

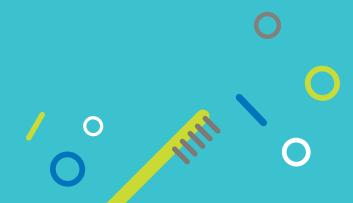
smile and the world smiles with you

At Ashland, we are committed to creating innovative ingredient technologies that improve the efficacy, usability and consumer appeal of oral care products. Toothpaste, mouthwash, and denture adhesives are just a few of the oral care products that benefit from the use of our ingredients. Today, Ashland's broad oral care ingredient portfolio includes bioadhesive polymers, teeth bleaching agents, stain removers, rheology modifiers, mouth moisturizers, and custom encapsulates.

Ashland solvers are focused on innovation and continue to see and understand the market activity and emerging trends around the world. In pursuit of new solutions, we bring all of the technical disciplines together, including molecular (synthesis) science, analytical, microbiology research, materials science, encapsulation technology, consumer evaluation and application/formulation development. New materials, tailor-made and custom grades are routinely evaluated by our global network of application and formulation scientists to solve technical challenges and delight consumers.

Our success depends on your success and we stand ready to solve with you at every step from innovative ingredients to technical service and awareness of market trends. We do more than just manufacture innovative ingredients to demanding quality standards; our products are supported by dedicated oral care solvers. We are committed to helping you grow.

Get to know us and you'll see how Ashland keeps the world smiling.



enhancing performance of oral care products

Ashland works to understand the properties of our ingredients and their performance in oral care formulations. With our global network of oral care laboratories staffed with experienced scientists, we routinely conduct *in vitro* performance evaluations of toothpaste, mouth rinse and denture adhesive formulations. We support all our ingredient solutions with formulation expertise and robust testing resources, including:

- assessment of actives delivery and retention to teeth and mucous membranes
- characterization of polymer effects on prevention of enamel demineralization from dietary acids
- measurement of rheology and complex flow behavior using advanced techniques
- formulation of laboratory-scale toothpaste batches and stability testing
- evaluation of teeth cleaning/stain removal, stain prevention or whitening by instrumental color measurement
- evaluation and formulation of teeth whiteners
- assessment of toothpaste using V-8 brushing machine and mouth wash on bovine enamel and artificial teeth
- in vitro evaluation of denture adhesive formulations performance as well as extensive formulation knowledge
- consumer panel testing of toothpaste and mouthwash formulations

We can help solve difficult formulating challenges and bring new formulations to market faster. Ashland will work with you to find new and better ways to deliver oral health and create beautiful smiles.



global capabilities

technical service scientists to help formulators bring new and improved formulations quickly to consumers

oral care *in vitro* evaluation of ingredients and formulations to provide new and improved end-product benefits

technical leadership in science of rheology and bioadhesion

innovative starter formulations and new market concepts

demonstration of consumer-perceivable benefits using consumer panels

synthesis of new polymers and evaluation using advanced analytical and material science methods for understanding of structure function relationship



formulation solutions from Ashland

Ashland is a leading supplier of innovative ingredients that solve complex formulation challenges in toothpaste, mouthwash, denture adhesives, denture cleanser tablets, tooth whiteners and mouth moisturizers.

solutions for high performance denture adhesives

For denture wearers, adhesives that hold dentures in place throughout the day are critical. Our polymers give the duration and strength of hold expected of modern denture adhesives creams, powders and pads. Aqualon™ and Blanose™ carboxymethylcellulose (CMC) gives initial tack to denture adhesives while Gantrez™ AN polymer salts such as MS-955 provide duration of hold in denture adhesives.

solutions for delivery and retention of actives

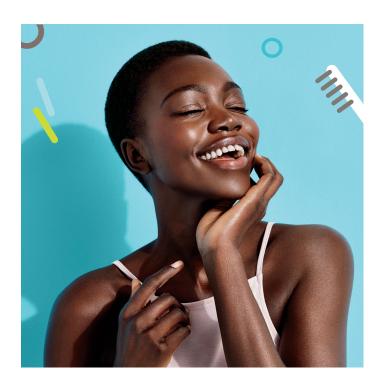
Delivering and retaining actives in the mouth are key for improving efficacy of toothpaste and mouthwashes. The combination of Gantrez S-97 polymer with a surfactant greatly enhances the buccal retention of active materials that are water insoluble and emulsifiable by the surfactant such as antimicrobial agents and flavors to provide long-lasting benefits.

