

5.1 – Cyanuric Acid Technology

Cyanuric acid was identified as a chemical substance over two centuries ago. However, it was not until the late 1950's that it attained industrial significance with the introduction of chlorinated isocyanurates by Monsanto and FMC. Although the majority of cyanuric acid production is used in the manufacture of chlorinated isocyanurates, some of it is also used as a swimming pool available chlorine stabilizer. Cyanuric acid is also used in the manufacture of specialty intermediates used in the production of plastics and coatings. The properties, chemistry, uses, etc. of cyanuric acid and chloroisocyanurates have been comprehensively reviewed (Wojtowicz 1993a and 1993b). This paper discusses the structure, properties, analysis, chemistry, manufacture, and uses of cyanuric acid.

Typical Analysis

Typical analysis of commercial cyanuric acid (CA) is shown in Table 1. The product also typically contains small amounts of ammonium sulfate or ammonium nitrate (<0.2%).

Structure

Cyanuric acid can exist in either of two structures as shown in Figure 1. The keto form predominates in the solid whereas the enol form predominates in solution. The keto form is techni-

Cyanuric Acid	>99%
Ammelide and Ammeline	≤0.5%
Water	~0.1%*
pH of saturated solution at 25°C	4.5-5.0

*Water content will vary with manufacturer; some products can contain up to 4% water.

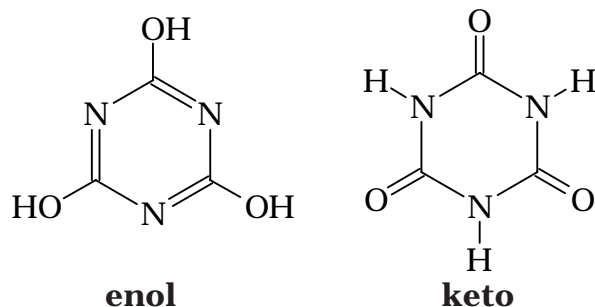
Table 1 – Typical Analysis of Commercial Cyanuric Acid

cally referred to as isocyanuric acid whereas the enol form is simply cyanuric acid. Both forms are collectively referred to as cyanuric acid.

Properties

Physical

Cyanuric acid is a white crystalline solid. Some of its physical properties are summarized in Table 2. The aqueous solubility data for CA in Table 2 refers to distilled water, consequently these solutions have a pH around 4.8. A plot of the data is shown in Figure 2. The extrapolated solubility of CA in distilled water at 0°C is 525 ppm. The solubility



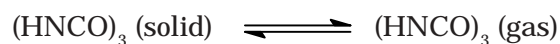
Cyanuric Acid Isocyanuric Acid
Figure 1 – Cyanuric Acid Structures

The Chemistry and Treatment of Swimming Pool and Spa Water

at pool pH would be much higher because of ionization to cyanurate, which amounts to 73 to 91 % over the normal pool range of 7.2 – 7.8.

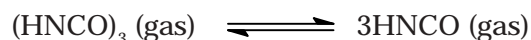
Sublimation

Solid cyanuric acid does not melt, instead it undergoes sublimation, i.e., it volatilizes directly from the solid to the gaseous state. Significant sublimation commences at about 350°C as shown by the reaction below, where (HNCO)₃ is a linear representation of the tricyclic formula of CA.



Dissociation in the Gaseous State

Heating gaseous cyanuric acid above 400°C causes dissociation into isocyanic acid as shown below.



Solid Forms	Granular, powder
Aq. Solubility @ 25°C	0.15% ^a
“ “ “ 50°C	0.70% ^a
“ “ “ 90°C	2.6% ^a
“ “ “ 150°C	10.0% ^b
Density (anhydrous)	1.75 g/mL
“ (dihydrate)	1.66 g/mL
Melting Point	Does not melt up to 350°C

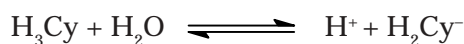
a) Nelson 1967

b) Zagranichnyi and Polyakova 1963

Table 2 – Some Physical Properties of Cyanuric Acid

Ionization in Aqueous Solution

Cyanuric acid (H₃Cy, where Cy represents the triisocyanurate anion) is a weak acid, even weaker than carbonic acid. The pH of a saturated solution is only 4.8. Ionization forms hydrogen and cyanurate ions as shown below:



