DOW COATING MATERIALS

ACRYSOL™ Rheology Modifiers

Product solutions guide



Rheology of coatings

Color trends may come and go, but rheology makes a lasting impression on consumer paint preference. How the paint feels when it is stirred, poured and applied to the wall creates a signature experience that helps to define and enhance your brand. Through experienced technical support and a robust line of rheology modifiers, Dow Coating Materials can help you create a rheology profile for your paint line that delivers a high-performance paint experience on and off the wall.

Low-shear

Low-shear conditions are typically experienced by the paint while it is in the can, during brush and roller loading, and immediately after it has been applied to the wall. During these phases, sufficient low-shear viscosity is needed to resist pigment settling, paint spattering and film sag. Brookfield viscosity is a common measure of a paint's low-shear viscosity.

Mid-shear

Mid-shear conditions are created during paint stirring and pouring, and some types of pumping. During these phases, mid-shear viscosity helps to facilitate good in-can appearance and handling properties and may also affect spattering. Stormer or KU viscosity are common measures of mid-shear viscosity. Rheology modifiers that are classified as KU builders generally offer good mid-shear viscosity.

High-shear

High-shear processes include brushing, certain aspects of rolling, and spraying. High-shear viscosity influences brush and roller drag, as well as film build and thus contributes to hiding. High-shear viscosity is also referred to as ICI viscosity. Rheology modifiers that are classified as ICI builders generally offer good high-shear viscosity.

Shear genius

A successful rheology package adapts to changing shear rates while supporting specific formluation goals.



Low
In the can and on the wall

Mid
Brush and roller loading

High
Brush drag, roller slip, and back pressure in spray applications

Key terms

Viscosity [cPs,P] is the resistance of a material to flow. It is defined as shear stress divided by shear rate.

$$n = \frac{\tau(shear\ stress)}{D(shear\ rate)}$$

Shear stress [dyn/cm^2] is the force per unit area used to move a material. It is defined as force divided by area.

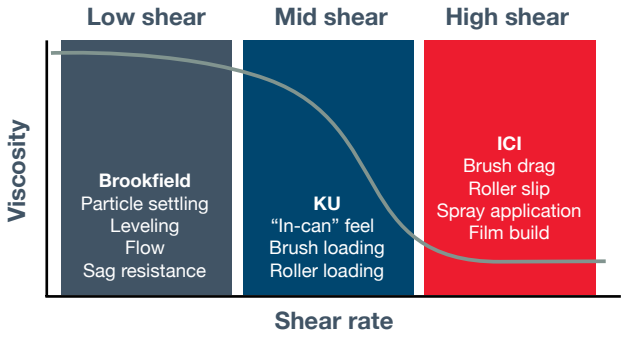
$$\tau = \frac{F(force)}{A(area)}$$

Shear rate [1/sec] is the velocity gradient in a flowing material. It is defined as velocity divided by thickness.

$$D = \frac{V(velocity)}{h(thickness)}$$

Ranges of viscosity (typical waterborne paint)

With every change in shear rate, paint undergoes a change in viscosity. To better understand how a paint behaves at different shear rates, we typically look at three different types of viscosity measurements.



Brookfield viscosity

Measures low-shear flow and is indicative of paint viscosity when it is in the can and after it has been applied to the wall.

KU viscosity

Measures mid-shear flow and is indicative of paint viscosity when it is being loaded onto the brush or roller and as the brush or roller leaves the wall.

ICI viscosity

Measure of high-shear flow and is indicative of paint viscosity when it is being rolled or brushed onto the wall.

All three shear rate regions should be considered when building an optimum rheology profile.

How rheology modifiers thicken

Volume exclusion thickeners (figure 1) employ water-soluble polymers that swell with water and take up space in the paint. Cellulose ethers, such as CELLOSIZE™ Hydroxyethylcellulose (HEC), fall into this category. These types of thickeners create viscosity through chain entanglement and particle flocculation. Their ability to thicken is directly proportional to their molecular weight and concentration in the paint formulation. The greater the molecular weight, the more efficiently they thicken.