solutions for whiter teeth

With consumers around the world wanting whiter and brighter teeth, Ashland offers Plasdone™ K-29/32 polymer to gently and effectively lift staining agents during brushing or rinsing, leaving teeth measurably whiter. For teeth bleaching, Peroxydone™ complexes are very stable, powder complexes of hydrogen peroxide and polymers that release hydrogen peroxide on contact with saliva in the mouth. These novel polymers can be formulated into a wide range of product forms including liquids, gels, tablets, strips and films for whiter teeth.

solutions to modify and control rheology

Ashland offers the widest range of cellulose ether and synthetic polymers to modify and control rheology. As toothpaste formulations have become diversified, driven by new actives and need for increasing performance, we have responded with tailor made grades and types of rheology modifiers to meet the needs of specific applications.



solutions for mouth lubrication and moisturization

With the increasing use of medications around the world, a growing number of consumers seek artificial saliva or mouth moisturizing gels, sprays and rinses to address dry mouth. Mouth moisturizer formulations are designed to have the flow and lubricity similar to natural saliva as well as high mucoadhesion to stay in the mouth between applications.

Ashland oral care ingredient portfolio overview

We invite formulators to explore our commercial ingredients.		Ар	plicat	ion						Fund	tion				
our commercial ingrealents.	Toothpaste	Mouthwash	Denture Care	Teeth Whiteners	Mouth Moisturizers	Actives/Flavors Delivery	Bioadhesion	Hydrafion	Oxidative whitening	Protectant	Rheology Control	Stain Removal	Tablet binding	Tartar Control	Visual Enhancement
Polymers — Synthetic															
Gantrez™ AN polymers			•				•								
Gantrez S polymers	•	•	•		•	•	•			•				•	
Gantrez MS-955 polymer			•				•			•					
Plasdone™ K polymers	•	•	•	•	•		•				•	•	•		
Plasdone S-630 polymer			•		•		•			•			•		
Polyplasdone [™] polymers	•		•								•				
Polymers — Cellulose Ethers															
Aqualon™, Blanose™, and Bondwell™ sodium carboxymethylcellulose	•		•		•		•				•				
Klucel™ hydroxypropylcellulose	•	•		•	•						•		•		
Natrosol™ hydroxyethyl cellulose	•	•			•						•				
Polymer Complexes															
Peroxydone [™] complexes			•	•		•	•		•		•	•			
Encapsulation Technology		,						,							
Captivates [™] HC encapsulates	•	•	•			•									•
Captivates GL encapsulates	•					•									•
Hydrogels															
Lubrajel* BA hydrogel		•			•			•			•				
Other															
Allantoin	•	•	•		•					•					

 $^{{\}rm *Lubrajel} \ {\rm is} \ {\rm a} \ {\rm registered} \ {\rm trademark} \ {\rm of} \ {\rm United\text{-}Guardian}, {\rm Inc.}$



an introduction to Ashland oral care ingredient portfolio

polymers — synthetic

Gantrez™ AN polymers

Gantrez polymers are a family of synthetic copolymers based on methyl vinyl ether (MVE) and maleic anhydride that offer excellent bioadhesive properties. The anhydride powders (AN grades) are the base polymer for making polymer salts used as bioadhesives in denture adhesive applications. The AN grades are available in a range of molecular weights, but are not used directly in oral care applications.

Grade	Structure	Approximate Molecular Weight
AN-169	-(CH ₂ -CH)n OCH ₃ OOO	2,000,000

Gantrez S polymers

INCI Name: PVM/MA copolymer

Gantrez S polymers are the free acid form of copolymers of MVE and maleic anhydride utilized for their excellent film-forming properties; highly-effective chelation and exceptional bioadhesive performances in wet environments. Gantrez S polymers are available in a range of molecular weights.

Toothpastes and Mouthwashes

Gantrez S polymers are an excellent mucosal adhesive for delivery and retention of antimicrobial agents, colors and flavors. In addition, Gantrez S polymers impart tartar control, anti-demineralization, and dentin tubule flow reduction. Gantrez S polymers are available as aqueous solutions and/or powder, depending on the grade.

Denture Cleansers

In denture cleansers, Gantrez S polymers provide active and flavor delivery.