Effect on Swimming Pool Water Alkalinity

Addition of cyanuric acid will lower the pH of pool water. When the pH is restored to the normal range, total alkalinity will be increased, due to formation of cyanurate ions. Cyanuric acid is 73–91% neutralized at pool pH. Total alkalinity is corrected for cyanurate alkalinity by the following equation to yield carbonate alkalinity (Wojtowicz 1995):

$$\text{Alk}_{\text{CORR}} = \text{Alk}_T - 1/3 \cdot \text{CA}$$

Toxicity

Cyanuric acid is essentially non-toxic to humans, animals, wild-life, and aquatic life. The toxicology of cyanuric acid and chlorinated isocyanurates have been reviewed (Hammond *et al* 1986). The acute toxicity (oral LD₅₀) is >10 g/Kg for rabbits.

Biodegradability

Cyanuric acid undergoes biodegradation by some soil bacteria (Bagnall *et al* 1984).

Analysis of Cyanuric Acid

Solid Cyanuric Acid

Solid cyanuric acid dissolved in water can be titrated with sodium hydroxide solution using a

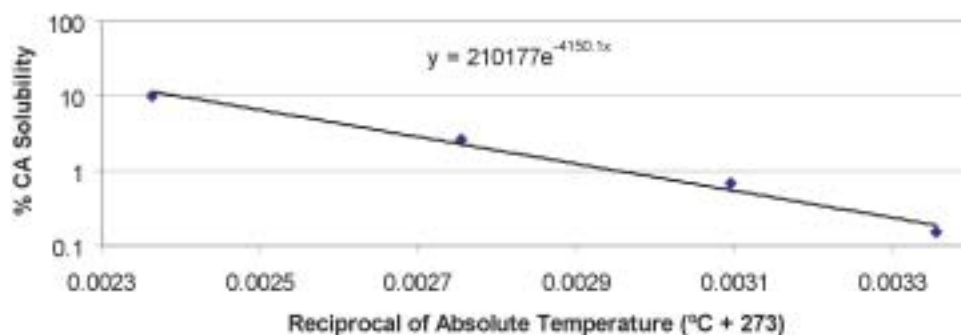
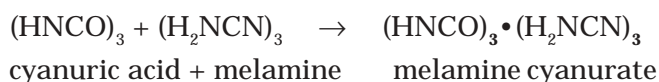


Figure 2 – Cyanuric Acid Solubility

recording pH meter; the equivalence point is at about pH 8.8–9.0. Ammelide and ammeline are also titrated (Wojtowicz 1974). Ammelide and ammeline do not interfere if the titration is performed in a dimethyl sulfoxide (DMSO)–benzene mixed solvent using tetrabutyl ammonium hydroxide instead of sodium hydroxide (Morales 1968). Ammelide and ammeline can be determined by gas chromatography after dissolving cyanuric acid in trimethylsilylacetamide (Wojtowicz 1974).

In Swimming Pool Water

By Test Kit – The swimming pool test kit analysis is based on the turbidity caused by precipitation of cyanuric acid as melamine cyanurate. Since melamine cyanurate has a small solubility (5–10 ppm), the method is not suitable for very low cyanuric acid concentrations (<10 ppm). The accuracy of the test kit method is ±10%. The reaction is shown below.



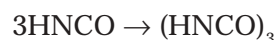
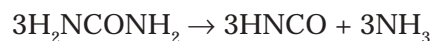
Other Methods – Dilute aqueous solutions of cyanuric acid can also be analyzed by liquid chromatography (Downes *et al* 1984), ion chromatography (Wojtowicz 1985), uv spectrophotometry (Downes *et al* 1984), and differential pulse polarography (Struys and Wolfs 1987). These methods are more accurate than swimming pool test kits.

