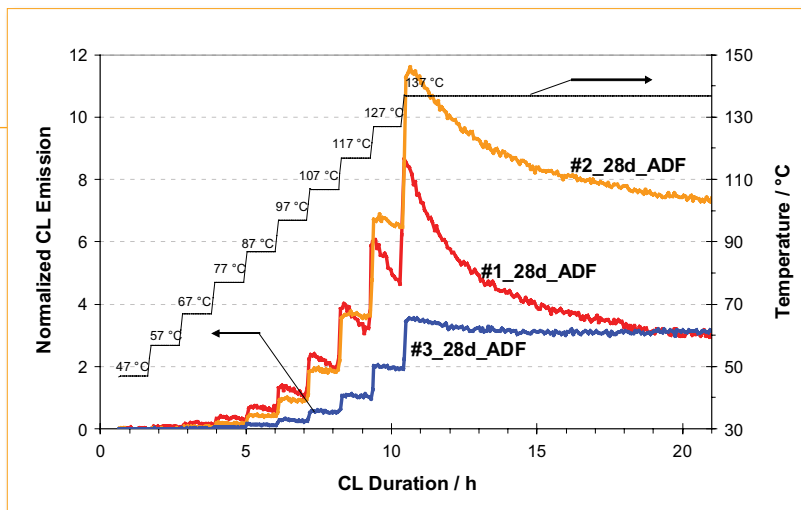
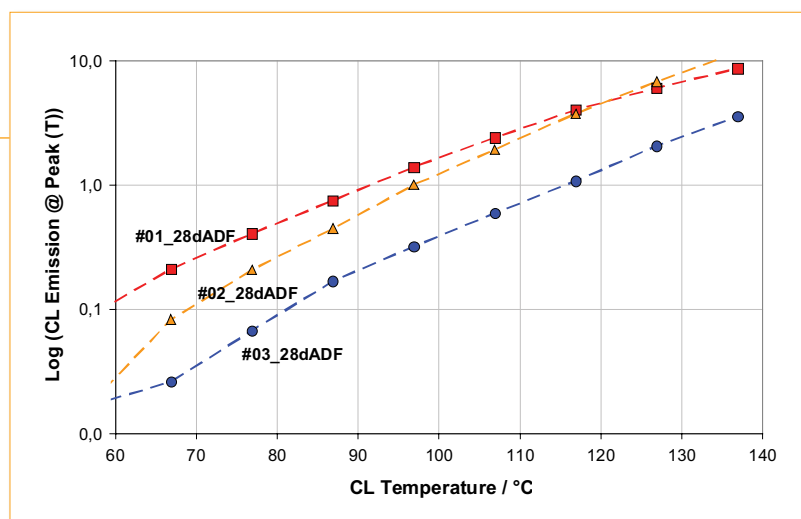


Figure 15—Normalized CL emissions after 28 days of the artificial ADF weathering test as in Figure 14, but logarithmic CL emission of peak value at each respective temperature step is shown for scaling reasons only (#1: TSA; # 2 and #3: PUR).



for temperatures between 115°C and 140°C, the stability ranking is #3>#1>#2. As temperatures on real car surfaces can reach up to 90°C, the region up to this temperature and below it is considered most relevant.

More comprehensive recent studies of the weathering effects of automotive coatings using the CL evaluation¹² showed that the duration of the artificial weathering could be reduced by at least a factor of 2–3 compared to macroscopic evaluation techniques like visual assessment or haze and gloss measurements. This implies, however, that the demands to rank correlation are reduced to screening group correlations of good, medium, and low performances.

SPECIAL CL MODES AND COMBINATIONS WITH OTHER TECHNIQUES

The signal derived with CL often is able to reveal very sensitively if a change in the oxidative stability of a material occurs. However, work only

starts at that point to investigate what actually caused the change chemically. A few possible techniques that can be used to gain further information are listed as follows:

Spectrally Resolved CL

Whereas the CL discussed so far was exclusively examined as wavelength integral signal, either sets of bandpass filters or monochromators can be used to split the signal into wavelength ranges.

Theoretically, the additional spectral information could be used to identify the reacting species. However, in most cases the spectral resolution does not help further since signal intensity is often insufficient and, with reacting species in high concentrations in condensed matter, energy transfer will occur and only the species with the highest quantum efficiency will determine the observed spectrum. Moreover, at least spectra of polymers show very few and broad bands and do not give much information for differentiation.¹⁸

Imaging CL¹⁹

By means of imaging onto an array of photon detectors (mostly CCD), heterogeneities within the oxidation of the surface of the sample can be investigated. In this way, for instance, inhomogeneous distributions of components of the sample or inhomogeneously damaged areas of the sample can be identified.

Since this surface of the sample could be prepared as the cross-section of a material, this can be used to investigate oxidation profiles.²⁰

Combination with Other Analytical Techniques

Due to the complexity of the quantum efficiency determination, only relative reaction rate values can be compared for the different samples. To evaluate the absolute reaction rate (for instance, to determine the concentrations of oxidation products), additional techniques have to be applied.

By combining the information from CL with the information gained from other techniques, an interpretation of CL measurements only then becomes possible.

An interesting addition in this sense, oxidation uptake has emerged over the last couple of years,²¹ as well as carbon dioxide evolution,²² while combination or coupling with established techniques like IR²³ or DSC²⁴ have already been in use for a longer time.

CONCLUSIONS


The CL signal monitors the ongoing oxidation reactions very sensitively and selectively. As most aging reactions are related to oxidation reactions, CL is suited to follow aging. These properties enable CL to shorten the long duration of weathering tests of polymeric materials including paints and varnishes.

The observed CL signal in response to a temperature program is the result of the superposition of the temperature dependence of the reaction rate constant, the aging process, and transport phenomena.

Normally, weathering tests aim at certain macroscopic properties. As these macroscopic properties need a high number of damages to accumulate before a change can be detected, weathering tests of very long duration result. However, with a sensitive substitute property like CL, a change can be detected much earlier. The substitution means that only ranks can be compared. In addition, the detection and an earlier

state of the aging reaction can mean that ranks can be different until the later stage that was needed for the macroscopic property that was to be substituted.

For the evaluation of the CL signal, either its course over time can be used and certain critical points like the end of induction time, or reaching the maximum emission can be determined, or a comparison of absolute emissions can be applied. The latter approach allows shorter duration of the test and lower temperatures to be applied during the CL test but necessitates accounting for the different quantum efficiencies of different samples.

To determine mechanisms, the investigation of the CL signal has to be complemented using other analytical techniques such as IR. 

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