Grade	Structure	Approximate Molecular Weight
S-97	OCH ₃ 	1,500,000
S-96	O=C C=O OH OH	700,000

- offers bioadhesion to enable delivery of actives to mucous membranes
- delivers and retains oral care actives in the mouth for up to 12 hours
- holds flavors, botanicals, colors, coolants and other water-insoluble actives in the mouth
- gives tartar control
- forms film to reduce flow to dentin tubule

Gantrez™ MS-955 polymer

INCI Name: calcium/sodium PVM/MA copolymer

Gantrez MS-955 polymer is a mixed sodium and calcium salt of MVE and maleic anhydride copolymer supplied as an off-white powder. The polymer is slowly soluble in water, resulting in amber-colored solutions with high viscosity and adhesion.

Denture Adhesives

Gantrez MS-955 polymer delivers the long-term hold expected of modern denture adhesives. It is used in denture adhesive formulations with Aqualon $^{\text{\tiny M}}$ or Blanose $^{\text{\tiny M}}$ CMC.

Grade	Structure	Approximate Molecular Weight
MS-955	OCH ₃ CH ₂ -CH - CH	1,000,000

Key Benefits:

- offers excellent bioadhesion in wet environments
- provides long term hold to denture adhesive creams and powders

Plasdone™ K polymers

INCI Name: PVP

Plasdone polymers are pharmaceutical-grade homopolymers of N-vinyl-2-pyrrolidone (NVP) supplied as white, free flowing powders. Available in a range of molecular weights, they are characterized by K-value. PVP polymers are soluble in water, highly adhesive and form glossy, transparent, oxygen permeable films.

Toothpastes and Mouthwashes

Plasdone K-29/32 polymer delivers non-abrasive and non-oxidatitve teeth whitening for brighter, whiter smiles. As PVP polymers are well-known to hydrogen bond with phenolic compounds, Plasdone K-29/32 polymer will form complexes with many of the chemicals that cause teeth stains resulting in a water-soluble complex that is easily removed during rinsing.

Denture Cleansers

Plasdone polymers are highly effective tablet binders for denture cleanser tablets.

Grade	Structure	Approximate Molecular Weight
K-29/32	$-\left(CH_2-CH\right)_n$	58,000
K-90		1,300,000

Additional grades are available.

- complexes with common staining agents to whiten teeth
- reduces in vitro teeth staining from cationic antibacterial and stannous compounds
- acts as a tablet binder resulting in tablets with high breaking force and low friability
- modifies solution viscosity
- o forms water-soluble films
- adds lubricity



Plasdone™ S-630 polymer

INCI Name: VP/VA copolymer

Plasdone S-630 polymer is a pharmaceutical-grade 60:40 linear, random copolymer of NVP and vinyl acetate. The addition of vinyl acetate to the vinylpyrrolidone polymer chain reduces hydrophilicity and glass transition temperature (Tg) of the copolymer relative to PVP. As a result, Plasdone S-630 polymer is an excellent adhesive material and a tougher, more flexible film former than PVP.

Denture Cleansers

Plasdone S-630 polymer is a highly effective tablet binder for denture cleanser tablets. Because of their large size and high inorganic content, denture cleanser tablets need a highly adhesive tablet binder to increase tablet breaking force and reduce friability. In addition, the binder should be water soluble so that the consumer experiences, a clear, haze-free solution, upon tablet dissolution. Plasdone S-630 polymer delivers the performance required.

Grade	Structure	Approximate Molecular Weight
S-630	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	47,000

Technical grades are also available.

Polyplasdone™ polymers

INCI Name: PVP

Polyplasdone polymers are insoluble, crosslinked homopolymers of NVP that differ by particle size. The nonionic polymer swells on contact with water.

Toothpastes

With the increasing number of active ingredients that are not compatible with water, there is a growing need for thickeners for anhydrous systems. Polyplasdone polymer is an excellent choice for modifying rheology of an anhydrous toothpaste system.

Denture Cleansers

Polyplasdone polymers combine multiple mechanisms to achieve rapid tablet disintegration at low use levels.

