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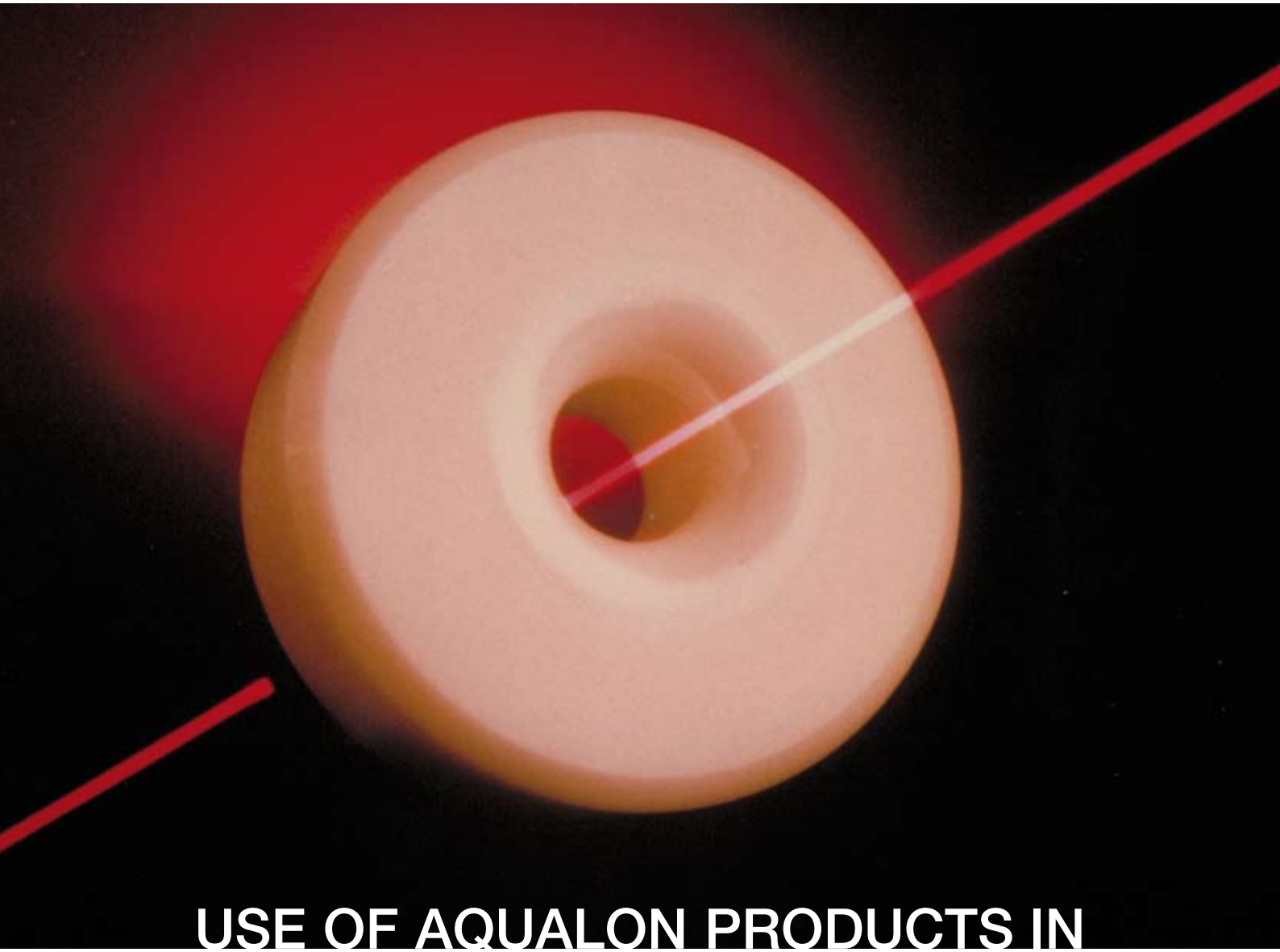