Associative thickeners (figure 2) also employ water-soluble polymers, but they do not thicken through water absorption. Instead, these polymers contain hydrophobic groups that interact with one another and with the latex particles in the formulation to create a three-dimensional network. Thickening results because this network restricts the motion of the latex particles.

Key terms

Newtonian describes a viscosity that is constant, regardless of the shear rate. Simple fluids such as water, solvent and oil are examples of Newtonian fluids.

Non-Newtonian describes a complex relationship between shear stress and shear rate that results in viscosity being dependent on shear rate. Paint is a non-Newtonian fluid.

Pseudoplastic describes a non-Newtonian fluid that loses viscosity when shear rate increases, but recovers that viscosity when the shear rate decreases.

Figure 1.

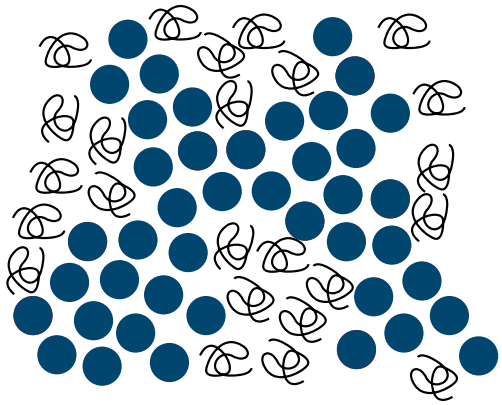
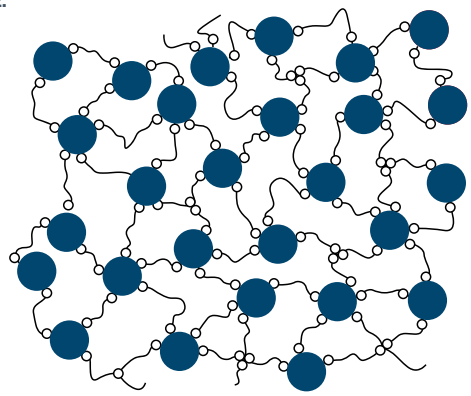


Figure 2.



ASE chemistry overview

Rheology modifiers that thicken by volume exclusion include cellulosic ethers and ASE alkali soluble (or swellable) emulsions. Cellulosic ethers are nonionic, water-soluble polymers derived from natural fibers. They thicken by absorbing water and creating chain entanglement and flocculation. Cellulosic ethers are efficient and shear-thinning, but their dry powder form can be difficult to handle in commercial-scale production.

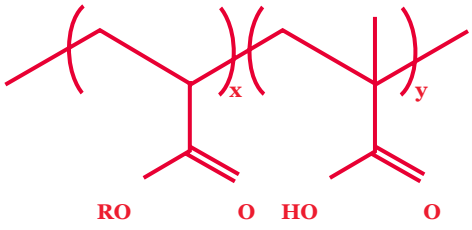


Figure 3. Alkali soluble/swellable emulsions (ASE) contain copolymer chains of methacrylic acid and acrylate ester in a ratio at or near 50:50.

Next-generation ASE thickeners are copolymers of methacrylic acid and ethyl acrylate ester (figure 3). They were developed to mimic the rheology properties of cellulosics, but facilitate an easier-to-use, more cost-effective product. Like cellulosic ethers, ASE products thicken via water absorption and swelling. Different rheological characteristics are achieved by manipulating the molecular weight, as well as the types and amounts of acid and ester monomers.

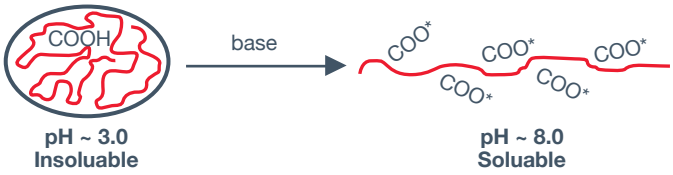


Figure 4. pH-triggered thickeners are insoluble at low pH and soluble at high pH. ASE and HASE rheology modifiers are pH-triggered thickeners.