Product/ Trade Name	Structure	Typical Average Particle Size (microns)
XL	SOFTER	110–140
XL-10	(CH ₂ -CH) ₁₁	25–40

Key Benefits:

- acts as a tablet binder resulting in tablets with high breaking force and low friability
- forms tough, clear, flexible films with high substantivity to skin

- swells on contact with water and solvents to modify rheology
- thickens anhydrous systems
- o acts as rapid tablet disintegrant

polymers — cellulose ethers

Aqualon™, Blanose™, Bondwell™

sodium carboxymethylcellulose (CMC)

INCI Name: cellulose gum

Aqualon, Blanose and Bondwell CMC are anionic, water-soluble cellulose ethers, produced by reacting alkali cellulose with monochloroacetic acid under controlled conditions. A variety of grades with different degrees of substitution(DS), viscosities and particle sizes to meet specific formulation requirements are available. Based on the local regulatory requirements of the final product formulation, grades that comply to food and pharmaceutical requirements are offered. Ashland provides CMC under the tradenames Aqualon CMC, Blanose CMC and Bondwell CMC depending on site of manufacture.

Toothpastes

CMC is used to modify rheology, bind water for the prevention of syneresis and impart desirable flow properties to the formulation. CMC provides excellent rheology properties such as shear thinning for ease of filling tubes and dispensing onto brush as well as excellent stand up, clean ribbon cut-off and smooth non-stringy appearance.

Selecting the CMC grade for your formulation will depend on the desired properties of the toothpaste formulation. Many grades are available. In general, Aqualon or Blanose 9M31F or 9M31XF CMC are good starting points. The Ashland team can help you select the optimum CMC grade.

Denture Adhesives

In denture adhesive powders and creams, CMC provides the initial wet tack necessary for holding dentures in place. To get started, Aqualon or Blanose 7H3SXF CMC are suggested.

Aqualon/Blanose CMC Grade	Degree of Substitution	Typical Brookfield Viscosity (mPa.s) at 25°C	Suggested Application
7MF, 7MXF	0.7	400-800 (2%)1	Cream or liquid toothpaste
7H3SXF	0.7	1,000-2,800 (1%)2	Denture adhesives
9M8F, 9M8XF	0.9	400-800 (2%)2	Baking soda, cream or gel toothpaste
9M31F, 9M31XF	0.9	1,500-3,100 (2%)2	All toothpaste types
12M31F, 12M31P, 12M31XP	1.2	800-3,100 (2%)2	Clear, cream, and baking soda toothpaste

Structure is idealized structure of CMC with degree of substitution (DS) of 1.0. Grades designated with "X" have finer particle size. Viscosity in aqueous solution with concentrations noted (). Additional grades are available. The above chart lists common grades.

"Soludle number 2. 30 rom

²Spindle number 3, 30 rpm

- acts as a thickener for aqueous systems
- provides shear-thinning rheology properties
- o inhibits syneresis formation
- provides initial wet tack to denture adhesive



Bondwell™ CMC Grade	Degree of Substitution	Typical Brookfield Viscosity (mPa.s) at 25°C	Suggested Application
TH10A	≥1.0	200-600 (1%)1	All toothpaste types
TH9A	0.90-1.05	200-600 (1%)1	All toothpaste types
9M	0.85-1.0	1500-3000 (2%)1	All toothpaste types
9H4F U	≥0.85	2500-4500 (1%)2	All toothpaste types
8M23F	0.75-0.90	2000-3000 (1%) ³	All toothpaste types

The chart lists common grades. Viscosity in aqueous solution with concentration noted in $(\tt).$

Klucel™ HPC

INCI Name: hydroxypropylcellulose

Klucel HPC is a nonionic water-soluble cellulose ether with a remarkable combination of properties. It combines organic solvent solubility, thermoplasticity, and surface activity with the aqueous thickening and stabilizing properties characteristic of other water-soluble cellulose polymers. HPC films are flexible without plasticizers and non-tacky at high humidity.

Key Benefits:

- thickens anhydrous systems (all grades thicken propylene glycol and ethanol; low molecular weight L and E grades thicken polyethylene glycol)
- binds tablets

Grade	Structure	Typical Brookfield Viscosity (mPa.s) at 25°C	Approximate Weight Average Molecular Weight
Н	он он	1,500–3,000 (1%)¹	1,150,000
М	OCH2CHCH3 OH OCH2CHCH3 OH CH2 OCH2CHCH3 CH2 OCH2CHCH3	4,000-6,500 (2%)2	850,000
G		150-400 (2%) ³	370,000
J	CONTRACTOR OF THE CONTRACTOR O	150-400 (5%) ³	140,000
L	осн ₂ снсн ₃ сн ₂ осн ₂ снсн ₃ сн ₂ /п	75–150 (5%)4	95,000
Е	Öн осн₂снсн₃ он осн₂снсн₃ Осн₂снсн₃ он Он	300–600 (10%) ^s	80,000

Small and regular particle size grades availability. Viscosity in aqueous solutions with concentration noted (). Additional grades are available. The above chart lists common grades.