USE OF AQUALON PRODUCTS IN ADVANCED CERAMICS

Aqualon, a Business Unit of Hercules Incorporated

Aqualon

Cellulose and its derivates
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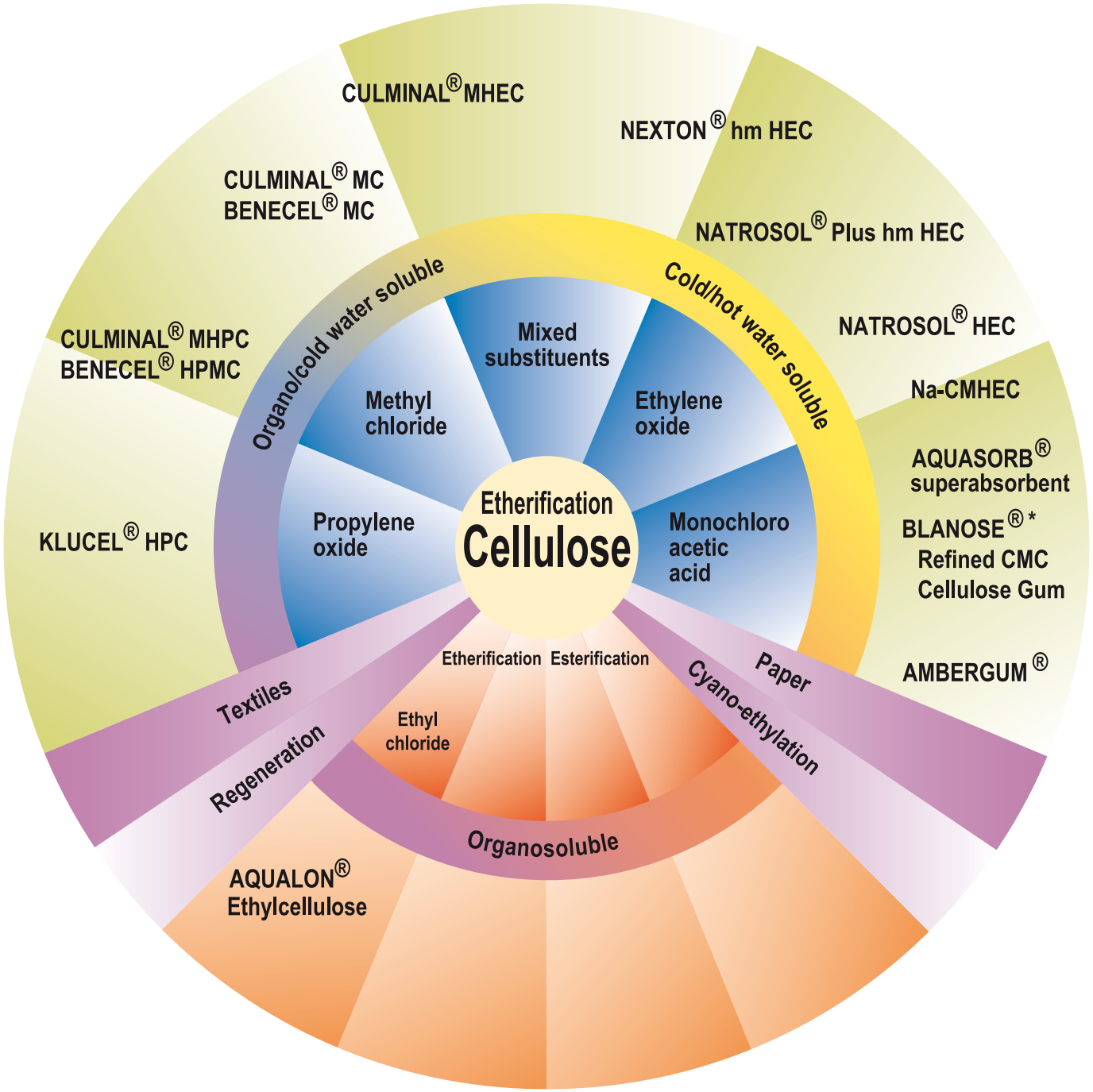


Contents

Introduction

Ceramic masses of nonplastic raw materials can only be given the plasticity required for shaping by the addition of organic binders. Binders improve the workability of the material and increase its mechanical strength.

Organic additives are of course also used in glazes and engobes to prevent sedimentation of solids and to achieve the required rheological properties. Binders improve the adhesion of the glaze or engobe and thus counteract any imperfections.

