CASE STUDY

The right combination of biocides & redox initiators for the retention of biocide stability

Abstract

Market requirements, driven by regulations and end-user preferences, demand polymer dispersions with maximum protection against microbes but minimal addition of biocides. The blanket solution sought by the paints and coatings market does not exist yet. How can microbial stability of polymer dispersions be guaranteed using in-can biocides despite this? And what influence does the correct selection of redox agents, as initiators for the polymerization process, play regarding the stability (it is well known that biocidal active ingredients are often destabilized by redox agents)? The companies SANITIZED AG and L. Brüggemann GmbH & Co. KG followed these questions in a study. The results of the study show that an appropriate combination of biocide and redox agent is required to avoid potential side reactions. Within the framework of the study, latex emulsions were used that were already pre-polymerized. For the post-polymerization different reducing agents and oxidation agents were added in several test series. After that, biocides were added and the stability of these biocidal active substances were analyzed.

Introduction

Guaranteeing the biocidal stability of polymer dispersions is a delicate issue: If antimicrobial active ingredients are strongly degraded by the use of initiators, typically peroxides and persulfates, an insufficient amount of biocide remains in the paint or coating. This means that the in-can protection against microbial contamination can no longer be fully guaranteed, thus increasing the risk of product failure. It is therefore necessary to increase the dosage of biocides in order to avoid germination and, in the next step, possible liability issues. However, regulatory restrictions and the general trend in demand for products with minimal biocide content are forcing manufacturers to proceed cautiously when adding in-can preservatives. As part of a joint collaborative project between the companies L. Brüggemann GmbH & Co. KG and SANITIZED AG, a series of tests were conducted to investigate how suitable redox initiator systems can be used to ensure the best possible biocide stability during post-polymerization. The results of the study provide concrete recommendations for action and underscore the complexity of the topic.

Redox systems in emulsion polymerizations

Redox systems are now widely used as initiators and radical starters of emulsion polymerization. In contrast to the classic, thermal initiation with peroxides at high temperatures, redox systems offer a much more controlled polymerization due to the possibility of temperature reduction. This not only leads to fewer residual monomers (and thus fewer harmful VOCs) in the finished binder, but also enables the targeted variation of parameters such as molecular weight and molecular weight distribution. Redox systems thus have a direct influence on the product properties of a finished paint or varnish.

Experimental part

Within the framework of, and with the aid of pre-screening with different latices and various biocide types (based on zinc pyrithione, BIT, CIT/MIT and bronopol), the specific parameters and active ingredients for the actual main study were determined. For this purpose, a styrene-butyl acrylate latex, the two biocides BIT and CIT/MIT, as well as an oxidizing agent and two reducing agents in the mixing ratios 1:1 and 2:1 were selected (see below).

The reducing and oxidizing agents were prepared as a 5% solution in deionized water for each series of experiments. The formulations with the additions of an oxidizing agent and/or reducing agent were calculated to 100 g, i.e. at a 1:1 ratio of oxidizing agent to reducing agent, 2 g of each of the 5% solutions were added to 96 g of latex. This corresponds to a redox amount of 0.1 % oxidizing agent and 0.1% reducing agent. The density of the 5% aqueous solution was approximately converted to volumetric units in mL using 1g/mL and added during post polymerization, whereby the oxidizing agent solution was dosed en bloc, while the reducing agent solution was dosed over a period of 30 minutes. The post-polymerization was performed in a beaker under constant stirring using a paddle or magnetic stirrer at 60 °C. At the end of the reaction, the final post-polymerized latex was divided and one of the different biocide systems was added to each part. GC-MS analysis also showed that no significant amounts of residual monomers were present as a result of post-polymerization. Thus, a possible influence from these monomers on the biocidal stability can be excluded. After a storage period of 14 days at room temperature, the biocidal active ingredient content was analyzed by using HPLC. The 14-day rest period ensures the complete removal of residual redox components.

The following chemical were used for the main study:

- Latex: LP 21-045 (styrene acrylate base)
- Deionized water
- tBHP (tert-butyl hydroperoxide) as an oxidizing agent
- Bruggolite® FF6M and Bruggolite® TP 1646 as reducing agents
- Sanitized® BIT20D (20% BIT active ingredient) and Sanitized® CI15 (1.5% CIT/MIT active ingredient) as biocides

Post polymerization procedure

1. Heating of the polymer latex to 60 °C while stirring (This stimulates the conditions during post-polymerization of a real polymer latex).
2. Addition of the oxidizing agent solution.
3. Dosing of the reducing agent solution over a period of 30 min.
4. Cooling phase to approx. 35 °C.

5. Addition of the biocide using a disposable pipette.
6. Storage at room temperature for 14 days.
7. Analysis of the residual amount of the biocidal active ingredient by HPLC.

