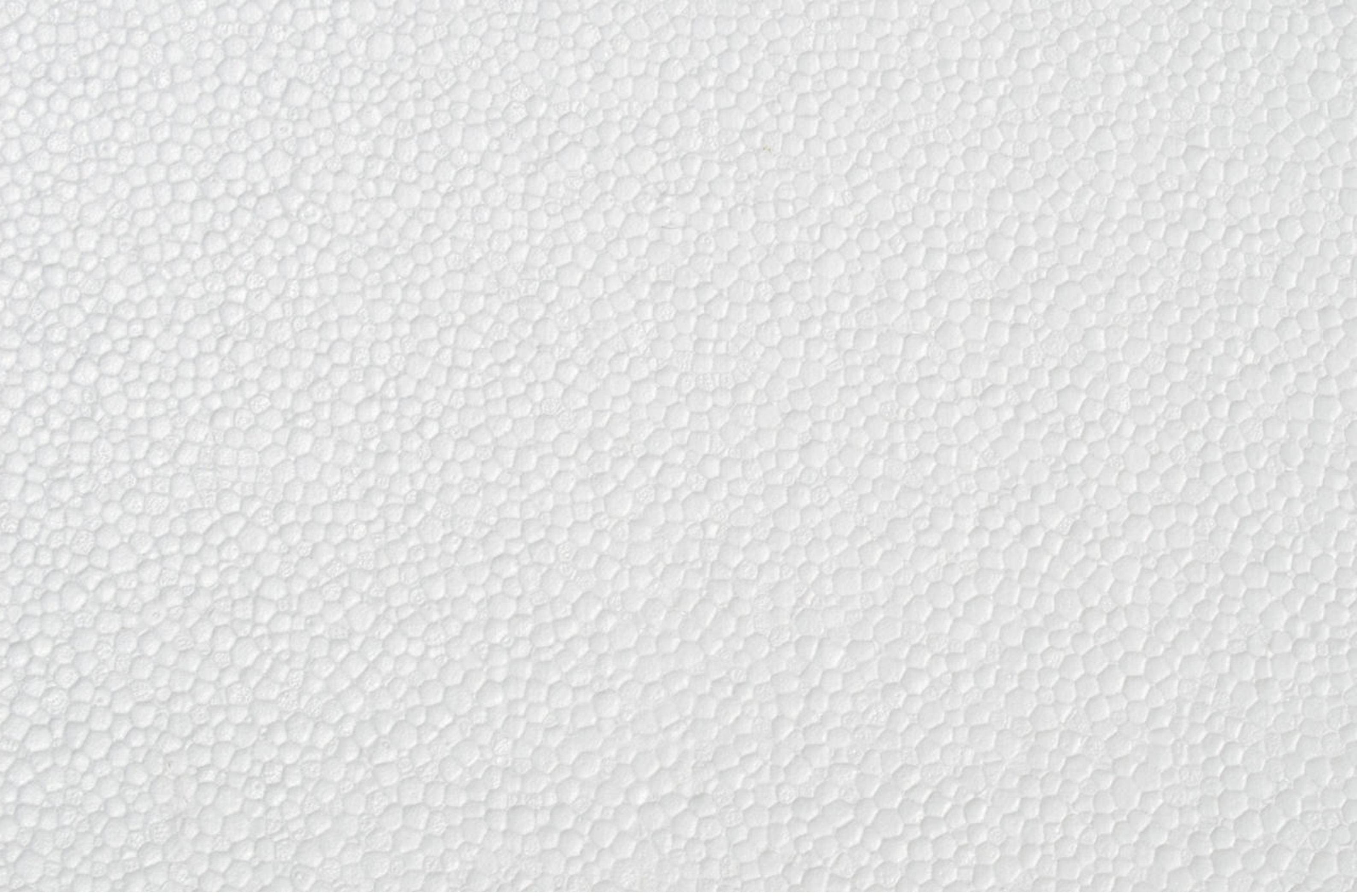


Application Note AN-PAN-1027

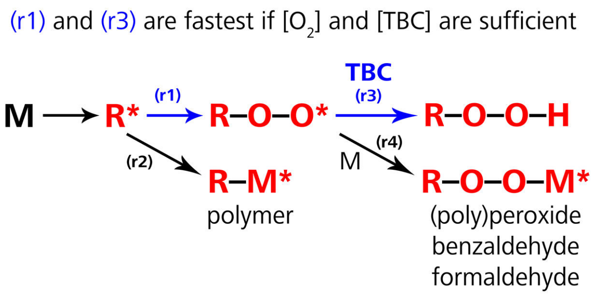
Online monitoring of TBC in styrene storage tanks according to ASTM D4590

In the production of styrene, butadiene, and vinyl acetate, the stabilizer 4-*tert*-butylcatechol (TBC) plays a crucial role in preventing premature polymerization during storage and transport.

In order to guarantee product quality, the TBC concentration in styrene must be maintained above 10–15 mg/L. Close monitoring of the concentration is necessary to control TBC levels.

This Process Application Note presents a solution for online colorimetric determination of TBC in styrene (as per ASTM D4590) with the **2060 TI Ex Proof Process Analyzer** from Metrohm Process Analytics.

More than 27 million tons of styrene monomer ($C_6H_5CH{=}CH_2$) are produced worldwide each year [1]. Styrene and other reactive monomers, such as butadiene and vinyl acetate, are inherently unstable during storage and transport due to their tendency to undergo spontaneous polymerization when exposed to environmental triggers like heat, light, or oxygen. Chemical stabilizers like 4-*tert*-butylcatechol are added to mitigate this risk. TBC acts as a free radical inhibitor to prevent the formation of long polymer chains that can lead to viscosity changes, blockages, or even runaway reactions in storage tanks.