ASE thickeners rely on a change from low to high pH (neutralization) to trigger thickening. The “trigger” is built into the copolymer by creating an approximately 50:50 ratio of methacrylic acid, which is soluble in water, and an acrylate ester, which is not soluble in water. When the acid is un-neutralized (low pH), the copolymer is insoluble in water and does not thicken. When the acid is fully neutralized (high pH), the copolymer becomes soluble and thickens (figure 2).

ACRYSOL™ ASE Rheology Modifiers are supplied at low pH (< 5) and maintain a low as-supplied viscosity (<100 cP) at solids of up to 35%. This is in stark contrast to cellulosic ethers, which develop a viscosity of several thousand centipoise even at solids as low as 2.5%. When subject to pH 8 or higher in the coating formulation, ASE copolymers solubilize, swell and thicken the formulated coating through volume exclusion. The degree of thickening is related to the molecular weight of the copolymer.

Because their performance depends on water absorption and swelling, ASE thickeners tend to be very high in molecular weight, which allows them to thicken efficiently. The rheology profiles they create are typically steeply shear-thinning (pseudoplastic), so ASEs are well suited to building high viscosity at very low shear rates.

ASE quick summary

ASE thickeners contain a balance of methacrylic acid and acrylate ester. They are supplied at high volume solids in liquid form. Thickening is triggered by a change from low to high pH. ASE thickeners are steeply shearthinning and well suited to high-viscosity, thick-film applications such as caulks, mastics, EIFS finishes, driveway sealers and craft paints.

HASE chemistry overview

HASE stands for hydrophobically-modified alkali soluble emulsion. These are tertiary polymers that build on the ASE chemistry by adding a hydrophobic acrylic ester monomer to the polymer composition.

HASE rheology modifiers retain the pH dependent behavior and easy handling advantages of their ASE counterparts, but in addition to absorbing water, HASE rheology modifiers also thicken via hydrophobe association. This mechanism, known as associative thickening, offers performance properties over a wider range of shear levels and facilitates a wider range of rheology profiles than is possible with volume exclusion thickeners such as ASE and cellulosic offerings.

HASE quick summary

HASE thickeners build viscosity through the association of hydrophobes. They are supplied in easy-to-handle liquid form at high volume solids. HASE offerings are generally lower in molecular weight than ASE offerings. They are better suited than ASE to more water sensitive applications and offer a wider variety of rheology profiles. Collectively, these characteristics make HASE thickeners well suited for flat through gloss paint formulations to facilitate sag resistance, spatter resistance and brush/roller drag.

HEUR chemistry overview

HEUR is an acronym for hydrophobically-modified ethylene oxide-based urethane. This category of rheology modifier was developed after the introduction of ASE and HASE to address limitations in flow, leveling and water sensitivity. HEURs offer a wide range of rheological properties, from Newtonian (very little shear-thinning) to quite pseudoplastic (strongly shear-thinning). Unlike ASE or HASE thickeners, HEURs are non-ionic and soluble at any pH. This solubility is due to the polymer's ethylene oxide backbone (figure 5), which is water soluble and makes up the majority of the polymer structure.

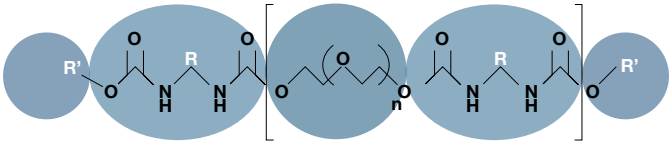


Figure 5. HEUR morphology features repeating polyethylene glycol units at the center and hydrophobic groups on either end. Isocyanate linkers on either side of the polyethylene oxide connect the polymer backbone to hydrophobic end groups.

