Polymers & Intermediate Petrochemicals

INGOLD
Leading Process Analytics

5 Ways to Optimize Production

1 Predict Maintenance
of pH Sensors

Eliminate Unplanned Downtime

2 Prevent Product Discoloration
Stop Unwanted Polymer Oxidation

3 Simplify Maintenance
and Control

Reduce Process Interruption

4 Ensure Safe Storage
of Hazardous Chemicals

Avoid Runaway Polymerization Reactions

5 Optimize Exhaust Monitoring
Averting Problems at Scrubbers

METTLER TOLEDO

Switching to Condition Based Maintenance
"Indispensable" Sensor Technology at Mitsubishi

Failure of pH sensors in processes was a costly and concerning issue for Mitsubishi. The ability to see when sensor maintenance or replacement will be needed has transformed their pH measurement operations.

World leading chemical company

The Mitsubishi Chemical Corporation (MCC) is Japan's largest chemicals manufacturer. Its product range spans industrial chemicals, petrochemicals, solvents, methyl methacrylate and acrylonitrile. MCC has the world's largest market share of acrylic resin raw material.

The need to know when a sensor will need exchanged

At the corporation's Mizushima plant near Okayama, pH measurement during the neutralization of strong acids is closely monitored. For this important measurement Tsutomu Ishikawa and Naoto Ogura, engineers at the plant's Instrumentation and Engineering Department, were not satisfied with the performance of the pH sensors they were using. Mr. Ishikawa said: "The conditions in the process are harsh: pH is in the range of 5 to 12, and temperature swings between 40 and 80 °C. Typically, a pH sensor survives for three months, but sometimes a sensor becomes unusable after just one. The unexpected interruption of processes affects product quality, so the reliability and stable operation of measuring instruments is an important factor."

For this reason sensors were regularly exchanged at the plant to minimize the chance of failure in the process. But the operation cost was high and Mr. Ishikawa and Mr. Ogura needed a better solution. Specifically, they required to know in advance when a pH sensor would need to be cleaned, calibrated or replaced: "We wanted to grasp how deposits forming on the pH sensors would affect the timing of sensor maintenance and exchange."

"Knowing the correct remaining sensor life is a major advance in Plant Asset Management."

Diagnostics predict sensor maintenance and replacement

Intelligent Sensor Management (ISM®) provides exactly this ability. By continuously monitoring process conditions, sensor slope and reference system impedance value ISM pH sensors can predict their remaining lifetime and when calibration and cleaning should be performed. Further, ISM's predictive diagnostic tools (displayed on the connected transmitter) are dynamic, so as process and sensor conditions change, the diagnostics readjust.

Mr. Ishikawa and Mr. Ogura were impressed with a demonstration of ISM and could immediately see its potential. Mr. Ogura stated: "In our existing operation method, sensor state is confirmed on site or periodic sensor maintenance is performed on a Time Based Maintenance rule of thumb. Using the Condition Based Maintenance function provided by the algorithms in the ISM sensors means we could implement an efficient and more appropriate maintenance plan. In short, systems equipped with ISM technology would be indispensable."

To test ISM at the facility, two pH measurement systems comprising InPro 4260i sensors and M400 transmitters were installed on neutralization equipment. The METTLER TOLEDO solutions functioned extremely well and further ISM pH systems were installed for monitoring organic solvents.

High satisfaction leads to major replacement program

Mr. Ishikawa and Mr. Ogura are delighted with the sensor performance and particularly ISM's Dynamic Lifetime Indicator: "Knowing the correct remaining sensor life is a major advance in Plant Asset Management."

Such is their satisfaction that Mitsubishi are now considering replacing 200 pH measurement points at their Mizushima plant with ISM solutions.

Get a free white paper on ISM:
► **www.mt.com/ISM-chem-wp**

ISM simplifies pH sensor workflows from start-up to maintenance to replacement

Avoiding Discolored Plastic
with In-line Oxygen Measurement

Polyethylene terephthalate (PET) is one of the most abundantly used polymers. Its versatile nature allows for an extensive range of bulk applications such as drinks bottles. Oxidation of PET can easily occur during its production, leading to unwanted color changes. Measurement of oxygen with in-line amperometric sensors provides instant warning of out-of-spec production.