The organic binders discussed here are temporary additives, which, on firing, burn off before sintering starts. These additives improve workability without affecting the physical properties of the final ceramic product.

Traditional Ceramics

- Traditional ceramics are generally made from natural deposits of minerals and clays.
- The end products are sold for aesthetic or commercial value.

Advanced Ceramics

- Advanced ceramics are generally made from costly, highly refined raw material powders.
- The end products are priced according to performance and quality value.
- Advanced “fine“ ceramics are made to exhibit unique, functional characteristics.

Product range

AQUALON offers the following product ranges:

BLANOSE®	carboxymethylcellulose (CMC)
CULMINAL®	methylcellulose (MC)
	methylhydroxyethylcellulose (MHEC)
	methylhydroxypropylcellulose (MHPC)
NATROSOL®	hydroxyethylcellulose (HEC)
KLUCEL®	hydroxypropylcellulose (HPC)

These products are also available with extremely low salt content and in several grain sizes and viscosities. The properties of these water-soluble polymers and their functions in the usual ceramic forming process are tested in our modern technology and research centres.

Aqualon products are used in the following:

- injection molding
- tape casting
- spray drying / pelletisation
- slip casting
- plastification / extrusion
- rheology (glazes)

Cellulose ethers are binders designed to improve water retention. This property offers the following advantages:

in shaping

- ensures plasticity of non-plastic materials
- improves lubrication and slipping properties
- reduces equipment wear and tear
- improves firmness of the wet mass after extrusion (wet green strength)
- improves mechanical strength after drying (green strength).

in drying

- ensures uniform, controlled drying
- prevents thermogelling cellulose ethers from migrating to the surface during drying
- prevents formation of cracks and blisters.

Effect of binders on green strength

Green strength is achieved by adsorption of the binding agents on the ceramic particles. Green strength is affected by the following factors:

- concentration of the binding agent
- chemistry of binding agent used
- distribution of the binding agent
- wettability of the ceramic solids surface
- adhesion of the binder after drying
- cohesion in the material
- compactability of the powder
- water-absorbent properties of the binding agent.

These factors are in turn dependent on the type of forming process (e.g. extrusion, slip casting, injection molding, tape casting, spray drying / pelletisation).

An appropriate binding agent is chosen primarily on the basis of the following criteria:

- mixability
- concentration
- flocculation
- lubrication
- drying time and water retention
- virtually complete burnout
- good solubility
- low fibre content
- low salt content
- homogeneity of binder quality
- adhesion and strength
- efficiency.

Thermal gelation

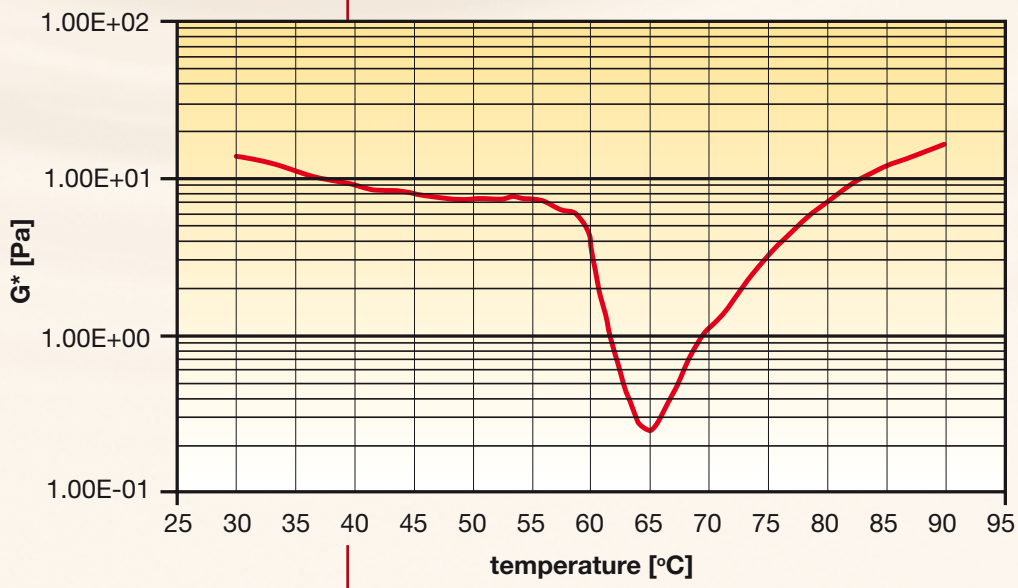
Thermal gelation is a term used to describe the rapid increase in viscosity caused by a rise in temperature. The process is reversible during cooling.

