EPCEd Five Part Series - September/October: Impact of Redox on Biocides

Did you know……………….there is valuable information available about the use of redox systems for effective reduction of residual monomers/VOCs used in emulsion polymerization? EPCEd is partnering with Brüggemann for this fourth in a series of *Did You Know* issues for 2023 to highlight best practices for redox application in emulsion polymers, including reaction kinetic data and guidelines for best practices. This issue focuses on the impact of redox on biocides.

Previous issues in this series highlighted the fundamentals of redox systems typically used for emulsion polymer chase, discussing dosage, rate of addition, rate of reduction of residual monomers, initial screening tests for selection of the best reducing agent/oxidizer for the polymer recipe, and redox optimization for the chase.   Less often considered is the effect a chosen reducer or oxidizer can have on a given biocide. With increased regulatory restrictions and the general trend in demand for products with minimal biocide content, any degradation from reducers or oxidizers can be costly.

First, a study on the impact of various reducers on chloromethylisothiazolinone (CMIT) was performed with a model system using a 1:1 weight ratio with tertiary-butyl hydroperoxide. The redox pairs were fed into an aqueous solution with a pH of 4 at 60°C under agitation over a period of one hour to a final concentration of 0.1%. The reaction was cooled to 30°C, pH adjusted to 8.5 with NaOH, biocide charged and mixed for 30-minutes.

Reducer	Oxidizer / Reducer Molar Ratio Used	State	Remaining CMIT (PPM)	Final pH
SMBS	2.1 : 1.0	Oxidative	0	8.5
Isoascorbic Acid	0.98 : 1.0	Reductive	58	6.4
Bruggolite® FF6M	1.06 : 1.0	Oxidative	47	8.1
Bruggolite® FF6M	2.0 : 1.0	Oxidative	7	8.2
Bruggolite® E28	1.47 : 1.0	Oxidative	33	8.2

Figure 1: CMIT degradation over 15 days. Starting value – 150 ppm.

Given that each redox pair was used at a 1:1 weight ratio, the vastly different molecular weights of each reducer hadn't been considered. However, as illustrated in Figure 1, it was found that the molar redox ratio, as calculated from the molecular weights of each redox pair, was an impactful variable on CMIT stability. The trend in Figure 1 shows that the more oxidative the environment, the greater the degradation of biocide illustrating the importance of understanding the stoichiometric levels of redox in your formulation. Also, data suggests that CMIT is best preserved under acidic environments, thus the pH shift noted in the isoascorbic acid sample likely had a positive impact as well. Logically, one may first investigate the redox package used in post-polymerization, or chase, as a first step. However, the source of radical generation for initiation and main polymerization should also be considered. Often, thermal initiation with a persulfate is utilized, but when strictly relying on temperature for the cleavage and degradation of such oxidizers, time must be considered given the reliance on half-life in this case. If this method is used for initiation, it should be understood that there will be residual, unreacted oxidizer when entering the chase step. While the redox package used for chase may be stoichiometrically balanced, the residual oxidizer from main polymerization yields an imbalance of overall redox. This, however, is not a concern for balanced reactions which utilize chemically generated radicals via redox for initiation and main polymerization. A separate, but similar study looked at the effects on benzisothiazolinone (BIT) and isothiazolinone blends (CIT/MIT).

In this second study, a styrene-acrylic latex with a pH of about 4 was used to test different redox pairs and dosages. All of the oxidizer was charged at once and the reducer was fed over 30 minutes at 60°C. Biocide was charged after cooling to 35°C and the latex was kept at room temperature for 14 days. Biocidal active ingredient content was tested via HPLC after this period. Figure 2 shows the results of testing a few different reducers at various weight ratios with tBHP, as well as tBHP alone. The final column shows the experimental

value of biocide that was found after the 14-day period, while the initial value was theoretical based on the biocide dosage.

