Ashland
always solving

BULLETIN VC-5673

formulating washcoats

with ashland products

background

A washcoat is a liquid formulation acting as carrier for a variety of catalytic materials. The formulation should be stable and keep the components suspended to allow a dispersion of the ingredients over a large surface area.

Aluminum oxide, titanium dioxide, silicon dioxide, or a blend of silica and alumina are used. The catalytic materials are suspended in the washcoat prior to applying to the core. Aiming for an increased surface area, washcoat materials are selected to form a rough, irregular surface, as the substrate area is mainly smooth. There can be several layers or different areas that are coated, always followed by a calcination step (figure 1).

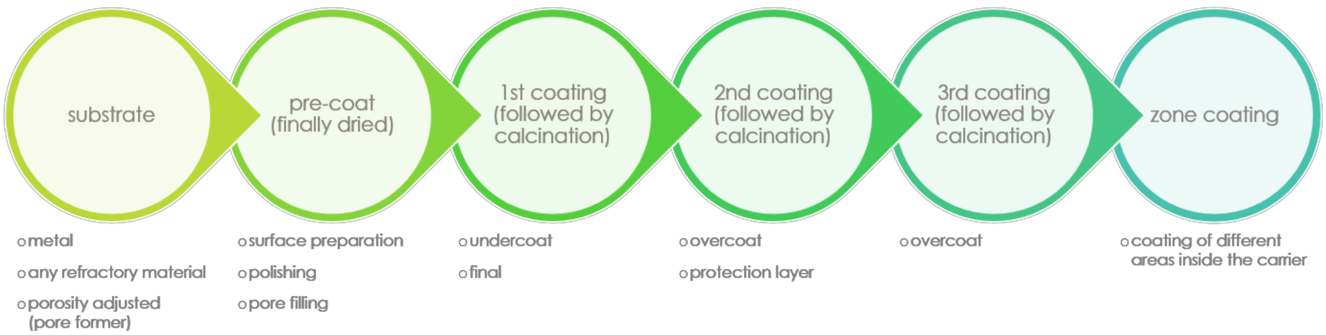

figure 1: schematic of washcoat application possibilities

Of course, it has to be differentiated between the used substrates if it is a flow-through or wall-through application (figure 2), nevertheless always to maximize the catalytically active surface available to react with the engine exhaust. The coat must retain its surface area and prevent sintering of the catalytic metal particles even at high temperatures.

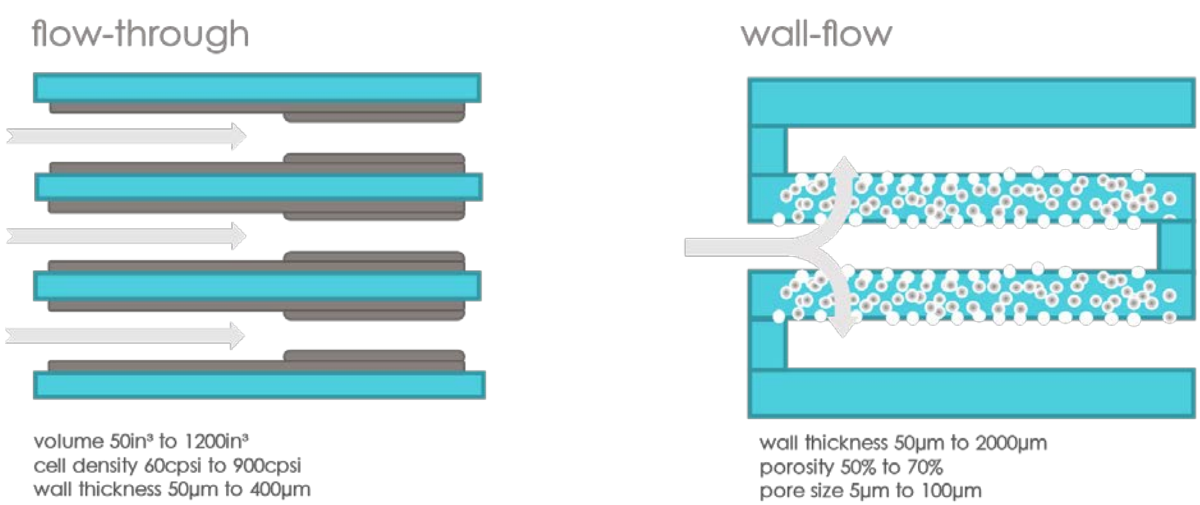

figure 2: difference in the application of the washcoat (flow-through left; wall-through right)

