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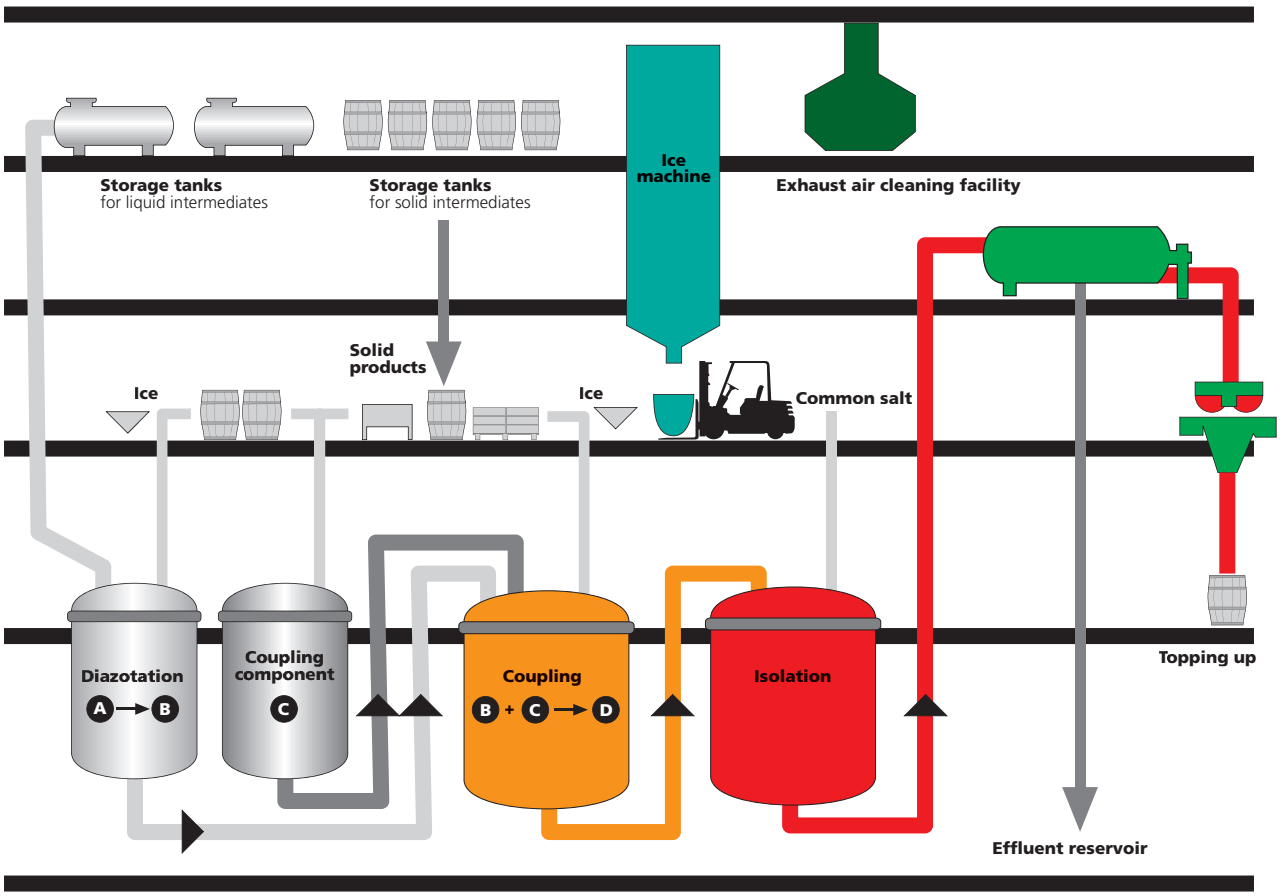
Knick

Application Report

pH Measurement During Dye Synthesis

Azo dyes

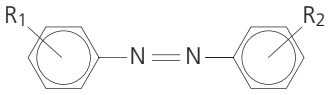
Procedure



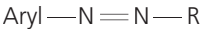
Background:

Azo dyes make up the largest group of synthetic dyes by number.
They are used as food dyes, artists' colors, basic colors for four-color printing (yellow and magenta), as well as textile dyes on a large scale. Over 350.000 t of azo dyes are used worldwide only for the dyeing of natural fibers.