Background

PET is the fourth most produced polymer making up 18 % of the world's polymer production. The key to its versatility comes from its repeating molecular makeup: long chains of ethylene terephthalate. This accounts for its chemical inertness and ability to be crystalized or made into an amorphous glass-like material, depending on the chosen polymerization process. Further modifications can be made through strict control of the polymer chain length, degree of cross linking between the chains, addition of modifying agents and heat treatments. Thus, strict reaction and process control is required to produce the specific characterizations for the desired application.

Process

The two chief routes for PET production are through transesterification and direct esterification. In transesterification, dimethyl terephthalate (DMT) is heated to a reaction temperature of 125 – 220 °C in a closed vessel with a catalyst. Since water is a by-product and the reaction is reversible, constant removal of the water is required and can be accomplished by vacuum, inert gas or inert solvent. For direct esterification, the raw material for PET is chiefly terephthalic acid synthesized from crude oil-based paraxylene, along with ethylene glycol. The reaction is performed under a pressure of 2.7 – 5.5 bar and temperatures of 220 – 260 °C without the need for a catalyst. This reaction also similarly requires continuous removal of water due to the equilibrium shift. After the reaction is completed to the desired

molecular weight, the remaining solvents and precursors are removed in a drying step where the resultant polymer can be spun into fiber or pelleted into small solids.

In both methods, and throughout the production, the materials must be under inert conditions free of oxygen. Oxidations, which can occur throughout the process, will interrupt the polymerization as well as producing undesired color changes. Yellowing is a serious risk at higher temperatures as it will render the product unacceptable for white or clear applications. Furthermore, in spinning, pelleting and hopper storage, yellowing can still occur, so it is important to keep all headspace oxygen-free.

Analysis of oxygen levels are thus required, and this is best achieved with an in-line system. An in-line solution supplying continuous measurements will give the real-time value of oxygen in the pipe, tank or vessel and does not require sampling equipment. The in-line system must also have precise and accurate reading at low levels of oxygen.

Oxygen sensor predicts its own maintenance

The InPro® 6950i G is an amperometric-type trace oxygen probe which has the ability to detect even 5 ppm oxygen in the vessels and process pipes of PET production. With a real-time response, even small amounts of oxygen can be detected quickly allowing rapid remedial action. Use of an M400 2-wire transmitter also allows for measurement in hazardous areas.

Diagnostics of the sensor's health is available from the probe's Intelligent Sensor Management (ISM®) technology. ISM sensors feature a Dynamic Lifetime Indicator (DLI) to show the sensor's remaining lifetime. The DLI changes according to the measurement conditions and displays on the connected transmitter a value in days before sensor replacement will be required. Further, the Time To Maintenance and Adaptive Calibration Timer also show how many days until servicing will be needed.

Automated sensor cleaning maximizes uptime

For ease of cleaning, an InTrac® 777 retractable housing can be used which includes a flushing chamber for rinsing any potential fouling build-up on the sensor, ensuring consistent performance without process interruption.

- **www.mt.com/InPro6950iG**
- **www.mt.com/ISM-chem**

Seamless Process Monitoring at Nalco
with ISM Technology

For Nalco, a world leading chemical company in water treatment, process analytical systems are vital for ensuring product quality remains high and manufacturing effluent meets regulatory requirements. Intelligent Sensor Management provides the assurance they require and makes maintenance easier.

Background

Nalco was founded in Chicago in 1928 as the National Aluminate Corporation. It formed from the merger of the Chicago Chemical Company and Aluminate Sales Corporation, two companies whose main business was selling sodium aluminate for water treatment. Chicago Chemical Company sold primarily to municipal utilities and industrial plants for boiler feedwater treatment. Aluminate Sales Corporation made most of its sales to railways for processing the water needed for steam generation. Today, Nalco is the world's leading supplier of chemicals for water treatment and conditioning, with 70,000 customers in 130 countries.