Thermal gelation is particularly pronounced with MC, but also occurs with MHEC and MHPC products.
The gel strength and gel point are dependent on the various parameters listed below.

Properties of cellulose ethers

	gel strength	water retention	wet bonding strength	gel point/ temp
↑ molecular weight	↑	↑	↑	↓
↑ degree of substitution	↑	-	-	↓
↑ PO substitution	↓	↑	↑	→
↑ EO substitution	↓	↑	↑	↑
↑ concentration	↑	↑	↑	↓

Gel curve of a CULMINAL® MHPC



Binder migration

In ceramic processing, it is important that the binder remains homogeneously distributed within the body until sintering. As the green body dries, the migration of water to the surface creates a capillary effect which will carry a binder with weak gelation to the ceramic surface.
This migration can cause voids or blistering of ceramic surfaces on burnout, substantially reducing ceramic strength.

Binder migration can be reduced by the following procedures:

- use high viscosity cellulose ethers
- use less liquid and reduce the interconnective water channels
- use thermally gelling binders
- use finer particle sizes.

Aqualon cellulose ethers are very effective in preventing migration.

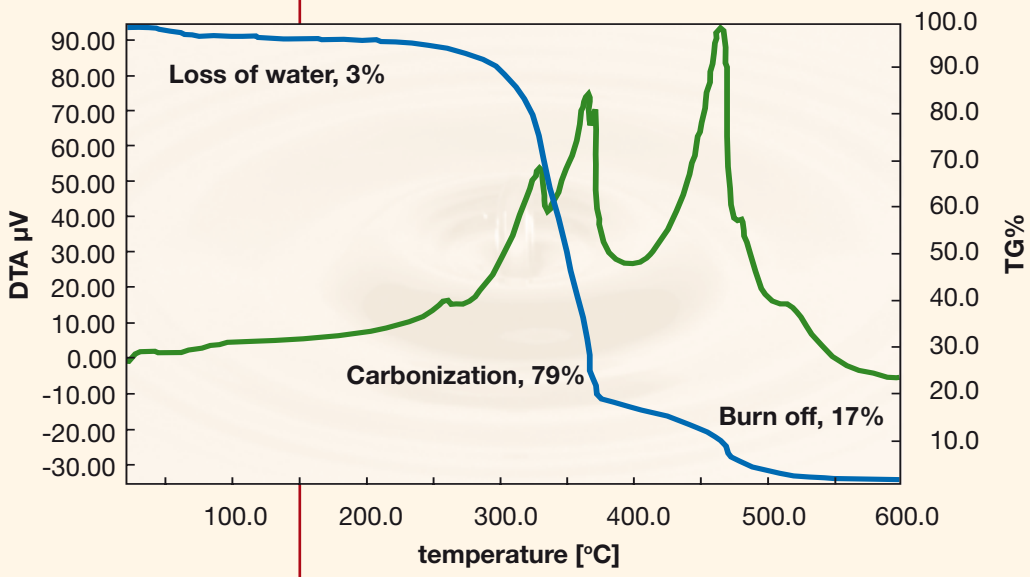
CULMINAL® gels thermally, forming a molecular network within the ceramic body.
NATROSOL® and KLUCEL® create high, localised viscosity around the ceramic particles, preventing migration of the binder.

Reduced binder migration results in a slower, controlled dryout of the wet body.

Burnout properties

Because of their organic nature, nonionic cellulose ethers will burn out virtually completely. In an oxygen atmosphere complete burnout occurs below 600°C. Under the same conditions in an inert atmosphere, between 80 and 90% of the binder will burn out. Longer heating times at higher temperatures are necessary to ensure complete combustion.

