Strong bonds. Trusted solutions.

The History of Kymene™ Wet-Strength Resins: 60 Years of Success

Kymene turned 60 in 2017. That makes it older than the internet, DNA testing, and seedless watermelons.

Two thousand seventeen marks a momentous occasion for Solenis — the 60th anniversary of Kymene™ wet-strength resins. It's fitting that the traditional theme for a 60th anniversary is diamonds, as the first generation of Kymene, released in 1957, was a rare gem that revolutionized the papermaking industry forever. Since then, our scientists have continued to refine the basic chemistry of Kymene, creating newer generations of the resin that are better for the environment and better for our customers. We're proud to say that, after more than half a century, Kymene remains the most trusted wet-strength resin on the market today.

Back to the Beginning

It all started in 1944 when research chemist Gerald Keim joined Hercules, Solenis' legacy company. Keim initially focused on developing modified urea-formaldehyde (UF) resins, the standard wet-strength technology at the time, which only worked in acidic environments. Some UF resins were anionically charged and required the use of another product, often an acid rosin size-alum complex, to provide the necessary catalytic environment to allow retention of the UF resins onto the paper fiber, thus creating wet strength. With the advent of neutral pH papermaking conditions in the paper industry in the 1950s, however, UF technology could no longer provide wet strength. Something new was required to provide wet strength under neutral pH conditions, so Keim went to work exploring alternative chemical platforms to replace UF resins.

In 1957, success came when his experiments involving the reactants diethylenetriamine, adipic acid and epichlorohydrin yielded a chemical that could impart superior wet strength in neutral pH conditions. That chemical was polyamidoamine-epichlorohydrin (PAE) resin, and it initiated the modern era of wet-strength paper manufacturing. Hercules filed its first patent for PAE resin in 1957 and then introduced it to the market as Kymene 557 wet-strength resin. Kymene 557 was an immediate success. In the first year, Hercules sold 7 million pounds of Kymene 557, and sales increased to 70 million pounds by 1964.

The reaction between diethylenetriamine and adipic acid generated a low molecular weight polymer or "prepolymer," which would then be functionalized by reaction with epichlorohdrin. The reactive characteristics of this prepolymer

A History of Chemical Innovation

1957

First patent application filed for polyamido-amine-epichlorohydrin (PAE) resin technology, ushering in a new era with Kymene 557 wet-strength resin.

1980s

Development begins on products containing less than 1,000 parts per million (ppm) of 1,3-dichloropropanol (1,3-DCP).

1990

Kymene SLX wet-strength resin—a G2 resin with less than 1,000 ppm 1,3-DCP—launches in Europe.

1993

Kymene ULX wet-strength resin is introduced in Europe. This product takes advantage of "biodehalogenation" to become the first G3 wet-strength resin.

1999

Another first is launched—the first G3 resin allowing papermakers to manufacture products with reduced or non-detectable levels of 3-monochloropropan-1,2-diol (3-MCPD) and 1,3-DCP.

was the basis of the Hercules wet-strength portfolio for the next 40 years. Researchers continued to refine the chemistry during this time to improve cost-effectiveness by increasing solids. By the mid 1980s, Hercules was selling a family of five PAE resins based on Keim's original work, now referred to as Generation 1 (G1) PAE wet-strength resins.

A Cleaner, Kinder Kymene

Despite its initial success, the first generation of Kymene resins had its drawbacks, most notably that the resins contained harmful by-products — primarily 1,3-dichloropropanol (DCP) and 3-monochloropropane-1,3-diol (CPD). With the classification of these by-products as potential carcinogens, Hercules scientists went back to work in a major effort to reduce the level of by-products in Kymene resins. As a result of significant developments in process chemistry, the first in a series of second generation (G2) PAE technologies — Kymene SLX — was launched in 1990, and was widely accepted by the industry. Ninety percent of the European wet-strength resin market switched to the new Kymene in its first year.

With the ultimate goal of providing the paper industry with Kymene resins that were completely free of harmful by-products, Hercules scientists set out again to develop the next generation and turned to a new method: biodehalogenation.

With help from the University of Kent, United Kingdom, Hercules used physiochemical methods to isolate microbes that were capable of metabolizing DCP and CPD to glycerol, which the microbes then used as food. Unlike other methods used to reduce and remove epichlorohydrin by-products, biodehalogenation consumes very little energy, requires no additional chemicals and generates no additional waste stream. Generation 3 (G3) went full scale with this technique in 1994.

Membrane separation technology is perfected, making it possible to manufacture higher-solids, higher-efficiency G3 wet-strength resins.

2008

2012

The G2.5 and G3 portfolio gets refreshed with the introduction of Kymene LHP and GHP wet-strength resins.

G1.5, a low VOC high performing resin, with excellent storage stability launches in North America.

2017

A completely new wet-strength resin category—G2.5—is created when Kymene 217LX wet-strength resin launches.

2005

2010

The G1 portfolio gets updated to have much lower 1,3-DCP and 3-MCPD.

EMEA portfolio refreshed with G2 and G2.3 products now containing <500 ppm of 1,3-DCP.

2015 **2016**

Around the same time, Hercules scientists also developed more reactive prepolymers, which allowed for a new range of G2 wet-strength resins with higher solids and functionality. These updates were also applied to the G1 portfolio of resins to provide upgraded product offerings to the North American market. Further developments of the basic prepolymer design in the late 2000s allowed upgrades to the Kymene product portfolio yet again. But Hercules scientists were still on the hunt for the perfect high-solids, low-by-products solution.

From Microbes to Membranes

The development of the biodehalogenation process to reduce levels of DCP and CPD to undetectable levels was a truly "out of the box" route to cleaner PAE technology. However, biodehalogenation also limited the level of solids and required a serious maintenance regimen to avoid "infection" from other microbes. At times, this made the process unpredictable.

To overcome these limitations, Hercules scientists investigated nanofiltration (membrane separation) technology in the mid 2000s. This process takes a Kymene resin that has been treated to destroy polymer-bound CPD (PB-CPD) and passes it through a nanofiltration device, essentially removing all by-products while retaining high solids and functionality. As a result, our latest G3 Kymene technologies are able to maximize wet-strength performance while minimizing levels of DCP, CPD, PB-CPD and overall AOX (adsorbable organic halides) at higher solids.

Moving Forward

Ultimately, Solenis and Kymene have come a long way — from inventing a new wet-strength additive in the lab to mass-scaling the product and distributing it across the globe. PAE resins account for 90 percent of the current wet-strength market, with nearly half bearing the Kymene name. Solenis offers the broadest portfolio of wet-strength resins in the world, with different product configurations to accommodate any mill's compliance standards, and we'll continue to refine and introduce next-generation wet-strength resins that improve the sustainability and profitability of our customers.

CELEBRATING 60 YEARS
KYMENE™
WET-STRENGTH RESIN
ESTABLISHED 1957