Overview of the results from HPLC analysis

Trial number	Oxidizing agent (Ox) tBHP (tert-Butyl hydroperoxid)	Reducing agent (Red)	Ratio Ox:Red w/w%	Biocide	Active ingredient content in %	Initial value (Target value) in ppm	Actual value in ppm
1	-	-	-	Sanitized® BIT20D	20 % BIT	200	229
2	-	-	-	Sanitized® CI15	1.5 % CIT/MIT	140	141
3	tBHP	Bruggolite® FF6 M	2:1	Sanitized® BIT20D	20 % BIT	200	82*
4	tBHP	Bruggolite® FF6 M	2:1	Sanitized® CI15	1.5 % CIT/MIT	140	122
5	tBHP	Bruggolite® FF6 M	1:1	Sanitized® BIT20D	20 % BIT	200	199
6	tBHP	Bruggolite® FF6 M	1:1	Sanitized® CI15	1.5 % CIT/MIT	140	87*
7	-	Bruggolite® FF6 M	-	Sanitized® BIT20D	20 % BIT	200	22*
8	tBHP	-	-	Sanitized® BIT20D	20 % BIT	200	9*
9	-	Bruggolite® FF6 M	-	Sanitized® CI15	1.5 % CIT/MIT	140	9*
10	tBHP	-	-	Sanitized® CI15	1.5 % CIT/MIT	140	146
11	tBHP	Bruggolite® TP 1646	2:1	Sanitized® BIT20D	20 % BIT	200	176
12	tBHP	Bruggolite® TP 1646	2:1	Sanitized® CI15	1.5 % CIT/MIT	140	155
13	tBHP	Bruggolite® TP 1646	1:1	Sanitized® BIT20D	20 % BIT	200	189
14	tBHP	Bruggolite® TP 1646	1:1	Sanitized® CI15	1.5 % CIT/MIT	140	155

60°C polymerization temperature

*Significant deviation from the target value

Figure 2. Effects of Redox on BIT and CIT/MIT blends.

A redox ratio of 2:1 between tBHP (oxidizing agent) and Bruggolite®FF6M (reducing agent) resulted in a strong degradation of the active ingredient BIT from 200 ppm to 82 ppm (Trial 3), whereas an adjusted ratio of 1:1 (Ox:Red) of the two redox components allowed the most complete preservation of BIT from Sanitized® BIT20D (Trial 5) similar to the findings with CMIT. The use of either reducing agent (Trial 7) or oxidizing agent (Trial 8) *alone* resulted in significant degradation of BIT in each case. In contrast, when the reducing agent was changed from Bruggolite®FF6M to TP 1646, a consistently high active ingredient content was analyzed for both redox ratios (Trials 11 and 13).

In contrast to the findings with BIT, a ratio of 2:1 between tBHP (oxidizing agent) and Bruggolite®FF6M (reducing agent) did not lead to a strong decrease in the active ingredient content when Sanitized® CI15 (1.5% CIT/MIT) was used (Trial 4), but degradation occurred on the other hand - and also in contrast to the studies with BIT - with a ratio of 1:1 (Trial 6). The sole use of a reducing agent also led to a strong decrease in the active ingredient content with CIT/MIT (Trial 9), but this was not the case for the sole use of the oxidizing agent (Trial 10). When the reducing agent was changed from Bruggolite®FF6M to TP 1646, again a consistently high active ingredient content could be analyzed for both redox ratios (Trials 12 and 14).

In summary, it can be said that the redox components had less influence on the CIT/MIT stability than on the BIT stability. And in combination with the study on CMIT, we can see that there is no single solution for all systems. Rather, it is essential to use a suitable redox ratio and package for the selected biocide. Furthermore, as previously noted, residual oxidizer from a thermally initiated system that is not taken into account can have potentially devasting results on biocide stability.

EPCEd Five Part Series - September/October: Impact of Redox on Biocides

    As always, we invite your questions and comments by going to *info@epced.com* . Additionally, we invite you to go to Brüggemann's Institute of Redox Chemistry (see link at end) – a collection of tutorials on redox chemistry for emulsion polymerization, providing greater detail of redox combinations and process optimization techniques. For more information, contact Brüggemann, *BCUS_Sales@brueggemann.com*