Post polymerization setup

Finished polymerized and preserved latex (after addition of biocide)

Results

The findings from the present study are summarized in Table 1. The values marked with an * refer to the polymerization tests that showed a significantly reduced active ingredient content (target value in ppm) after storage. This indicates that the combinations of redox initiators used had a negative influence on biocidal stability. Conversely, the unmarked values refer to the redox combinations which did not have a negative influence on biocidal stability.

In addition to the mixing ratios of the reducing agent to the oxidizing agent (1:1 or 2:1), the type of reducing agent and the biocide used also play a decisive role:

Influence of redox components on BIT (Sanitized® BIT20D)

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 (experiment 3), whereas an adjusted ratio of 1:1 (Ox:Red) of the two redox components mentioned above allowed the most complete preservation of BIT from Sanitized® BIT20D (experiment 5). The use of either reducing agent (experiment 7) or oxidizing agent (experiment 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 (experiments 11 and 13).

Influence of the redox components on CIT/MIT (Sanitized® CI15)

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 (experiment 4), but degradation occurred on the other hand - and also in contrast to the studies with BIT - with a ratio of 1:1 (experiment 6). The sole use of a reducing agent also led to a strong decrease in the active ingredient content with CIT/MIT (experiment 9), but this was not the case for the sole use of the oxidizing agent (experiment 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 (experiments 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.

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

Table 1

Conclusion

In the present study, the stability of biocides for in-can preservation in polymer dispersions was investigated while using suitable combinations of different redox initiator systems. Depending on the use and ratio of said redox components as well as the applied biocides, a certain tendency how biocides are affected by a given redox system can be identified. However, it is clear that there is no single solution for all polymer dispersions. It is essential to use a suitable ratio of oxidizing to reducing agent and to select a biocide that is compatible and stable in the polymer latex. A strategy adjusted to the system and the components used is therefore required to ensure the best possible stabilization of the biocide.

The knowledge gained from this study as well as future test series with various other industry-related polymer dispersions can additionally contribute to the use of in-can preservatives in a targeted manner and in the necessary (ideally low) dosage.

For follow-up studies and individual questions regarding the selection of redox initiators and suitable biocides, representatives from SANITIZED AG and L. Brüggemann GmbH & Co. KG are at your disposal. By combined efforts, the challenges posed by ever-increasing regulatory requirements can be tackled together.

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More information about the companies

About SANITIZED

Sanitized®: adding value since 1935

Sanitized® enhances the usefulness of textiles, plastic products, paints, and coatings. The company develops its groundbreaking technologies in Switzerland and sells them worldwide. Sanitized® delivers odor-free textiles while responsibly protecting paints and coatings and giving long-term hygiene function and material protection to polymers.

Our all-inclusive service for customers is second to none: standardized tests at the TecCenter, technical and regulatory consulting, marketing assistance. Manufacturers and customers have trusted the world-renowned Sanitized® brand for decades. Sanitized® allows you to stand out on the market and delivers tangible added value.

www.sanitized.com

About Brüggemann

Since 1926, Brüggemann has been successfully manufacturing and distributing sulfur-based reducing agents marketed under the Bruggolite® brand name worldwide. With the introduction of Bruggolite® FF6M, Brüggemann became the first manufacturer of a sulfur-based, formaldehyde-free reducing agent. Other similar, environmentally friendly products soon followed. We are constantly developing our water-soluble reducing agents in response to new market requirements and possible applications. Today, reducing agents are mainly used as initiators in the production of polymer dispersions - an increasingly important and demanding field.

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Redox Chemistry for Effective Reduction of Free Monomer in Emulsion Polymerization

SpecialChem – Jun 24, 2021

TAGS: Sustainability / Natural Coatings

Reducing residual monomer contents has become a must for every emulsion polymer manufacturer in order to meet standard quality criteria. Products with no or very low levels of residual monomers simply have a **positive commercial appeal** as they guarantee:

- Low VOC
- No odor, and
- Enhanced mechanical properties

There are several techniques for reducing residual monomer contents. The most elegant technique is a post-reaction by redox-initiated emulsion polymerization, which is a highly versatile method of polymer production used for the synthesis of more than one-third of the polymers produced in total.

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Webinar

Redox Optimization for Emulsion Polymer Post Reaction

Brüggemann

This is a Past Webinar

Reduction of free monomer content is required in the manufacture of emulsion polymers to lower VOC emissions. This has become more critical as consumers are demanding formulations with reduced odor.

Conventional post polymerization techniques using redox pairs can achieve low levels of residual monomers, but this can increase production time, add cost, and reduce production capacity.

A post-polymerization redox optimization study was conducted on a production latex made with a persulfate to thermally initiate the main polymerization. Various redox combinations were tested in the post-polymerization stage at different dosage levels and feed rates to minimize redox quantity, residual monomers, and time.

This webinar will show with a redox optimization study that the mentioned hurdles can be overcome and excellent results are within reach.

Presented By: Matthias Lubik

Length: 60 min