¹Spindle number 2, 30 rpm

²Spindle number 3, 30 rpm

³Spindle number 5, 50 rpm

¹Spindle number 3, 30 rpm

²Spindle number 4, 60 rpm

³Spindle number 2, 60 rpm

⁴Spindle number 1, 30 rpm ⁵Spindle number 2, 30 rpm

Natrosol™ HEC

INCI Name: hydroxyethylcellulose

Natrosol 250 HEC, a nonionic, water-soluble polymer, is derivatized from cellulose. Dispersible in polyols and completely soluble in water, Natrosol HEC is available in a wide variety of molecular weights.

Toothpastes

Natrosol HEC is used as an effective rheology modifier and syneresis control agent where high di- and tri-valent salt tolerance is required. In addition, Natrosol HEC is stable with quaternary salts and other cationic actives such as Olaflur. In general, Natrosol 250 M PHARM HEC and Natrosol 250 H PHARM HEC are good starting points.

Key Benefits:

- offers excellent tolerance to mono-, di-, and tri-valent cations
- o provides rheology properties such as shear-thinning for ease of filling tubes during manufacture and ease of dispensing onto brush
- o imparts glossy, smooth ribbon appearance
- o inhibits syneresis formation
- o is nonionic resulting in compatibility with wide range of actives

Grade	Structure	Typical Brookfield Viscosity (mPa.s) at 25°C	Approximate Molecular Weight
нн, ннх	T T	3,500-5,500 (1%)1	1.3 x 10 ⁶
H, HX	H ₂ C OH CH ₂ OH	1,500–2500 (1%)²	1.0 x 10 ⁶
М	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4,500-6,500 (2%)3	7.2 x 10⁵
G	H_2C H_2C H_2C H_2C H_2C H_2C	150–400 (2%)4	3.0 x 10⁵
L	HOCH HOCH	75–150 (5%) ^s	9.0 x 10 ⁴

The structure shown above is idealized chemical structure of Natrosol HEC with 2.5 degree of molar substitution (MS). Natrosol HEC grades designated with "PHARM" are compliant with the monograph requirements of the USP, EP and JPE.

 $X = Smaller\ particle\ size\ grades.$ Viscosity in aqueous solutions with concentration noted in ().0

Spindle number 4, 30 rpm

²Spindle number 3, 30 rpm

³Spindle number 4, 60 rpm

⁴Spindle number 2, 60 rpm ⁵Spindle number 1, 30 rpm







polymer complexes

Peroxydone™ complexes

INCI Name: PVP [and] hydrogen peroxide

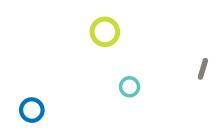
Peroxydone complexes are a family of stable, hydrogen-bonded complexes on vinyl pyrrolidone-based polymers with hydrogen peroxide. Peroxydone complexes are very stable, solid complexes that release hydrogen peroxide on contact with water or saliva in the mouth to provide oxidative teeth whitening. As Peroxydone complexes retain the properties of the base polymer, these unique complexes offer a range of solubility, substantivity, viscosity and filmforming benefits.

Teeth Whiteners

Consumers want whiter and brighter teeth, but not all stains can be brushed away. Bleaching products that penetrate into and oxidatively whiten teeth provide effective results and, therefore, are popular with consumers. Peroxydone complexes are the logical choice for delivery of hydrogen peroxide to teeth. They provide excellent substantivity, bioadhesion, filmforming and thickening with excellent formulation stability without odor or taste, unlike other solid forms of hydrogen peroxide. Peroxydone complexes can be formulated into a wide variety of product forms, including liquids, gels, tablets, strips and films.

