Application Note

pH in Diazo Coupler

Industry: Petrochemical, Chemical
Product: pH/ORP Process Liquid Analyzers

Introduction

Diazonium Coupling (Diazo Coupling, Azo Coupling):

Due to their positive charge, diazonium cations, which are generated by treatment of aromatic amines with nitrous acid and a stronger mineral acid, may participate in an electrophilic aromatic substitution as an electrophile. The electrophilic reaction center is the terminal nitrogen of the -N=N group. As a result, two aromatic compounds are coupled by a -N=Ngroup. This is known as the azo group (diazo group). The corresponding reaction is called diazonium coupling (diazo coupling, azo coupling). However, the electrophilicity of diazonium ions is only relatively weak, as their positive charge is delocalized. The unsubstituted benzenediazonium cation may react only with strongly activated aromatic compounds, such as phenolates and amines.

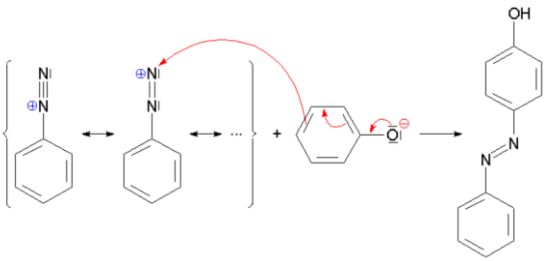

Figure 1. Diazonium coupling with a phenolate[1]

Azo coupling is the most widely used industrial reaction in the production of dyes, lakes and pigments. Aromatic diazonium ions acts as electrophiles in coupling reactions with activated aromatics such as anilines or phenols. The substitution normally occurs at the para position, except when this position is already occupied, in which case *ortho* position is favoured. The pH of solution is quite important; it must be mildly acidic or neutral, since no reaction takes place if the pH is too low.

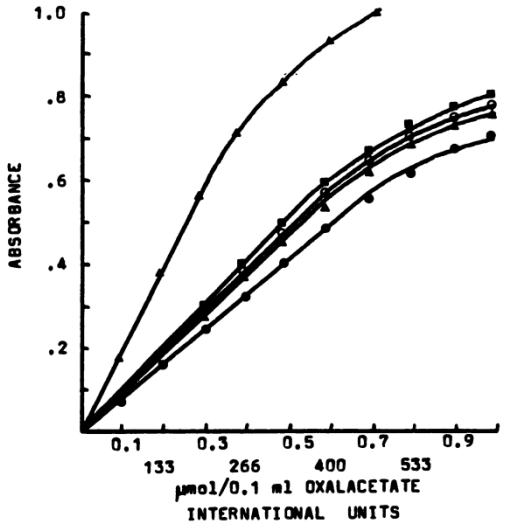

Fig. The effect of pH on standard curves of diazonium coupling with oxalacetate. Except for dye and pH, all parameters are as in described procedure
—○— Fast Red PDC, pH 4.2; —△— Fast Red PDC, pH 7.5; —●— Fast Red RC, pH 4.2; —▲— Fast Red RC, pH 7.5; —■— Fast Red RC, pH 8.5

Figure 2. For this drawing: dependence of des Oxalacetates, pH value)

Application Information

Typical process details:

Chemical Composition - Coupler + Diazo
Coupler – 48 % caustic + Nepthol + Water
Diazo -36% HCL + Diecloro Anelene + Water
Operating Temperature – 55° C
Operating Pressure – 4 kg/cm2

Typical problems:

Limited life of sensor

Summary

The process is indeed quite aggressive so Glass is best material.

Product Recommendations

Measurement System

Process Liquid Analyzer:

- 2-wire FLEXA pH/ORP Analyzer

Features

Redundant system on dual sensor measurement

Easy touch screen operation on 2-wire type analyzer

- 4-wire PH450G pH/ORP Analyzer

Features

Easy touchscreen operation

Trending display up to 2 weeks

Sensor Selection:

Option #1: SC21C-AGC55 would be best, if it is possible to pressurize the electrolyte to 5 bar (72PSI).

Features for type SC21C-AGC55

Heavy duty pH sensitive glass.

Flowing reference system for pollution resistance, and highly stable reference potential.

Use in combination with the presurisable electrolyte reservoir to obtain a positive flow towards the process (K1500YA)

Option #2: FU20-FTS is possible if the cation (salt) content is stable during the pH control step.

Features:

The FU20-FTS is a differential pH sensor. This means that the reference is not a (liquid) junction but a glass sensor which does not respond to pH changes (within the applicable range of the sensor). Therefore the sensor is truly maintenance free and the output voltage of the sensor depends only on the salt concentration of the process.

The sensor responds to pH changes rather than analyses the accurate pH value. In that sense it is best to describe the sensor as pH control sensor rather than pH measuring sensor.

A pH sensor measures the voltage that the pH membrane measures as function of the pH value of the process sample. This voltage is then compared with the mV output of a reference cell that is independent on the pH value of the sensor.

In most pH control applications the salt concentration is rather constant, so the output of the FU20-FTS differential sensor is only dependent on the pH of the process.

A rule of thumb is that a change in salt concentration of +/- 25% has an effect of less than 0.1pH on the pH reading.

Tangible benefit:

More reliable and accurate analysis of pH which helps to improve end product quality

Note: For additional information on this application contact the local Yokogawa Process Liquid Analyzer Department

Footnote:

[1] Source:
http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/12/oc/vlu_organik/aromaten/reaktionen/reaktionen_aromaten.vlu/Page/vsc/en/ch/12/oc/aromaten/reaktionen/ar_se/azokupplung/azokupplung.vscml.html