The HEUR structure imparts viscosity almost exclusively through a three-dimensional associative network. This degree of associative thickening is notably higher than that for HASE polymers and is the reason that HEURS offer exceptional flow and leveling. This typically makes them an excellent choice for high-gloss and semi-gloss formulations. However the range of rheological properties that HEURs can create often make them suited for satin to flat formulations as well.

Because HEURs are soluble in water regardless of pH, it is often necessary to add solvent or surfactant to reduce as-supplied viscosity to manageable levels. ACID SUPPRESSION™ Technology takes the successful idea of pH-triggered thickening from ASE and HASE chemistry and applies it to HEURs, thus facilitating low-VOC formulations without added surfactant. This feature is accomplished via a slight modification of the end group to include a tertiary amine (figure 6.) At low pH, these amines are protonated, become charged, and repel, preventing the hydrophobe association that creates thickening. As a result, the assupplied product viscosity remains very low.

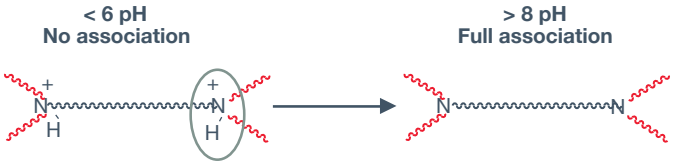


Figure 6. ACID SUPPRESSION Technology employs pH-triggered association and thickening in HEURs.

At the higher pH of a formulation, the amines de-protonate, become neutral, and allow hydrophobe association to occur. Thus, once added to the formulation, they thicken like traditional HEURs. The result is low viscosity (<2000 cP) in the as-supplied product, that can facilitate full thickening efficiency in the paint formulation.

HEUR quick summary

HEURs are low molecular weight associative thickeners comprised of ethylene oxide chains with hydrophobic end groups. They are water soluble across pH levels and offer excellent flow and leveling, high film build, spatter resistance, and brush/roller loading. HEURs are particularly well suited to high-gloss and semi-gloss formulations, as well as applications where water resistance is key. ACID SUPPRESSION™ Technology offers a solvent-free way to provide HEURs at low viscosity.

ACRYSOL™ ASE/HASE Rheology Modifier

ACRYSOL™ HASE Rheology Modifers are anionic alkali-soluble associative thickeners that offer an excellent cost/ performance balance and better flow than HEURs. They are compatible with multiple binder chemistries and are particularly suited to interior paints, where they offer a range of key performance properties, including flow and leveling, sag resistance and film build.

Product selector guide

ACRYSOL™ GRADE	Solids	Low-Shear Brookfield	Mid-Shear KU	High-Shear ICI	Benefits
HASE Rheology Modifier					
TT-615	30%				• Enhance spatter resistance for standard / economy spaces • Excellent sag resistance
TT-935	30%				• Broad utility in standard / economy spaces.
DR-73	30%				• Efficient thickener for PVA/VAE formulations • Could be used as a sole thickener
RM-7	30%				• Efficient ICI Builder for PVA/VAE formulations • Enhance cleansability
DR-6600	30%				• Excellent cleansability • Excellent application properties
DR-5500	30%				• Excellent application properties
ASE Rheology Modifier					
ASE-60	28.0%				• Excellent anti-settling properties • Excellent choice for texture coating