Manufacture of Cyanuric Acid

Pyrolysis Of Urea

Cyanuric acid is manufactured by pyrolyzing

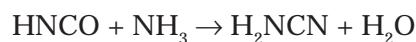
(i.e., heating) urea (see Figure 3). A molten or a concentrated aqueous solution of urea is sprayed onto a moving bed of crude cyanuric acid granules in a directly heated rotary kiln. The crude cyanuric acid is maintained at about 250°C for about one hour. About 90% of the crude cyanuric acid exiting the kiln is recycled to the front of the kiln. Urea dissociates into isocyanic acid and ammonia in the kiln. The isocyanic acid trimerizes to cyanuric acid.



The ammonia offgas from the kiln is scrubbed in the urea feed solution to remove small amounts of volatilized urea and cyanuric acid and can either be flared (i.e., burned) or recovered as ammonium nitrate by reaction with nitric acid for use as fertilizer.

Byproduct Formation

Pyrolysis of urea also produces undesirable aminotriazine byproducts which can form by reaction of ammonia with isocyanic acid to yield cyanamide.



Cyanamide can react with isocyanic acid or with itself to produce ammelide (Ad), ammeline (An), or melamine (Mm). The formulas for Ad, An, and Mm shown below are linear representations for the structural formulas shown in Figure 4. Crude cyanuric acid usually contains 80% cyanuric acid, 18% ammelide, 2% ammeline, and <0.1% melamine.

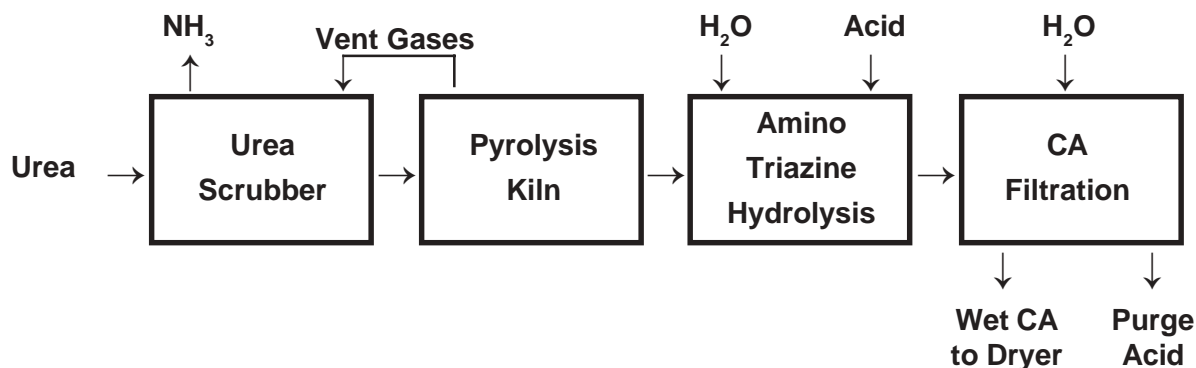
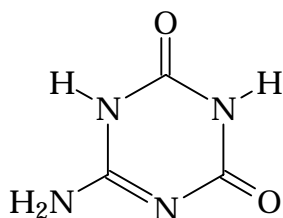
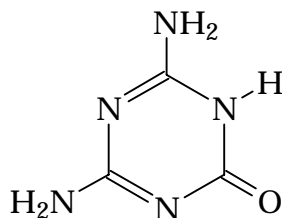


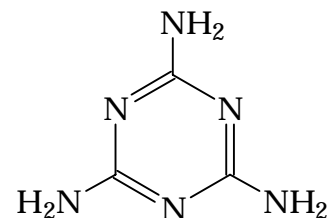
Figure 3 – Process Flow Diagram for Manufacture of Cyanuric Acid



Ammelide

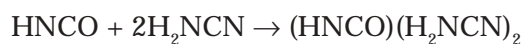


Ammeline

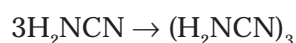


Melamine

Figure 4 – Structures of Aminotriazines



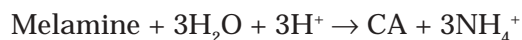
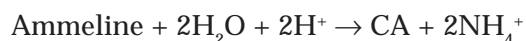
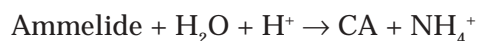
An



Mm

Hydrolysis of Aminotriazines

The crude cyanuric from the kiln is pulverized to a powder, slurried in dilute sulfuric (or nitric) acid, and heated at the boiling point for about one hour. This hydrolyzes the aminotriazines to cyanuric acid as shown below.