Azo dyes are characterized by the diazo group, which couples two molecular parts:

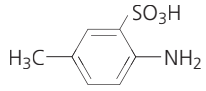


or more general

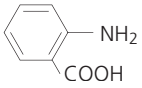


The diazo bridge connects the two components aryl, designated as diazo component, and R, designated as coupling component.

Modern diazo components are, for example:

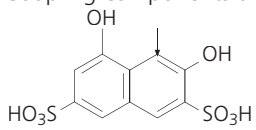


4B acid and

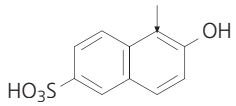


Anthranilic acid

Coupling components are:



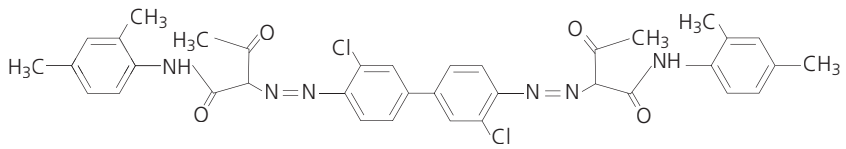
Chromotropic acid and



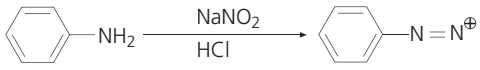
Schaeffer's acid

To increase solubility and adhesion to fibers such as wool, the sulfo group is introduced. The great variety of azo dyes results from the more or less free variation of substituents in the diazo components as well as in the coupling components:

Example for a modern azo dye:

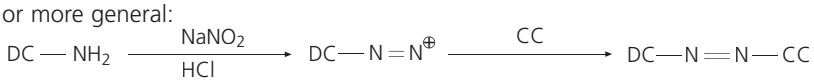


Start reaction is the diazotation in the presence of hydrochloric acid and sodium nitrite.



Aniline — Diazonium salt

or more general:



Diazo component — Diazonium salt — p-amino azobenzen

CC = coupling component

The reaction is exothermic and is therefore cooled with ice and it depends on the pH value. Now, the highly reactive diazonium salt reacts (couples to) the desired coupling components. These reaction steps, as well, depend on the pH.
The yield of this process is optimized via the pH value. The reactants are mixed stoichometrically. Fine tuning is achieved through the pH value. Therefore, pH measurement is required at each reactor vessel (diazotation and couplings).

Since the exhaust gases of the reactors are heavily contaminated (with hydrochloric acid, among others), they are cleaned in gas scrubbers. Here, as well, pH measurement is essential (cf. Application Sheet AB Gas V1 0305 en) In further reaction steps the product solubility is reduced by addition of sodium chloride and the product is precipitated. Through further washing procedures and the application of filter presses, a pure, typically pasty product is obtained, which is supplied to processing industries.

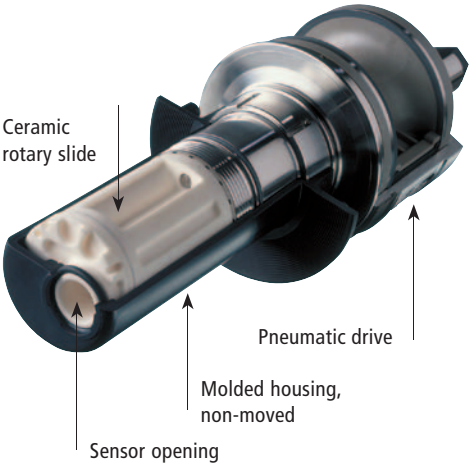
Measurement requirements:

Dye syntheses in modern plants run around the clock in 4 shifts.
Virtually all essential reaction steps are pH-dependent so that the optimization of product yield is based on a reliable, low-maintenance pH measurement. The diazotation reaction requires much hydrochloric acid and is therefore correspondingly corrosive. The reactors are protected by an enamel coating, the coupling reactors also by a rubber coating.
The extreme conditions for the measuring point are as follows:
pH = 1, hydrochloric
Temperature = 90°C,
Pressure = 6bars.
The pH electrodes have a service life of 8 h up to several weeks.
Automation of these measuring points with conventional retractable probes is only possible when Hastelloy C4 is used. Nevertheless, these expensive probes require high maintenance effort The probe must be removed and serviced several times a year.