Burnout behaviour of CULMINAL® MHPC



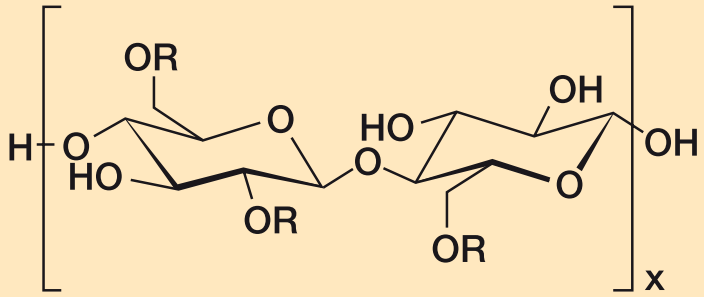
Product information

Cellulose ethers
Cellulose is a polysaccharide composed of anhydroglucose units, which are linked through beta-glycosidic bonds. Industrial cellulose ethers are alkyl, alkylhydroxyalkyl, hydroxyalkyl, and carboxyalkyl ethers derived from cellulose. Ethers are formed by substituting some of the hydroxyl groups. The use of one etherification agent in the substitution process results in a simple cellulose ether, whereas using different kinds of agents leads to mixed ethers.

Cellulose ethers are divided into ionic and nonionic types. The ionic cellulose ethers, e.g. BLANOSE sodium carboxymethylcellulose, contain substituents which are electrically charged. Nonionic cellulose ethers like CULMINAL methylcellulose and NATROSOL hydroxyethylcellulose carry electrically neutral substituents. Mixed ethers with ionic and nonionic substituents are classified according to their predominant features.

The number of substituted hydroxyl groups per anhydroglucose unit is expressed as DS or degree of substitution. The DS can vary between 0 and 3. As with all polymer reactions, this reaction does occur uniformly along the polymer chain.
The degree of substitution is therefore determined as mean over the whole polymer chain and expressed as average degree of substitution.

Constitution of cellulose ethers (example: DS = 1.5)



CE-type R

MC	methyl ($-CH_3$)
MHEC	methyl ($-CH_3$) + hydroxyethyl ($-CH_2-CH_2-OH$)
MHPC	methyl ($-CH_3$) + hydroxypropyl ($-CH_2-CH(OH)-CH_3$)
HPC	hydroxypropyl ($-CH_2-CH(OH)-CH_3$)
HEC	hydroxyethyl ($-CH_2-CH_2-OH$)
CMC	carboxymethyl ($-CH_2-COO-Na^+$)

	CULMINAL®			KLUCEL®	NATROSOL®	BLANOSE®
	MC	**MHEC**	**MHPC**	**HPC**	**HEC**	**CMC**
Gel temp. °C	40 - 70	60 - 90	50 - 90	NA	NA	NA
Flocculation point, temp. °C	50 - 70	70 - 90	60 - 90	45	NA	NA
Decomposition temp. °C	220 - 270	220 - 270	220 - 270	220 - 270	220 - 270	220 - 270
Typical ash content, wt-%	0,1 - 1	0,5 - 1	0,5 - 1	0,1 - 1,5	0,1 - 5,5	20 - 30
Cold-water solubility	yes	yes	yes	yes	yes	yes
Organic solubility	no	no	yes	yes	no	no

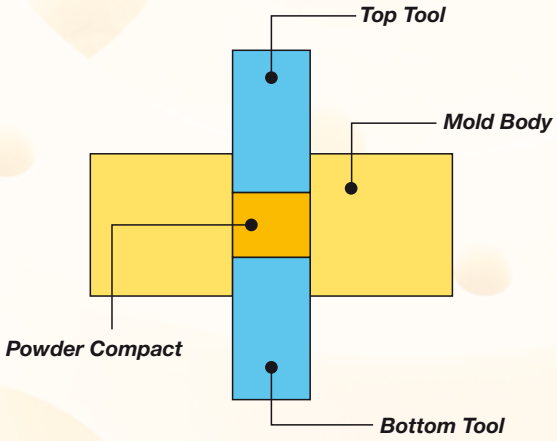
Die/rubber mold pressing

Die pressing can be divided into two different steps:
1. Granulation
2. Pressing

Functionality

1. Granulation.
   Cellulose ethers are used to stabilise the ceramic slip without increasing the viscosity too much.
   The resulting granules will also show increased inner strength.