In the periodic table, the platinum group (PMG) offers the most common used metals for catalysis. Platinum is the most active catalyst and is widely used as it can catalyze reduction and oxidation reactions, but it is not suitable for all applications because of unwanted additional reactions and high cost. Palladium and rhodium are common too. Rhodium is used as a reduction catalyst; palladium is used as an oxidation catalyst. There is research and development happening to optimize the reactions and utilize other metals, like cerium, iron, manganese, and nickel. Of course, each formulation needs to be adapted as the use of certain metals need to comply with regional regulations. E.g. Nickel can react with carbon monoxide into toxic nickel tetracarbonyl. An advantage of this manufacturing process is its ability to create consistent complex structures. Materials used can be powdered solids, inorganic, like ceramic oxides, concrete, clay, metal powders or even graphite. Due to the application as a liquid and therefore only compressive and shear stresses are applied the resulting products can have excellent surface appearances.

critical points in the washcoat formulation

- unreactive components => no side reaction with the ingredients
- purity => avoidance of any catalyst poisoning
- fast solubility / quicky viscosity development
- constant rheology profile
- adjustable rheology profile
- avoid sedimentation / good suspension properties
- full burn-out during calcination process

Ashland product offerings

There are many options for Ashland products as different product categories provide different properties in the formulations:

rheology additives
- Blanose™ / Aqualon™ carboxymethyl cellulose CMC
- Natrosol™ hydroxyethyl cellulose HEC
- Admiral™ FPS hydroxyethyl cellulose HEC
- Culminal™ / Benecel™ methyl cellulose derivatives MC / MHEC / MHPC
- Klucel™ hydroxypropyl cellulose derivatives HPC

suspension stabilizer
- Natrosol™ hydroxyethyl cellulose HEC
- Blanose™ / Aqualon™ carboxymethyl cellulose CMC
- Culminal™ / Benecel™ methyl cellulose derivatives MC / MHEC / MHPC

dispersant
- Polyvinylpyrrolidone PVP™
- Blanose™ / Aqualon™ carboxymethyl cellulose CMC
- Dextrol™ / Strodex™ phosphate esters

surfactants / wetting agents
- Dextrol™ / Strodex™ phosphate esters
- Surfadone™ alkyl pyrrolidone's

defoamers
- Drewplus* mineral oil based
- Drewplus* silicon based

coating of active metals
- Klucel™ hydroxypropyl cellulose HPC
- Culminal™ / Benecel™ methyl cellulose derivatives MC / MHEC / MHPC

pH independent gelation
- Culminal™ / Benecel™ methyl cellulose derivatives MC / MHEC / MHPC
- Klucel™ hydroxypropyl cellulose HPC

pore former / porogen
- Blanose™ / Aqualon™ carboxymethyl cellulose CMC
- Aqualon™ ethyl cellulose EC

crystallization optimizers
- Polyvinylpyrrolidone PVP™

lubricants
- Culminal™ / Benecel™ methyl cellulose derivatives MC / MHEC / MHPC

* Trademark owned by a third party

rheology optimization

An important factor is the flow behavior of the washcoat. As it can be more seen as a suspension with up to 40wt% solids, the rheology needs to comply with the different steps of the coating process.

water base (volume)
rheology agent for
- primary and secondary washcoat
- first oxidation layer / second oxidation layer

viscosity requirements
- between 100 mPas and 6000 mPas depending on shear rate and application profile

solid component (wt.%)
- inorganic alumina / silica (precoat)
- metal PGM, Ni, Ce, V, Cu (COX)
- carbon component to be reduced (NOX)