Nalco has been active in Germany since 1958 as Nalco Deutschland GmbH. Their Biebesheim plant, built in 1974, also focuses on water treatment. With 110 employees, the facility produces an annual volume of 50,000 metric tons of exclusively liquid products. It supplies a wide range of additives for corrosion protection, protection against micro-organisms, polymers for water treatment in sewage plants, and polymers for water treatment over the full spectrum of industrial applications.

Exhaust gas treatment

The exhaust gases generated during the production of water additives are treated in several stages at the Biebesheim plant. They are first passed through a sulfuric acid scrubber and are then neutralized by sodium hydroxide in a second scrubber. Following this, they are fed through an active carbon filter.

Two METTLER TOLEDO InPro 4260i pH electrodes, each with an M700 transmitter and InTrac retractable housing, are installed in the exhaust gas treatment system. Thanks to the retractable housing, the sensor can be withdrawn from the process stream whenever desired without requiring process shutdown. The InPro 4260i electrodes are members of the Intelligent Sensor Management (ISM) family of sensors and transmitters.

Convenient calibration

The most important aspect of the ISM concept is full integration of sensor diagnostics in the sensor. This makes probe maintenance easy and flexible.

pH electrode
InPro 4260i

All important sensor information, such as the most recent calibration data, is stored on an integrated microprocessor, so sensor calibration at the measurement system is not necessary. Using iSense software, ISM sensors can be calibrated in a lab or office and stored until they are required.

Nalco uses the InPro 4260i electrodes to help control alkali and acid dosing in the scrubber circuits, which varies depending on the contamination level of the exhaust. The main reason for using ISM sensors here is that they can be pre-calibrated in the lab and installed in the measurement system as necessary. At Nalco, this means that pre-calibrated pH electrodes are always available in the lab. If the electrodes in the process equipment need calibration, they are simply replaced with calibrated electrodes. As a result, interruption to process monitoring is significantly shorter than if in situ calibration were necessary. The replaced electrodes are subsequently recalibrated in the lab using iSense software and then put back into service at the next exchange event.

Monitoring raw materials

One of the raw materials used to produce polymers for water treatment is acrylamide. Nalco uses biological acrylamide, which means that it is prepared by the enzymatic hydrolysis of acrylonitrile. The biological acrylamide is stored in solution in a tank while waiting further processing. Measures must be taken to avoid autopolymerization during storage. Autopolymerization poses a threat because a lot of heat is released by this form of polymerization, and furthermore, acrylamide is of no use to Nalco after it has been polymerized. If polymerization begins in the tank, the pH value of the solution will shift, so to provide instant warning of this, an InPro 4260i pH electrode with an InTrac retractable housing is also mounted on this tank. If this electrode needs calibration, it is also replaced by a pre-calibrated electrode from the lab.

Further plans for ISM at Nalco

There are plans for using ISM sensors in other measurement systems in the future, such as determining the oxygen level during inertization. An oxygen sensor with ISM technology has already been purchased for this purpose, and it is intended to be put into service soon.

Find out how intelligent sensors can help your processes, at:

- ▶ **www.mt.com/InPro4260i**
- ▶ **www.mt.com/ISM**

Safe Storage of Acrylonitrile
and Other Hazardous Chemicals

Acrylonitrile is highly poisonous, flammable and susceptible to explosive polymerization; therefore, it must be produced and stored under strict conditions. Maintaining the pH of acrylonitrile below 7.5 during production and storage significantly reduces the risks. A pH measurement and sensor cleaning system from METTLER TOLEDO provides accurate, real-time data and prevents technician exposure to the hazardous compound.

Background

Acrylonitrile is an important precursor in many plastic end-products. The liquid monomer is used extensively in polymerization reactions to produce polyacrylonitrile (PAN), styrene-acrylonitriles, acrylonitrile butadiene styrene (ABS), as well as synthetic rubbers. The molecule is strongly polar and contains both a double-bonded carbon and a nitrile group, which allows for a wide range of reactions such as oxidations, reductions, esterification, hydrolysis, hydrogenations and cyclization. This reactivity, however, creates significant risk as many of the spontaneous reactions are also highly exothermic and can produce unsafe conditions. Polymerization reactions and auto-oxidations can lead to explosion hazard as well as the general flammability of the chemical. Further risks include the toxicity of acrylonitrile, which can affect human health.