2. Pressing.
   In the pressing process the binder is used to increase the strength of the pressed ceramic mass.



Recommended *low* viscous
Aqualon products:

CMC:	e.g. BLANOSE® Refined CMC 7 L
HEC:	e.g. NATROSOL® 250 L
MHPC:	e.g. CULMINAL® MHPC 50 and MHPC 100

Addition level: 0,5 - 1 wt-% (related to slip)

Slip casting

The ceramic suspension is poured into a porous mold, which sucks the water from the contact area into the mold.
Finally a hard layer of ceramic material is built up in the mold.

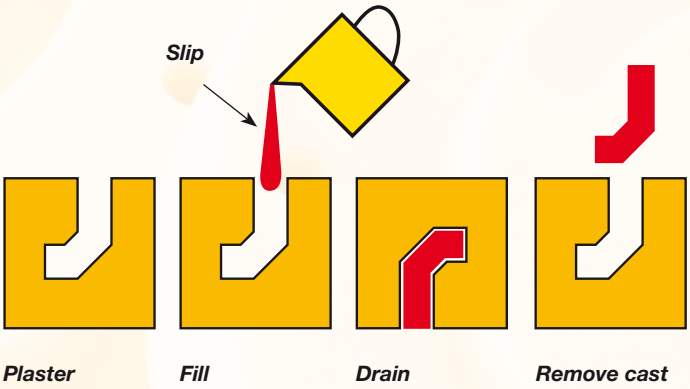
Functionality

The binders are used to stabilise the slip.

Recommended *medium* viscous
Aqualon products

CMC:	e.g. BLANOSE® Refined CMC 7 M
MC:	e.g. CULMINAL® MHPC 500PF
HEC:	e.g. NATROSOL® 250 G or M

Addition level: 0,5 wt-% (related to slip)



Tape casting

Components are mechanically dispersed with liquifiers. The binders are added and the slip is homogenised with ball mills.
After the air is removed by vacuum and the viscosity adjusted, the slip is casted on the belt with a wiper or doctor blade.
The cast layer is air dried and the cast layer is removed from the belt.

Functionality

The cellulose ethers:
- give green strength as well as elasticity to the thin and sensitive ceramic body
- improve drying behaviour
- allows controlled drying of ceramic product

Recommended *low* viscous
Aqualon products:

HEC:	e.g. NATROSOL® 250 L
MHPC:	e.g. CULMINAL® MHPC 100

Addition level: 6 - 7 wt-% (related to slip)

Injection molding

Ceramic powder is mixed with binder at 120-170 °C. Then the mixture is cooled down and granulated. The granulated product is fed into the injection molding device, where the mass is heated in the injection cylinder and subsequently sprayed.

Functionality

- The ceramic material has to be thermoplastic.
- Cellulose ether is used to create a thermo-plastic mass which can be injected in the subsequent molding process.

The thermoplastic binders used in this process must have the following properties:
- reversible thermo behaviour
- thermoplasticy
- wide burn out temperature interval (100 – 400 °C)

Recommended *high* viscous
Aqualon products:

Thermoplastic cellulose ethers	
HPC:	e.g. KLUCEL® H
MHPC:	e.g. CULMINAL® MHPC 20.000 S

Addition level:
5 - 20 wt-% (related to ceramic mass)