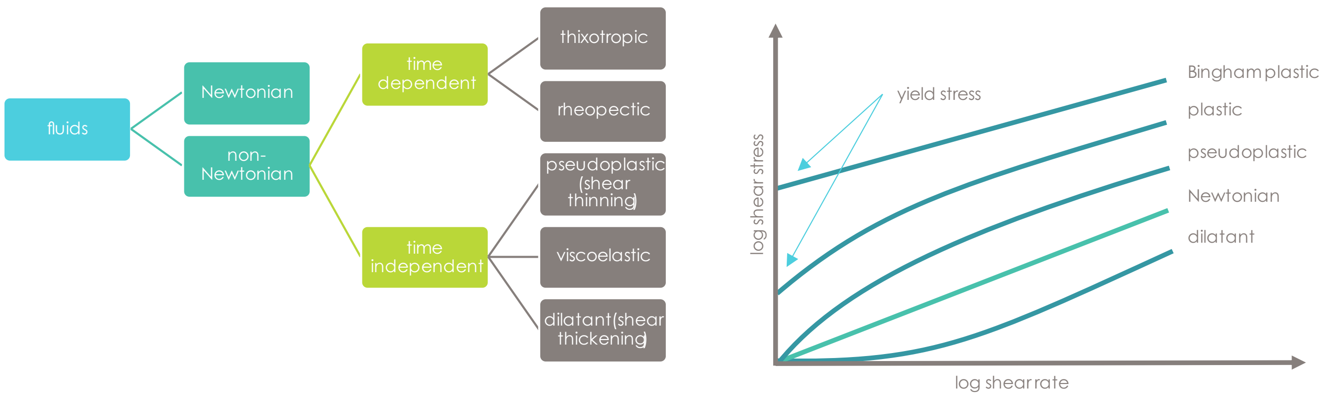

figure 3: rheological differences

The shear rate (γ) - shear stress (τ) relationship of time independent non-Newtonian fluids can be described graphically by a curve of shear stress as a function of shear rate (figure 3).

Some fluids require a threshold shear stress before they start to flow. This kind of fluid is called a plastic fluid. Once the particle network breaks down upon application of a critical yield stress, the polymer shows normal flow behavior.

Typically, low molecular weight grades result in a more Newtonian behavior, while high molecular weight grades offer more a pseudoplastic flow. The content of solids influences of course also the thixotropy and plastic properties.

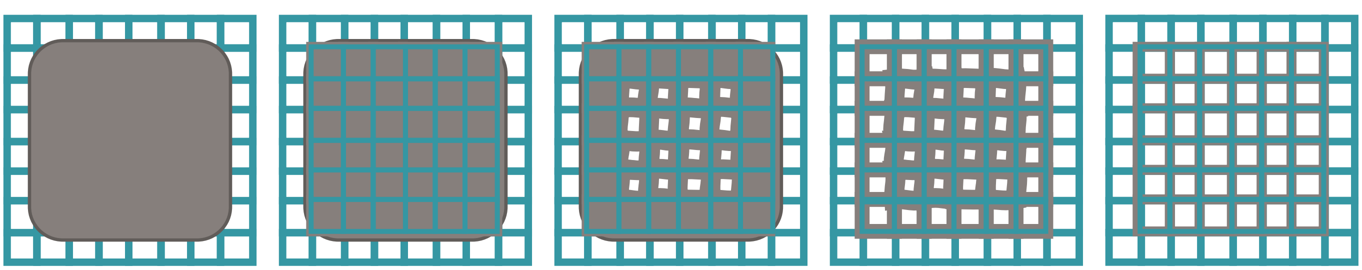

figure 4: washcoat application process on ceramic honeycomb

Typically, the washcoat formulation is either added on top of the substrate, where it rests, or sucked into honeycomb structure. It starts to penetrate the walls of the substrate either by gravity or under pressure or vacuum. A certain resting time is allowed to level the coating. Finally, the excess of washcoat needs to be removed.

recommended rheology modifier

The term cellulose ether describes a large family of derivatized cellulose with various substituents. The abbreviations MC, MHPC, MHEC, HEC, HPC identify the type of cellulose ether, its "chemistry".
The viscosity range is given in millipascal-seconds (mPa·s), measured at 2% concentration (bone-dry) in water according to the product family specification and method.