Process

Acrylonitrile is produced through the ammoxidation process. Propylene, ammonia and air are bought into contact with a solid powder catalyst in constant mixing at high temperatures. This is accomplished in a fluid-bed reactor which keeps the mixture in a continual 'fluid' state to provide a large surface area for the catalyst. The product then goes through numerous separation steps involving absorbers and distillation columns to remove by-products such as hydrogen cyanide (HCN) and acetonitrile.

The final product is either stored as a bulk chemical, or delivered for bulk storage via pipeline, railcar, truck or ship. When in storage, the risk of polymerization and explosion or flammability must be controlled. Certain conditions must be monitored and action immediately taken if changes are observed.

pH is one of the most important parameters to control when storing acrylonitrile. In the basic range, acrylonitrile can undergo polymerization resulting in the release of ammonia. Polymerization not only consumes valuable product and produce impurities, it significantly increases the risk of explosion due to the immense heat given off by the reaction. Furthermore, the ammonia produced is also incompatible with acrylonitrile, causing further side reactions.

To inhibit these reactions the pH should be kept below 7.5 at all times. If the pH increases to higher values, acidification with acetic acid is immediately recommended. Measurements of pH in acrylonitrile are very difficult due to water in the 0.25-0.45 wt% range of the stored product. These low levels of water will reduce the hydrated layer on the glass probe causing measurement instability. Therefore, a small volume side-stream must be diluted to 5% water to allow reliable pH determination.

METTLER TOLEDO solution

For continuous monitoring in storage vessels an in-line solution is required in order to have real-time information. The InPro® 3250i pH sensor is an ideal solution for such in-line measurements in polar chemicals. To avoid sensor contamination, the probe has pre-pressurized liquid electrolyte, ensuring that process chemicals cannot enter the internal reference system and produce false measurements.

For keeping the probe's glass layer hydrated, an EasyClean™ 400 system can insert and retract the sensor automatically, cleaning and rehydrating the measurement probe in the retracted position. While retracted, the sensor can also be calibrated, keeping the vessel contents isolated from the environment and, more importantly, keeping working staff separated from the toxic acrylonitrile. Control of cleaning and calibration as well as transmission of the pH value can be accomplished with an M700 transmitter. The complete system is certified for installation in hazardous areas

- **www.mt.com/InPro3250**
- **www.mt.com/EasyClean**

You're Scrubbing, but Are You Clean?
Analytical Measurements in Gas Scrubbers

Wet gas scrubbers prevent pollutants being released to the environment. Controlling scrubber solution strength via pH, ORP or conductivity measurements is central to scrubber performance, but the use of unsuitable sensors can result in costly problems. Thanks to advanced design, sensor maintenance costs can be cut by up to 90 % while scrubber efficiency is increased.

Wet gas scrubbers

Gaseous exhaust streams produced during certain chemical and petrochemical processes frequently contain polluting substances that must be removed before the exhaust is vented to atmosphere.

Wet gas scrubbers are designed to "wash out" or neutralize gases such as SO_2, NO_2, and HCl that would otherwise cause serious environmental damage, and corrosion to fixed equipment. Many wet scrubber designs exist, but all follow the same basic principle: The polluted gas stream enters a quenching zone where it is brought into contact with a scrubbing liquid (a combination of one or more chemical reagents in an aqueous solution) by spraying, forcing it through or by some other contact method. The pollutants are absorbed by the chemicals in the liquid which collects in a holding tank at the bottom of the scrubber. If the scrubbed gas is sufficiently clean it is expelled, if not it is processed further before release. Production of byproducts is common to all gas scrubbers.

