

Kymene™

Wet-strength Resin Innovations

Wet-strength Resin Production Facilities



Global Wet-strength Resin Leader

Solenis invented the modern era of wet-strength paper manufacturing with the introduction of Kymene[™] 557 wet-strength resin, the first polyamide-epichlorohydrin (PAE) resin chemistry ever brought to the market.

The product was an instant commercial success, both for its ability to function in neutral/alkaline pH papermaking processes and for its novel wetstrength capabilities. Like all PAE resins, the polymer in Kymene 557H contains azetidinium chloride (AZE), a quaternary amine ring species, that adsorb onto negatively charged paper fibers and continue to cross-link even as the paper dries and cures. This means the wet strength of paper treated with Kymene wet-strength resin continues to increase after it's been put into storage. Over the years, our researchers have modified the basic chemistry to make stronger-performing resins with reduced levels of organochlorine-containing by-products, 1,3-dichloropropanol (1,3-DCP) and 3-monochloropropan-1,2-diol (3-MCPD), as well as aminochlorohydrin (ACH) and polymer-bound CPD (PB-CPD). Solenis has led the industry in decreasing the organic chlorine content of its Kymene wet-strength resins without compromising their efficiency. Our scientists have developed manufacturing processes with greater control to maximize the efficiency of how epichlorohydrin is used to generate AZE while minimizing the levels of 1,3-DCP and 3-MCPD. We've also introduced innovative technologies that can be applied after the manufacture of the basic PAE resin to reduce the levels of these harmful by-products further.

Kymene[™] Wet-strength Resin Portfolio

Today, PAE resins account for 90 percent of the wetstrength market. Of this market, nearly half bear the Kymene brand name. One reason for the success of the product is a broad range of configurations that enable papermakers to customize their wet-strength programs to satisfy regional demands and regulatory requirements. Solenis has introduced market-leading technologies into each of the widely used industry descriptors of G1, G1.5, G2, G2.5 and G3 PAE resins, making it possible to address a full range of customer compliance needs while balancing cost-in-use.

Today, we offer the broadest portfolio in every region of the world and can provide solutions to satisfy even the most rigorous regulatory guidelines, including environmental labeling established by EU Ecolabel and recommendations issued by the German Federal Institute of Risk Assessment (Bundesinstitut für Risikobewertung, or BfR). Solenis' wet-strength resins can be supplied in a wide range of solids content — from 13 percent total solids to 30 percent total solids — to help our customers balance freight costs, shelf life and product stability concerns.



BfR XXXVI /1/2/3 **BfR XXXVI** Non BfR Non Total Chlorine Free **G1** 1.00% G1.5' G2 %AOX¹ (wet basis) 0.10% **Total Chlorine Free** G2.5 **G**3 0.01% 1 0 10 100 1000 10000 1,3-DCP ppm (wet basis)

Compliance Standards for Kymene Wet-strength Resins

We offer the broadest portfolio of wet-strength resins in the world, with different product configurations to accommodate any mill's compliance standards, regardless of location.

1 Adsorbable organic halogen ^ Only available in North America

A History of Chemical Innovation

In the late 1950s, Solenis scientists began a quest to find a wet-strength resin that could demonstrate good performance under neutral pH papermaking conditions. Their efforts led to polyamideepichlorohydrin (PAE) resin chemistry. Solenis filed its first patent application for PAE resin technology in 1957 and began to market Kymene™ 557, the first example of a G1 wet-strength resin. In the years that followed, this resin proved to be the most costeffective technology for providing wet strength in neutral pH conditions. However, 1,3-DCP and 3-MCPD, organochlorine by-products from the manufacturing process, are hazardous substances and are possible human carcinogens. These byproducts, together with the organochlorine species present on the backbone of the resin, ACH and PB-CPD, increased adsorbable organic halogen



(AOX) levels in the effluent of paper mills. As focus increased on the environmental and health impacts of using such technology, the use of this G1 PAE resin became more regulated, though the allowable levels of by-products varied greatly from region to region. Solenis scientists refined the manufacturing process to reduce the levels of organochlorinecontaining species and by-products. This led to the introduction of G2 wet-strength resins in Europe and North America, where the level of 1,3-DCP had been reduced by more the 90 percent.

As the levels of AOX permitted in effluent streams continued to be reduced, requirements were also placed on the use of PAE resins in food-packaging applications. To meet these requirements, further modifications were made to the chemistry and manufacturing process, leading to the introduction of Kymene 217LX, the first example of a G2.5 wet-strength resin. In recent years, there has been greater focus on managing and conserving resources in the paper industry, with less freshwater being used to make paper. This places greater demands on PAE technology to meet the requirements for food packaging grades and lower AOX emissions from the mill. Solenis has responded with the introduction of improved G2.5 wet-strength resins, Kymene 217LXE and Kymene 5720. With this most recent update of G2.5 technology, the level of 1,3-DCP has been reduced more than 98 percent compared to the original Kymene 557 resin developed 65 years earlier.