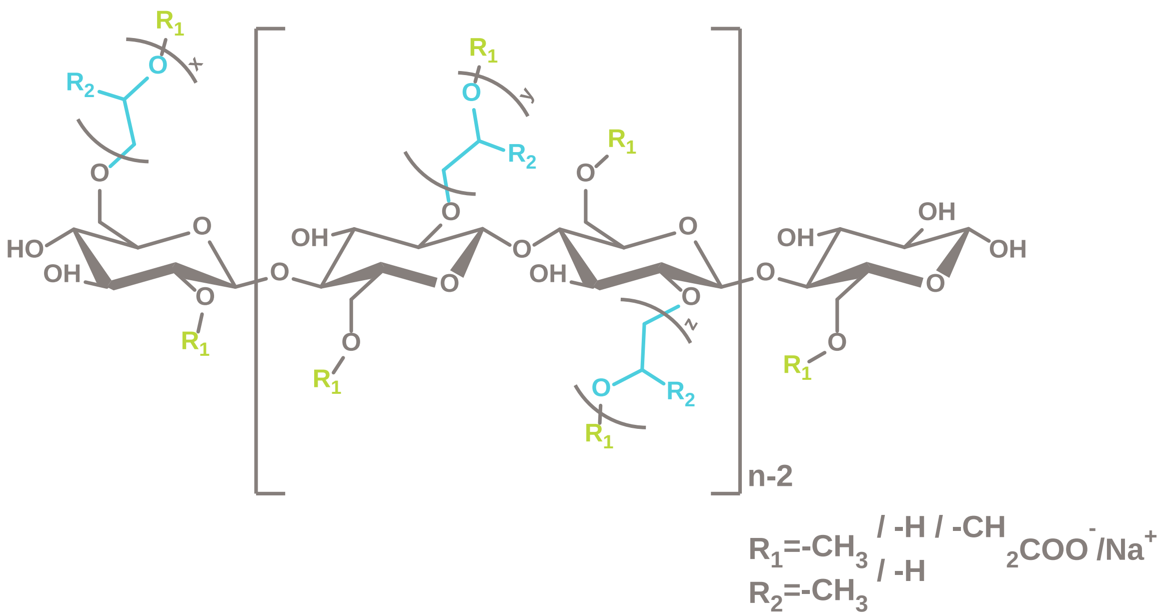

figure 5: chemical structure of cellulose ether derivatives

tradename	R_1	R_2	viscosity range
Blanose™ / Aqualon™ CMC carboxymethyl cellulose	-CH_2COO^-/Na^+	x=y=z=0	10mPas @ 6%-9000mPas @1%
Natrosol™ HEC hydroxyethyl cellulose	-H	-H	100mPas @ 5%-5000mPas @1%
Culminal™ / Benecel™ MC methyl cellulose derivatives	-CH_3	x=y=z=0	400mPas @ 2%-20000mPas @2%
Culminal™ / Benecel™ MHEC methyl cellulose derivatives	-CH_3	-H	2000mPas @ 2%-40000mPas @2%
Culminal™ / Benecel™ MHPC methyl cellulose derivatives	-CH_3	-CH_3	400mPas @ 2%-60000mPas @2%
Klucel™ HPC hydroxypropyl cellulose derivatives	-H	-CH_3	250mPas @ 10%-3500mPas @1%

fluidized polymer suspension solutions

Beside our powdered products, we offer also fluidized polymer suspensions. Using liquids offer a variety of benefits:

- **liquid form:** FPS is a unique liquid designed for easy handling in conventional equipment. Because it is a liquid, problems such as dusting or lumping, sometimes associated with powdered items are eliminated
- **very rapid dissolution:** FPS are designed to disperse, dissolve, and be fully functional in a matter of minutes when diluted in water with minimal agitation
- **aqueous medium:** FPS is water based
- **process / cost saving:** no pre-dilution or pre-activation is required. This significantly reduces preparation time compared with powdered polymers

purity

Remaining components after calcination or burn-out can influence the performance of the catalytic coating. Therefore, we try to eliminate all unwanted components and leave a very low ash content (figure 6).