Reaction 1 Mechanism for the inhibition of polymer formation in styrene monomer with the addition of TBC and oxygen.

Styrene monomers (M) form radicals (R*) when they are exposed to either light or heat (**Reaction 1**). These radicals can react with either oxygen (causing peroxide radicals) or other monomers to create polymer chains. This polymerization is exothermic. If left uncontained, it can lead to runaway polymerization in the styrene storage tank, resulting in serious consequences.

TBC is a free radical inhibitor that requires oxygen to prevent the monomers from polymerizing. Because monomers are present in the solution and in the tank headspace, a minimum concentration (10–15 mg/L) of oxygen (O_2) is required in both.

The O_2 addition is necessary to take advantage of different reaction kinetics (**Reaction 1**) – peroxide radical formation (r1) occurs much faster than styrene polymer formation (r2). In the presence of the correct amount of TBC, these peroxide radicals are scavenged (r3). Otherwise, the peroxide radicals react with styrene monomers to form peroxide chains (polyperoxides, r4) until the oxygen is completely depleted.

INTRODUCTION

These contaminations can be hazardous during the purification processes (distillation) due to the instability of peroxides at increased temperatures. Therefore, the TBC concentration in styrene must be maintained above 10–15 mg/L. Close monitoring of the TBC concentration is required to control its depletion.

While TBC is essential for preventing styrene and other reactive monomers from polymerizing prematurely, solely relying on laboratory analyses might be inadequate to guarantee consistent TBC levels within the required range.

Furthermore, the delay between sample collection, analysis, and results further magnifies the challenge of promptly addressing any deviations from optimal TBC concentrations. For operators tasked with maintaining TBC levels above the critical threshold of 10–15 mg/L, a more responsive and continuous monitoring approach is important to mitigate the risk of polymerization incidents and maintain product quality throughout the entire storage and transportation process.

A photometric process analyzer accurately tracks TBC reduction at the styrene storage tank inlet to maintain optimal conditions around the clock.

Metrohm Process Analytics offers the **2060 TI Ex Proof Process Analyzer** for monitoring TBC concentration in styrene (**Figure 2**).

APPLICATION

The method used is based on ASTM D4590 for the colorimetric analysis of 4-*tert*-butylcatechol (TBC) in styrene. The results are calculated based on a photometric determination at 490 nm.

Table 1. Parameter to monitor in styrene storage.

Parameter	Concentration [mg/L]
4-*tert*-butylcatechol (TBC)	0–50

REMARKS

Figure 2. 2060 TI Ex Proof Process Analyzer for monitoring TBC in styrene.

Due to styrene's sensitivity to light and heat, storage conditions can quickly become hazardous. Continuous monitoring is essential. In hazardous environments, only explosion-proof analyzers like the **2060 TI Ex Proof Process Analyzer** (**Figure 2**) ensure safe, real-time TBC control.

CONCLUSION

Online monitoring of TBC, as defined in accordance with ASTM D4590, is essential for maintaining product quality and safety during the production and storage of styrene, butadiene, and vinyl acetate. The presence of TBC prevents early polymerization, thereby avoiding potential hazards associated with unwanted polymerization reactions.

Maintaining TBC concentrations above the critical threshold of 10–15 mg/L is crucial. This requires close and continuous monitoring. Online process analyzers, such as the **2060 TI Ex Proof Process Analyzer** from Metrohm Process Analytics (configured for photometric analysis), offer a reliable solution for real-time TBC concentration monitoring. This ensures optimal storage conditions and product quality.

RELATED APPLICATION NOTES

AN-PAN-1007 Online analysis of peroxide in the HP-PO process

AN-PAN-1041 Inline monitoring of free isocyanate (%NCO) content in polyurethane

AN-PAN-1053 Monitoring of DOTP production via esterification with inline analysis

OTHER RELATED DOCUMENTS

WP-048 Utilizing online chemical analysis to optimize propylene oxide production

BENEFITS FOR ONLINE PROCESS ANALYSIS

- **Optimize product quality** and increase profit with fast response times to variation in process conditions.
- **Fully automated diagnostics**—automatic alarms for when TBC concentrations are outside of the specified parameters.
- **Safe working environment** and automated sampling.

1. Falcke, H.; Holbrook, S.; Clenahan, I.; et al. *Best Available Techniques (BAT) Reference Document for the Production of Large Volume Organic Chemicals. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control)*. JRC Publications Repository. https://publications.jrc.ec.europa.eu/repository/handle/JRC109279 (accessed 2024-03-06). https://doi.org/10.2760/77304

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CONFIGURATION

2060 TI Ex Proof Process Analyzer

El **2060 TI Ex Proof Process Analyzer** es un instrumento de análisis de procesos de química húmeda intrínsecamente seguro para la monitorización de procesos en entornos peligrosos en zonas con gases o polvos calificadas como zona 0, 1 y 2 o 20, 21 y 22. Cumple con las directivas UE 94/9/CE (ATEX95) y está certificado para áreas de Zona 1 y Zona 2. Su diseno combina un sistema de purgado y presurización con dispositivos electrónicos intrínsecamente seguros. La fase de purgado de aire y la sobrepresión permanente impiden que cualquier tipo de atmósfera potencialmente explosiva entre en la caja del instrumento de análisis.

El diseno del instrumento de análisis evita la necesidad de purgar grandes recintos protectores del instrumento, lo que permite instalarlo directamente en la línea de producción dentro de zonas peligrosas. También permite aplicar diversas técnicas como titulación en general, titulación Karl Fischer, fotometría, medidas con electrodos ion-selectivos y medidas directas.