The efficiency of wet gas scrubbers is measured by their consumption of chemicals and capacity to treat gas, and depends largely upon the condition of the scrubbing solution. If scrubbing efficiency is to be kept high, the quality of the scrubbing solution must be continuously measured and controlled. Reduced scrubber efficiency not only carries the risks of pollutants being released to atmosphere and corrosion of plant equipment, scaling of the scrubber vessel and plugging of pipes caused by a build-up of by-products reduces efficiency further and inevitably leads to expensive maintenance.

The use of inappropriate measurement equipment

pH, ORP, and conductivity sensors are commonly used on scrubbers to monitor the solution being fed to the scrubber and the condition of the scrubbed solution in the holding tank of the unit. However, to save on costs they tend to be of a design unsuited to the task. Scrubbers are challenging environments for analytical sensors, especially for ones that are inappropriate for the process conditions. The harsh measuring environment results in short sensor lifetime and hence regular replacement. In addition, build-up of solids and contamination of sensors cause the measurement value to drift, which leads to a more severe problem, particularly where pH electrodes are being used.

METTLER TOLEDO solutions for wet gas scrubbers

Robust conductivity cells

InPro 7250 inductive sensors for conductivity measurement are designed to handle aggressive solutions and are ideal for harsh, batch scrubber applications. As these sensors have no electrodes in contact with the sample and are not affected by coatings that foul traditional contacting conductivity sensors, they are very durable in scrubber applications. The InPro 7250 is available with a choice of polymer-coated body: PEEK for most scrubber applications, and PFA where HF is present as it offers better acid resistance.

Advanced pH electrode

For continuous scrubbers, pH is more suitable than conductivity measurement. The METTLER TOLEDO InPro 4800i with Intelligent Sensor Management (ISM®) is a patented pH electrode for dirty process applications. It features a PTFE diaphragm that repels dirt and particles, and a specially developed protection system for the reference electrode. The platinum-coated glass shaft provides, besides a solu-

tion ground, a parallel ORP measurement. The very long diffusion path between the diaphragm and the reference electrode, using two electrolyte chambers, gives excellent resistance to any poisoning effects from oxidizing agents or poisoning ions.

Drawing on METTLER TOLEDO's long experience in membrane glass technology, the electrode is designed for high accuracy measurement over the full pH range. The sensor is available with a choice of membrane glass to suit process conditions. The High Alkaline membrane glass features strong chemical resistance to abrasive particles and a minimal alkali error (deviation from the true pH value in highly alkaline solutions). For applications where HF is present in the measuring medium, the sensor is available with HF-resistant glass.

The inclusion of ISM technology in the sensor provides benefits such as Plug and Measure installation and advanced diagnostics that predict when sensor calibration and replacement should be performed.

Automatic sensor cleaning/ calibration systems

High-quality pH electrodes will perform particularly well in scrubbing applications if they are properly maintained. Retractable sensor housings in conjunction with manual or automatic sensor cleaning is highly recommended, especially if the measurement takes place in the scrubber holding tank where solids are present. Scrubbing sulfur dioxide with a lime solution requires frequent cleaning of the pH electrode to achieve good reliability. Best practice is to use a retractable housing made from chemical-resistant wetted materials (C-22 alloy or titanium), in combination with an automated sensor cleaning system using HCl as the cleaning agent. The EasyClean 400 system and InTrac 777 e housing from METTLER TOLEDO offer completely automatic and unattended electrode cleaning and rinsing, plus calibration.

► **www.mt.com/ISM-chem**

Inductive conductivity sensor InPro 7250 PFA

pH electrode InPro 4800i

Resources to Support Your Processes

METTLER TOLEDO is a market leader in process analytical solutions. To help you maximize your productivity and understand the role of real-time analytics, we have created a number of useful guides, white papers, etc.

pH Theory Guide – A Guide to pH Measurement Practice and Applications

What exactly is pH, why is it so important, and how do pH sensors work? Our complimentary guide has all the answers.

A Guide to Oxygen Measurement – Theory and Practice

In this free booklet we discuss the theory of oxygen measurement and its application in production processes.

Best Practice Guide to Process Analytics in the Chemical Industry

A collection of success stories from some of our many chemical customers.

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