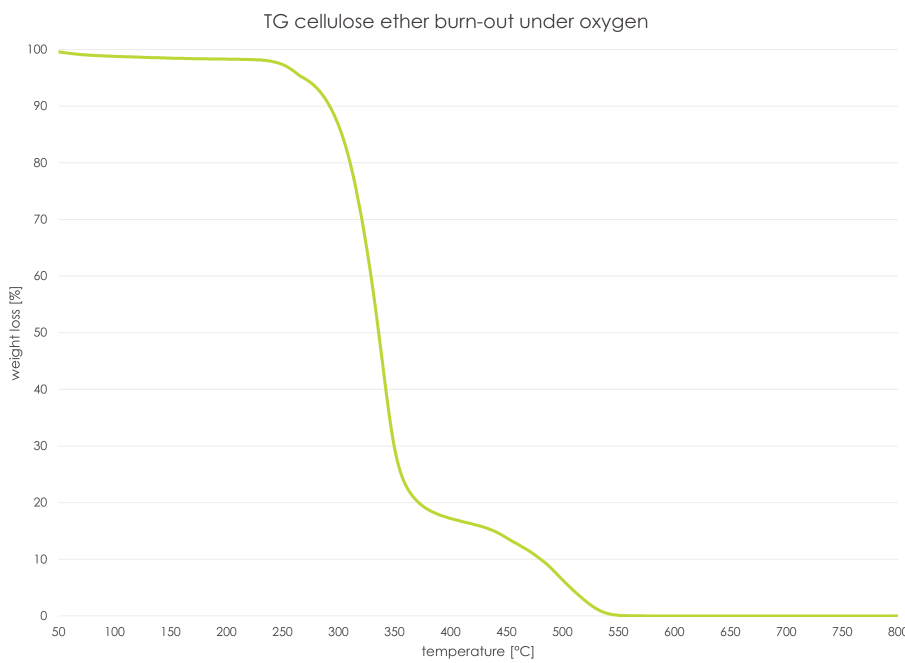

figure 6: thermogravimetric burn-out curve of a cellulose ether under oxygen

typical addition levels

1-5 wt% actives in formulation

dispersants and surfactants

The family of 2-pyrrolidones offered by Ashland have a variety of properties, primarily derived from the unique features of the lactam ring, modified by substitution on the nitrogen atom. The general characteristics of these compounds result from the polar N-C=O linkage in the five-membered ring. The reactivity, physical properties and stability of these molecules lay in the well-documented amide resonance. In anionic media, the partially positive nitrogen readily coordinates with negatively charged species while in acidic systems the electron-rich carbonyl oxygen is rapidly protonated.
The Surfadone™ alkyl pyrrolidones are hydrophobic in nature, functioning as excellent wetting agents and effective dispersing and cleaning aids. These are available in C8 and C12 alkyl chain length.

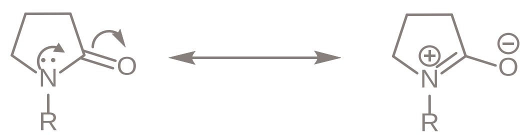

figure 7: Zwitterionic nature of the pyrrolidone ring

Polyvinylpyrrolidone is a hygroscopic, amorphous polymer supplied as a white, free-flowing powder or a clear aqueous solution. Available in several molecular weight grades, they are characterized by K-value, and used as effective suspension stabilizers.

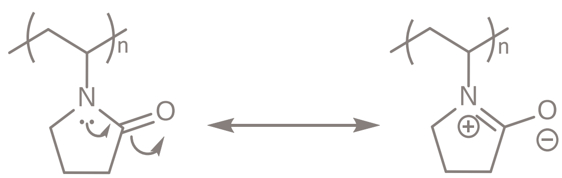

figure 8: utilizing the pyrrolidone ring as effective suspension stabilizer

Dextrol™ and Strodex™ phosphate ester surfactants exhibit superior wetting and emulsifying properties and are unique in that their compositions can be modified to achieve specific properties. Dextrol and Strodex phosphate ester surfactants demonstrate a strong viscosity profile and broad compatibility as well as good stability to a wide range of temperatures, pH and hard water. They are unique mono- and diester phosphates available as free acid or with ammonia, sodium or potassium counter ions. These specialty surfactants provide wetting, improve dispersion and emulsion stabilization, and corrosion protection.

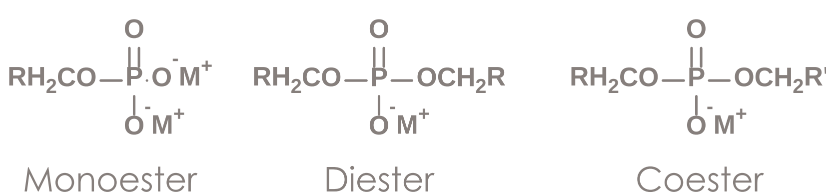

figure 9: general composition

product safety

Read and understand the Safety Data Sheet before using this product.