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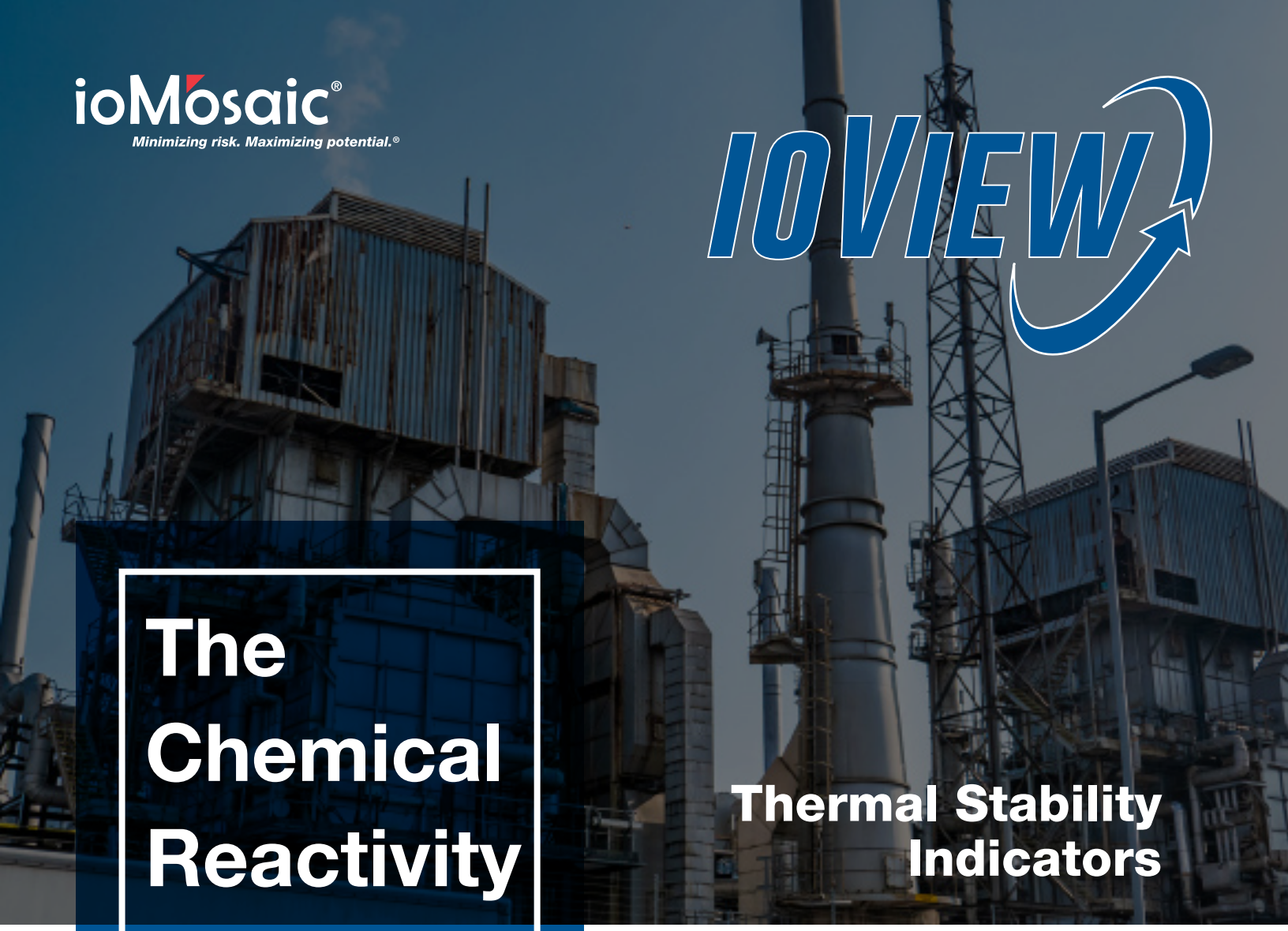

The Chemical Reactivity Issue

Methods, Tools, and Resources

Thermal Stability Indicators

By G. A. Melhem, Ph.D., FAIChE

Introduction

Chemical process hazards cannot be effectively managed if they first cannot be properly identified. This is especially true for reactive chemicals storage, processing, and management. Reaction rates can be significantly influenced by the presence of contaminants, inhibitors, incompatible chemicals, etc. Runaway reactions usually involve undesired reactions although many industrial accidents have occured because of desired chemistry runaway reactions.

Information pertaining to chemical reactivity is required under the Process Safety Information (PSI) element of the Process Safety Management (PSM) standard in the United States. This requirement is

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rarely satisfied by a safety data sheet. Information about chemical reactivity need to be provided for both desired and undesired chemistries. In addition to regulatory compliance, this information is used to develop safe operating limits for storage and processing.

This paper describes several thermal stability indicators that should be provided as critical PSI for reactive chemicals. This information often requires both laboratory measurements and computer modeling for proper scale-up to plant conditions.

Inhibitor Induction Time, *Lip*

Inhibitors are chemical substances that are used in small amounts to suppress the polymerization reaction of a monomer. An inhibitor has to be completely consumed before a polymerization reaction can proceed at normal rates. The time required to completely consume the inhibitor is often referred to as an ”induction” time. Inhibitors react with polymerization initiation radicals to produce products that cannot induce further reaction. Inhibitors are different from reaction ”retarders”. A retarder does not suppress the reaction but merely slows it down, i.e. the reaction continues to increase at a slower rate until the retarder is consumed. Some impurities in monomers can act as retarders.

Small amounts of inhibitors can substantially prolong the shelf life of a reactive monomer. Common polymerization inhibitors, typically antioxidants, include MEHQ (monomethyl ether hydroquinone), TBC (4-t-butylcatechol), HQ (hydroquinone), PTZ (phenothiazine), etc. The effectiveness of most commonly used inhibitors depends on the presence of dissolved oxygen to convert free radicals to peroxy radicals that in turn react with the inhibitor to stabilize the monomer. Both inhibitors and oxygen deplete over time. Understanding inhibitor requirements is essential for polymerization reactions safety.

An inhibitor effectiveness model is usually coupled with polymerization kinetic model(s) in order to properly develop relief requirements and also for accurate hazard assessment. In general, inhibitor effectiveness models correlate the induction time with temperature and initial concentration of...

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