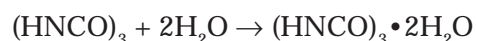
Recovery of Purified Cyanuric Acid

The purified cyanuric acid crystals from the hydrolysis step are filtered, washed with water to remove the digestion acid, and flash dried. The dry powder is compacted and granulated.

Reactions of Cyanuric Acid

Hydrate Formation

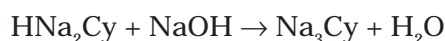
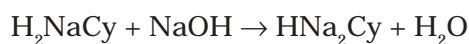
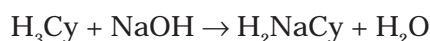
Cyanuric acid forms a dihydrate on reaction with water.



The dihydrate effloresces, i.e., it loses water on exposure to air of low to moderate humidity. When heated to 57°C, the dihydrate undergoes a transition to anhydrous cyanuric acid and water.

Neutralization (Salt Formation)

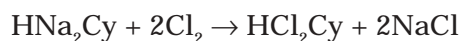
On reaction with sodium hydroxide, cyanuric acid forms a series of sodium salts, i.e., mono-, di-, and trisodium cyanurate as shown by the reactions below, where Cy represents the triisocyanurate anion, i.e., $(\text{CNO})_3^{3-}$.



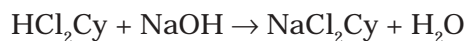
The solubilities of these salts are greater than that of CA, e.g., the solubilities of mono-, di-, and trisodium cyanurates are: 0.9, 5.7, and 14.1 g/100 mL of solution at 25°C.

Chlorination

Preparation of Dichlor – Chlorination of an aqueous slurry of disodium cyanurate produces dichloroisocyanuric acid.



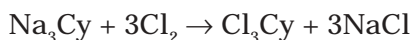
The dichloroisocyanuric acid is recovered by filtration and is washed with water to remove the byproduct sodium chloride. It is reslurried in water and reacted with sodium hydroxide to produce sodium dichloroisocyanurate (Dichlor).



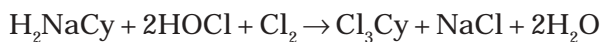
The sodium dichloroisocyanurate crystals are isolated by filtration. The crystals are flash dried with hot air to so-called anhydrous sodium dichloro-

isocyanurate (~2% water, ~63% available chlorine). The resultant powder is then compacted and granulated. Treatment with water converts anhydrous sodium dichloroisocyanurate to the dihydrate (12.5–13.0% water, 55–56% available chlorine). Dichlor is used primarily for spa sanitation. Another important use for Dichlor is in commercial dishwasher formulations.

Preparation of Trichlor – Reaction of an aqueous solution of trisodium cyanurate with gaseous chlorine yields trichloroisocyanuric acid (Trichlor).



Trichloroisocyanuric acid is also manufactured by reaction of an aqueous slurry of monosodium cyanurate with chlorine and hypochlorous acid.



The trichloroisocyanuric acid crystals are recovered by filtration and water washing to remove the byproduct sodium chloride. Flash drying with hot air gives a dry powder which is compacted and granulated and then pressed into 1" and 3" tablets as well as sticks for use in swimming pool sanitation.

Uses of Cyanuric Acid

Manufacture of Chloroisocyanurates

Most of the cyanuric acid produced commercially is converted to chloroisocyanurates. See above for a discussion of the chemistry.

Stabilizer for Available Chlorine

Cyanuric acid is used in swimming pools as a stabilizer for available chlorine. See below for a discussion of the mechanism of stabilization.

Other Uses for Cyanuric Acid

Cyanuric acid has a number of important non-pool uses which include preparation of

high performance magnet-wire enamels and in electrical varnishes, plastics with enhanced properties, flame retardant resins and solid lubricants, cross-linking and curing agent in the manufacture of plastics and coatings. CA is also used to reduce nitrogen oxides (NO_x) in stationary diesel engine exhaust gases.

References

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