Solution:

The Ceramat® WA 150 sensor lock-gate together with the Unical® 9000 automatic cleaning and calibration system allows complete automation of this difficult measuring point with maximum availability.
The Ceramat® probe consists of a corrosion-proof, ultrahard, superpolished, rotating ceramic part and a corrosion resistant, carbon reinforced, non-moved plastic (PEEK) housing.
After 24 months run time the Ceramat® did not show any wear on sealings, probe housing, or other parts.

Ceramat® WA 150
ceramic sensor lock-gate



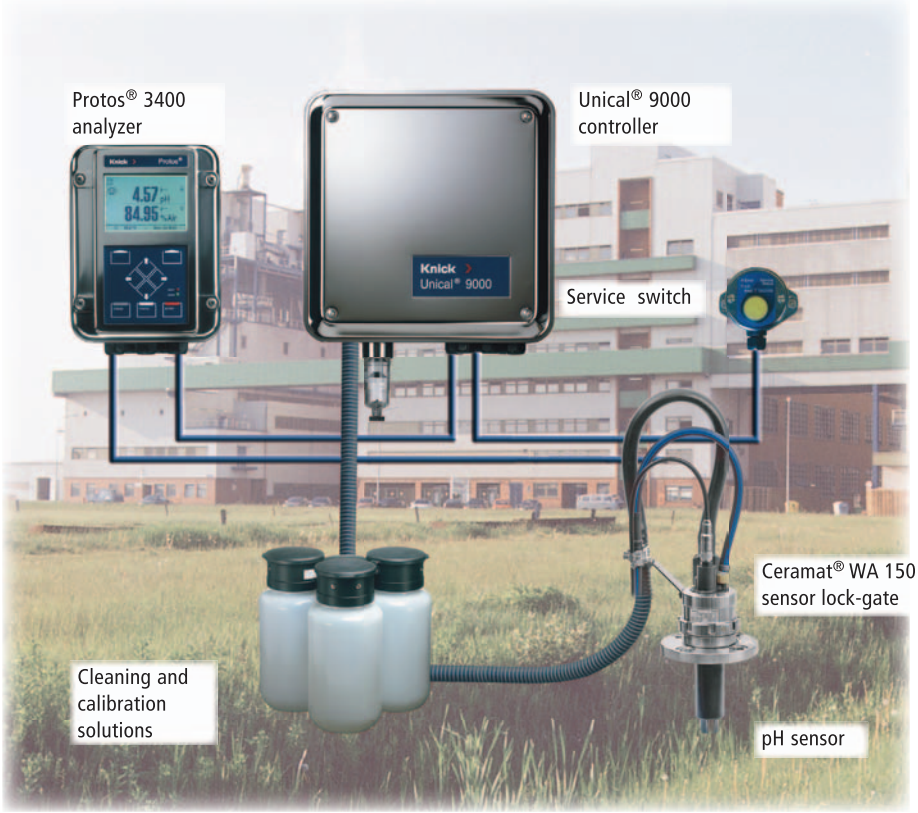
Typical measuring point
with Ceramat®

Knick

Knick
Elektronische Messgeräte
GmbH & Co. KG
Beuckestraße 22, 14163 Berlin
Phone: +49 (0)30 - 801 91 - 0
Fax: +49 (0)30 - 801 91 - 200
knick@knick.de · www.knick.de

The complete measuring system:

- Highest reliability
- Optimal process control
- Low cost of ownership



Applied Components

Ceramat® flange DN 50
WA150 –N0AAA1-000

Unical® 9000-NC301222CN000-000

Protos® 3400C
with Unical module PHU 3400-110

pH combination electrode SE 533/2
(225 mm)

Sensor cable VP ZU 0314

Buffer solutions pH 4,01 ZU 0200,
pH 7,0 ZU 0201 and pH 9,21 ZU 0202