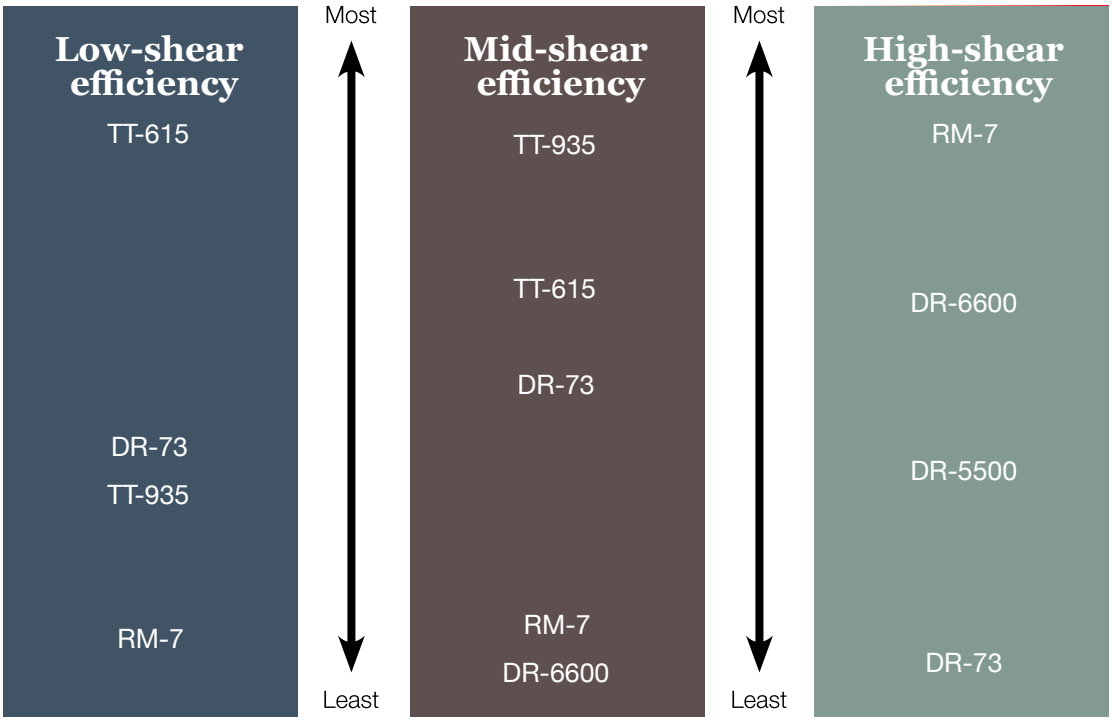
Slight contribution Moderate contribution Strong contribution

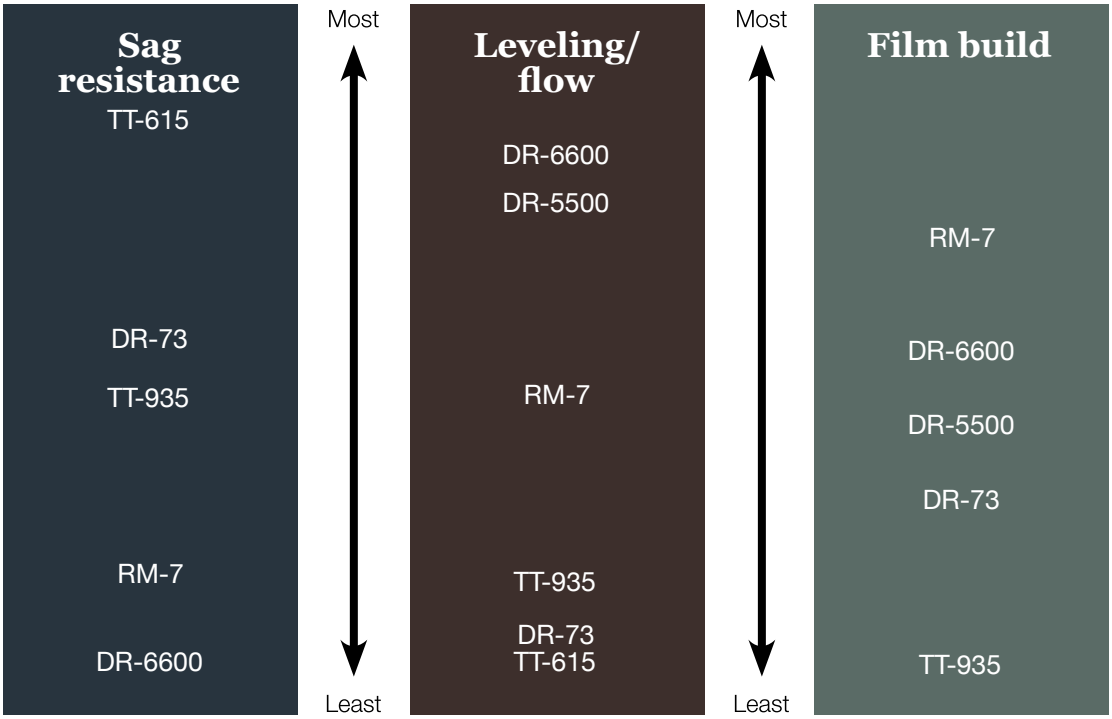
Dispersant recommendations for HASE-thickened formulations