The Synthesis of Kymene Wet-strength Resins

Although the basic reactions in the synthesis of wet-strength resins are well understood, we have introduced advanced process control and purification techniques to increase the efficiency of our products while lowering their environmental impact.









3-monochloro-1,2-propanediol (3-MCPD)

The Future of Innovation

While much has been done to reduce the levels of 1,3-DCP and 3-MCPD generated during the PAE resin manufacturing process, the most desirable product would be one completely devoid of these by-products. To achieve this, Solenis developed a unique purification process for PAE wet-strength resins, referred to as "biodehalogenation." This process relied on naturally occurring microorganisms to convert 1,3-DCP and 3-MCPD to glycerol, which the same microorganisms then used for food. Biodehalogenation used very little energy, required no additional chemicals and did not generate an additional waste stream. This was the first example of a G3 PAE wet-strength resin. However, the process did limit the solids content and level of AZE functionality of the resins, impacting the performance papermakers could gain from this product.

To overcome these constraints, Solenis scientists searched for alternative purification techniques. This has led to the application of membrane separation technology to PAE resins to reduce the level of by-products to very low levels. This process overcomes the limitations of the biodehalogenation process, allowing for resins with higher solids and

Membrane Separation Technology

A decade of research has led to revolutionary membrane separation technology, which can help paper mills decrease levels of both 1,3-DCP and 3-MCPD and overall AOX. higher levels of AZE functionality. This class of G3 resins allows papermakers to maximize wetstrength performance while decreasing levels of both 1,3-DCP and 3-MCPD and overall AOX in their processes.

Both the biodehalogenation process and membrane separation technology are examples of post-reaction techniques requiring dedicated equipment to purify a PAE resin. Solenis has continued to develop the main PAE manufacturing process further, resulting in the launch of a new G3 wet-strength resin, Kymene[™] 888ULX, that does not use a post-reaction purification technology.



Wet Strength: Satisfying Consumer Demand

Solenis' ongoing commitment to wet strength reflects an increasing demand among consumers for paper products that remain strong even when wet. Today, any grade of paper that needs to maintain



its integrity after becoming wet relies on the application of a wet-strength agent. These grades include tissue (facial, kitchen towel, wipers, napkins and tableware), packaging (liquid packaging, aseptic container, carrier board, and other forms of food packaging), and specialty (tea bag, coffee filter, labels, currency, laminating grades, etc.).

Solenis' PAE resin inventions established the modern wet-strength platform and helped to clarify the fundamental chemistry. Wet-strength resins are a class of chemicals that adhere to pulp fibers and form linkages between fibers through covalent bonding. These linkages supplement and reinforce the natural hydrogen bonding in the dry sheet and, because they're covalent, cannot be broken by soaking in water and are resistant to cleaning chemicals. Papers treated with these resins, such as kitchen towels and wipers, typically have a wet breaking strength of 30 percent or greater of their dry breaking strength.

Wet Strength by the Numbers



Wet-strength papermaking is vitally important because of the prominence these grades have in day-to-day consumer activities and because governments carefully monitor any paper and board that comes into contact with food.

Kymene[™] Wet-strength Resin: Active Patents

G3:		G3
US9719212	CN106574445	US7
EP3180474	AU2015301636	US8
		EP2

G3 via membrane separation:

US7932349 US8101710 EP2064265 CA2663054 KR101387870

The Future of Wet Strength

As consumer needs and regulatory requirements continue to evolve, wet-strength chemistry must evolve with it, which is why the Kymene story is far from being over. Solenis scientists continue to explore and refine the chemistry we invented at the same time that we research commercially viable alternatives, with the goal of introducing nextgeneration wet-strength products that:

- Increase solids so significantly that paper mills can cut their deliveries by half, thereby significantly improving sustainability.
- Improve functionality to significantly increase the wet-strength-to-dry-strength ratio papermakers can achieve.
- Remain far ahead of all regulatory compliance issues by further reducing 1,3-DCP, 3-MCPD and total AOX.

All of these innovations will lead to a better Kymene product line that helps our customers adapt to

changing industry requirements, deliver products that are both functional and safe for consumers, increase sustainability and minimize associated environmental impacts.







To learn more about how Solenis can help address your toughest challenges and more, please visit **solenis.com**