Grade	Base Polymer	Structure
K-30	D. /D	H-0,
K-90	PVP	
XL-10	Crosslinked PVP	

- releases hydrogen peroxide for oxidative whitening
- are supplied as very stable powders
- act as excellent film formers, tablet binders or disintegrants
- provides a range of solubilities, substantivity and viscosities











encapsulation technology

Captivates™ HC encapsulates

Captivates HC encapsulates series are small particles that contain an active ingredient, or core material, surrounded by a shell and are produced using a complex coacervation process. During brushing when pressure is applied, the capsules break to release the core material. Capsule wall thickness, color, capsule size and core material can be customized to meet the desired properties of the applications.

Toothpastes and Mouthwashes

Captivates HC encapsulates enable the opportunity to create unique sensory experiences that appeal to consumers. Visible capsules have a minimum diameter of 500 microns to provide striking visual impact while delivering core materials. Encapsulates are non-identifiable to the naked eye in the 15 to 50 micron range. HC encapsulates are custom formulated; however, several standard starting point grades are available. The typical use level is 0.5-2.0%.

Grade	Function	Appearance
HC0004	Provides peppermint flavor burst	Silver capsule
HC56051	Releases a cooling flavor with hints of gentle warming	Blue capsule
HC5773	Delivers malodor suppression flavor	White capsule
HC5774 ²	Releases refreshing citrus flavor	Yellow capsule
HC5884 ³	Adds a refreshing green tea flavor	Orange capsule

All prototype capsules have typical average diameter of approximately $900~\mathrm{microns}$

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Captivates™ GL encapsulates

Captivates GL encapsulates series are small particles that contain materials dispersed in a continuous hydrogel matrix. The GL encapsulate are made using JetCutter™ technology, which forms a hydrogel matrix that can entrap insoluble powders, oils and water-soluble actives. The process produces a uniform bead matrix, ranging from 250 to 3,000 microns, with high levels of encapsulated materials. Naturally derived materials such as chitosan, alginates and carrageenan can be used as the matrix material. Delivery triggers vary from dilution to pressure and temperature.

Toothpastes

Captivates GL encapsulates enable the use of color in new and unexpected ways in toothpaste. These encapsulates can be designed to slowly soften and release color during brushing providing a gradual color-changing signal.

Key Benefits:

- o adds exciting visual effect
- delivers flavor
- provides texture and sensory signals
- isolates and protects ingredients

- adds exciting visual effect
- delivers color for signals during brushing



¹HC5605 contains Blue 15. Not approved in oral applications in USA, Canada, Japan, Korea and Taiwan

 $^{^2\}mathrm{HC}5774$ encapsulate is not approved for use in oral care applications in Japan and Turkey

³HC5884 is not available in Korea and Philippines

hydrogels

Lubrajel* BA hydrogel

Lubrajel BA hydrogel is a clathrate of glyceryl acrylate and glyceryl polyacrylate that encloses water molecules via hydrogen bonding and Van der Waals forces. As supplied, this unique hydrogel contains about 50% water.

Mouth Moisturizers and Mouthwashes

As it binds moisture, Lubrajel BA hydrogel helps provide relief from the feeling of a dry mouth. It imparts a combination of high mucoadhesion, hydration, and non-Newtonian rheological properties to mouth rinses, gels and sprays.

Grade	Chemical Description	Theoretical Structure
ВА	Water, Glycerin, Butylene Glycol, Sodium Polyacrylate, Polyacrylic Acid, Benzoic Acid, EDTA	Carboxyvinyl backbone

^{*}Lubrajel is a trademark of United-Guardian, Inc.

Key Benefits:

- provides hydration
- adds shear thinning characteristics, just like natural saliva
- enhances mucoadhesion to help hold moisture in the mouth
- provides cohesive rheological properties
- supplies lubricity for pleasant saliva-like mouth feel

other

Allantoin

INCI Name: allantoin

Allantoin, a white odorless crystalline powder, has been widely used in various dental preparations, such as toothpastes and mouthwashes. Allantoin is a skin protectant agent with both soothing and moisturizing properties.

Grade	Chemical Description	Structure
Allantoin USP	glyoxyldiureide	$H \longrightarrow N \longrightarrow H$ $NH \longrightarrow C \longrightarrow NH_2$ 0

- o promotes a healthy environment
- provides emollient properties
- protects mucous membranes

committed to healthier, beautiful smiles

At Ashland, we are committed to making your oral care formulations delight consumers. We go beyond an innovative ingredient portfolio to provide local technical and sales support.

Ask us how we can help you achieve your formulation objectives.