TAMOL™	Salt	Solids	Use level (on pigment)	Benefits
Polyacid dispersants				
945	Na	45%	0.3 - 1.0%	Excellent cost/performance balance. Excellent color acceptance with high reproducibility. Low odor. Low-foam generator.
1254	Na	35%	0.3 - 1.0%	Broad formulating latitude and cost/performance balance. Low-foam. Good color acceptance and stability with active pigments including ZnO.
851	Na	30%	0.6 - 1.0%	High efficiency with low-foam generation. Excellent stability in paints containing ZnO and other reactive pigments.
901	NH_4	30%	0.6 - 1.0%	Low-foam generator. Excellent stability. Ammonia version of TAMOL™ 851 Dispersant.
963	NH_4	35%	0.3 - 1.0%	Low-cost, low-foam generator. Good water resistance.
Hydrophilic copolymer dispersants				
1124	NH_4	50%	0.5 - 1.0%	High-gloss potential. Broad formulating latitude. Cost/performance balance. Low-foam generator.

ACRYSOL™ HASE Rheology Modifiers

Performance comparison





ACRYSOL™ HEUR Rheology Modifier

ACRYSOL™ HEUR Rheology Modifers offer excellent flow and leveling, high film build, stability, spatter resistance and syneresis control in a wide variety of latex binders, including large- and small-particle-size acrylics, vinyl acrylics, styrene acrylics and vinyl acetate ethylene polymers (VAEs).

For all binder systems

ACRYSOL™ GRADE	Solids	Low-Shear Brookfield	Mid-Shear KU	High-Shear ICI	Benefits
RM-12W	19%				• High sag resistance for spray application
RM-995	23.5%				• Great viscosity retention for high colorant systems • Excellent application properties
RM-725	18%				• Excellent balance of sag resistance and leveling • Excellent surface smoothness
RM-735BF	22.9%				• High efficiency with excellent sag resistance and leveling • Enhanced applied hide
SCT-275	17.5%				• Excellent for PVA/VAE formulations • Can be used as a sole thickener. Contains solvent.
RM-8W	21%				• Wide utility KU builder with ease of incorporation • Excellent flow/leveling
RM-825	25%				• High efficiency mid-shear builder. Contains solvent.
RM-845	27%				• High efficiency mid-shear builder.
RM-6000	17.5%				• Highly efficient ICI builder • Great choice for PVA/VAE systems
RM-5000	18.5%				• Lower efficiency than RM-6000
RM-3030	20.5%				• Newtonian ICI builder with broad formulation latitude • Excellent syneresis resistance • Enhance performance with formulation flexibility
RM-3000	20%				• Improved efficiency vs. RM-2020NPR
RM-2020NPR	20%				• Wide utility ICI builder
RM-1600	25%				• Newtonian ICI builder for small particle size, high volume solids, and/or composite systems