Extrusion

Applications in traditional ceramics

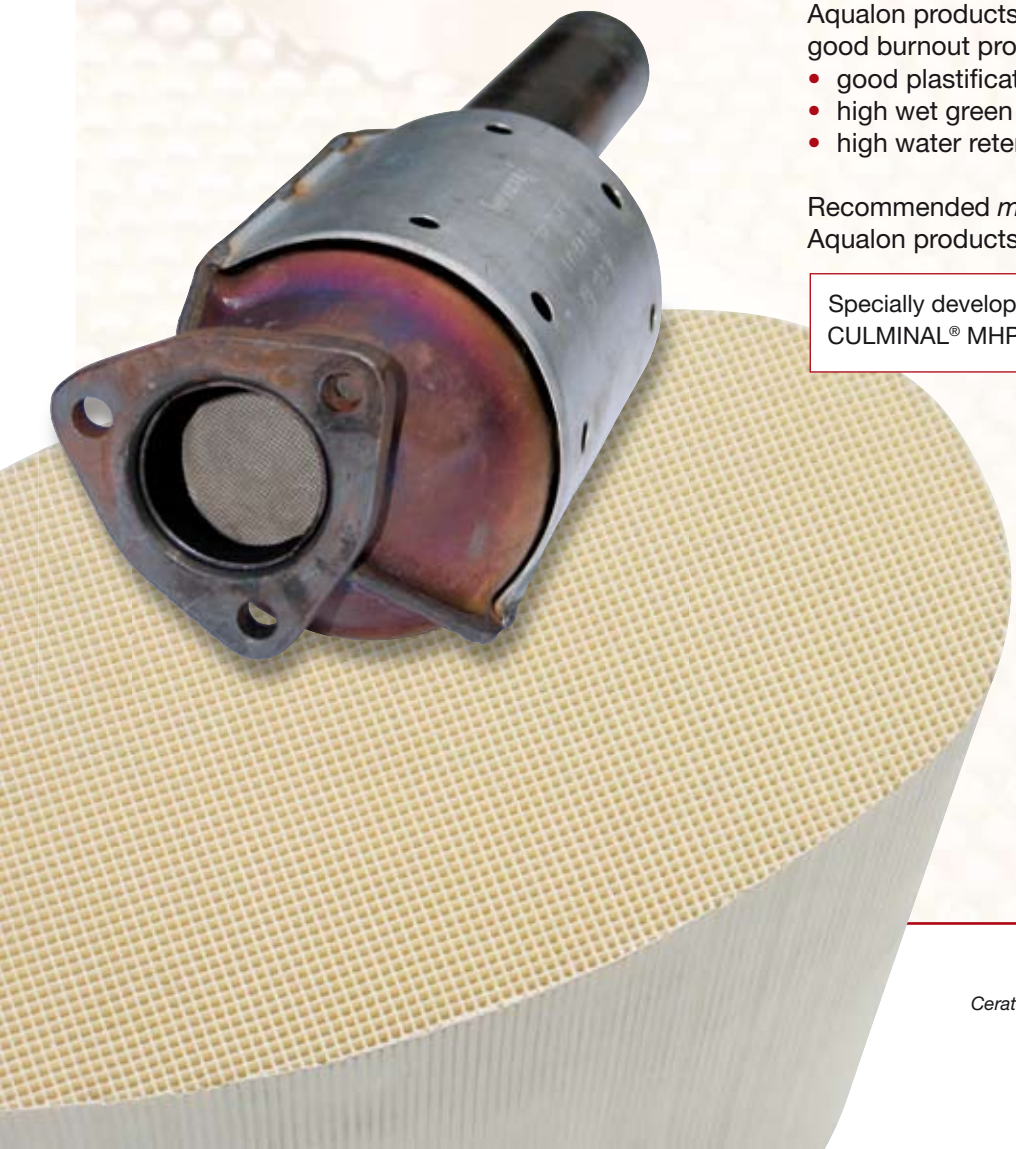
- split tiles
- roof profiles
- pottery

Applications in technical ceramics

- reactor pipes
- honeycombs used for catalytic converters in automobiles
- molten metal filters

The extrusion process can be divided into four steps:

1. Plastification
2. Extrusion
3. Drying
4. Burning / sintering.



Procedure

1. ***Plastification***
   - The dry mixture is mixed with water to obtain a kneadable, plastified material.
   - Due to friction during the mixing process, the temperature of the ceramic mass will increase.
2. ***Extrusion***
   - The kneadable, plastified mass is extruded through a die to shape the ceramic material.
3. ***Drying***
   - Water is removed from the ceramic body.
   - After drying, the extruded ceramic body develops sufficient green strength.
4. ***Burning/sintering***
   - The cellulose ethers are burnt out.

Functionality

Aqualon products in advanced ceramics display good burnout properties and provide:

- good plastification of ceramic material
- high wet green strength / green strength
- high water retention

Recommended *medium* to *high* viscous Aqualon products:

Specially developed CULMINAL® MHPC grades

Pictures of ceramic applications by the courtesy of:
Dynamic-Ceramic Ltd/UK, www.dynacer.com
Ceratec Technical Ceramics BV/The Netherlands, www.ceratec.nl

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