Slight contribution Moderate contribution Strong contribution

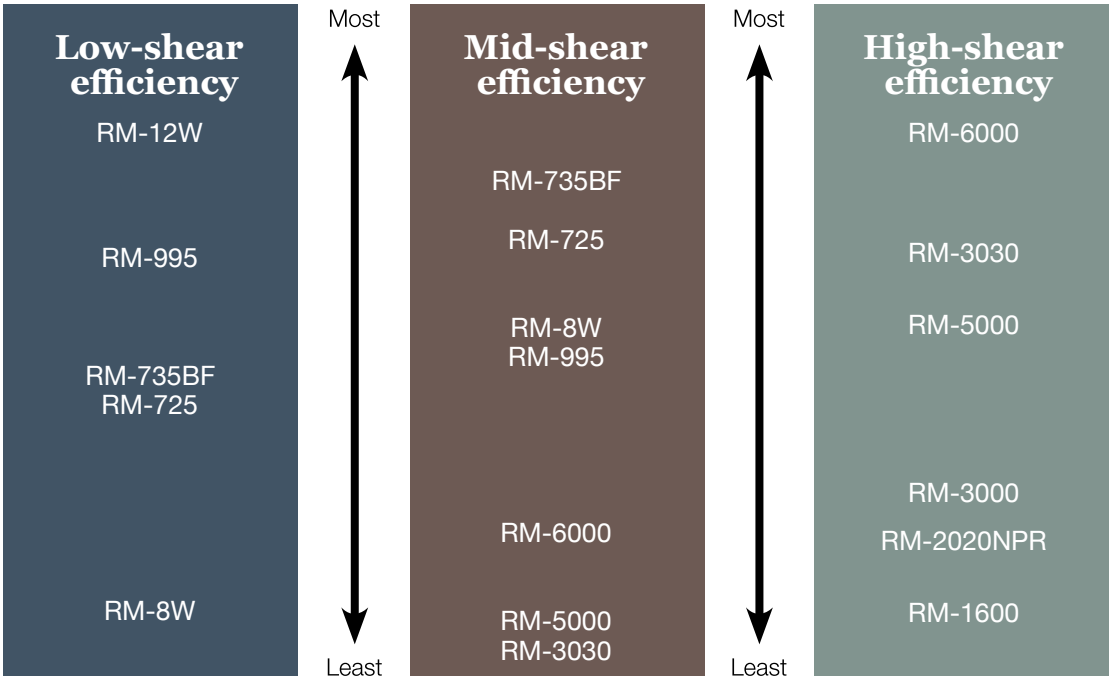
Dispersant recommendations for HEUR-thickened systems

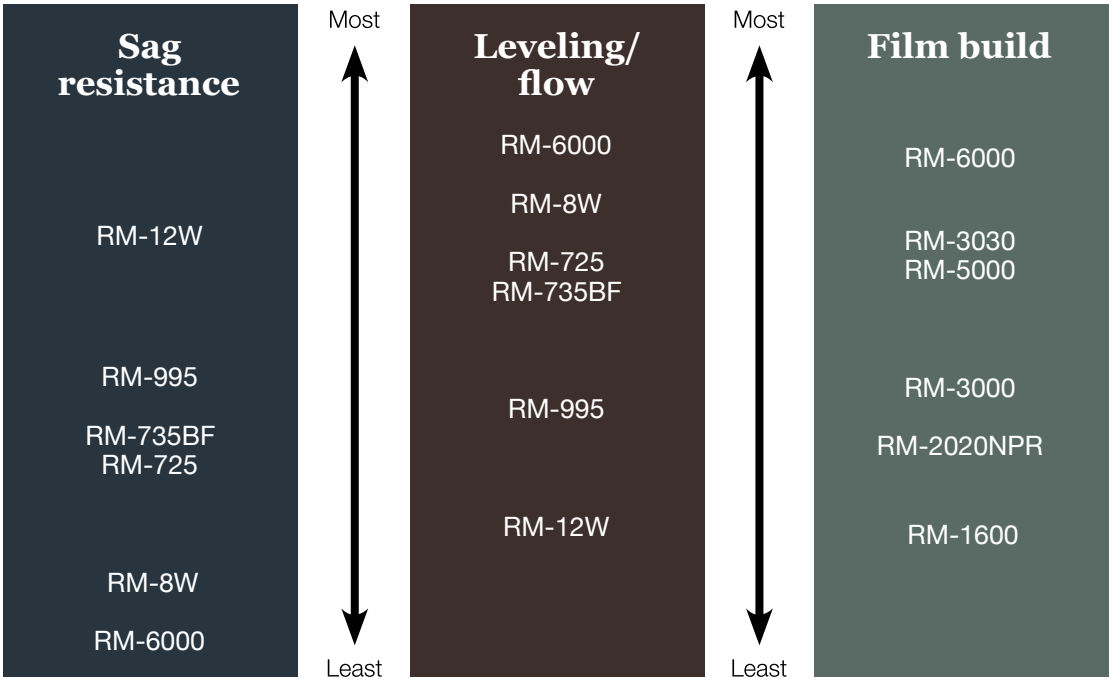
TAMOL™	Salt	Solids	Use level (on pigment)	Benefits
Hydrophobic copolymer dispersants				
165A	NH_4	21%	0.6 - 1.0%	Excellent early blister resistance and wet adhesion. Good color acceptance. Good gloss development and corrosion resistance.
731A	Na	25%	0.7 - 1.0%	Excellent overall compatibility. Good pigment wetting. Highly efficient performance.
681	NH_4	35%	2.0 - 5.0%	Maximizes gloss potential. Good stability in paints containing ZnO and other reactive pigments. Good corrosion resistance.
2011	K	23%	2.0 - 5.0%	Low-odor. Maximizes gloss potential. Good stability with ZnO. Good corrosion resistance.
2002	n/a	27.5%	2.0 - 5.0%	Low pH to allow for neutralizer choice. Low-odor, solvent-free* capability. Maximizes gloss potential. Good stability with ZnO. Good corrosion resistance.
Hydrophilic copolymer dispersants				
1124	NH_4	50%	0.5 - 1.0%	High-gloss potential. Broad formulating latitude. Cost/performance balance. Low-foam generator.
Universal Dispersant				
2028	Specialty	40%	Varies*	Suitable for both organic and inorganic pigment types. Great for waterborne pigment concentrates. Excellent color properties.

* Suggested dosage level (Dispersant solids / Pigment solids): Titanium dioxide (TiO2): 1.5-5%; Inorganic pigment: 1.5-12%; Organic pigment: 8-30%; Carbon black: 16-60 %

ACRYSOL™ HEUR Rheology Modifiers

Performance comparison





Starting point formulations

Choosing the optimum package is a balance among many paint properties beyond KU, including application feel, touch-up, surface smoothness and applied hide. In the table below, there are multiple starting point suggestions. The optimum for a specific situation will be dependent on the desired balance among properties such as those just listed.

Segment	Formulation	Performance properties	ACRYSOL™ KU-builder	ACRYSOL™ ICI-builder
Premium	Acrylic and EVOQUE™ binder Above 38% VS	Optimum flow/sag balance and high film build	RM-8W RM-995	RM-3030
Premium Standard	Acrylic, Sty-acrylic 32%-38% VS	Premium feel, application, touch up, high sag resistance, excellent flow	RM-995 RM-725 RM-735BF	RM-3030
Premium Standard	Acrylic, Sty-acrylic 32%-38% VS	More Newtonian rheology. Excellent flow and film properties. Increase sag with ACRYSOL™ RM-12W if needed	RM-8W	RM-3030 RM-2020 NPR
Standard	Lower VS acrylic and sty-acrylic	Good balance of efficiency and flow/sag	TT-935 RM-725 RM-735BF	DR-6600
Standard	PVA+acrylic blend	Good sag/flow balance with improved house-hold stain resistance vs. all HEUR system; improved MPI properties	RM-725 RM-735BF	DR-6600 RM-7
Standard Economy	VAE/PVA, PVA+acrylic blend	Good efficiency and improved water resistance and flow vs. an all-HASE system	TT-935 DR-73	RM-6000
Economy	VAE/PVA, PVA+acrylic Sty-acrylic	Excellent spray and spray/backroll application; balanced overall application performance with excellent touch up	TT-615	DR-6600 RM-6000

Red - HEUR rheology modifier Blue - HASE rheology modifier

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