

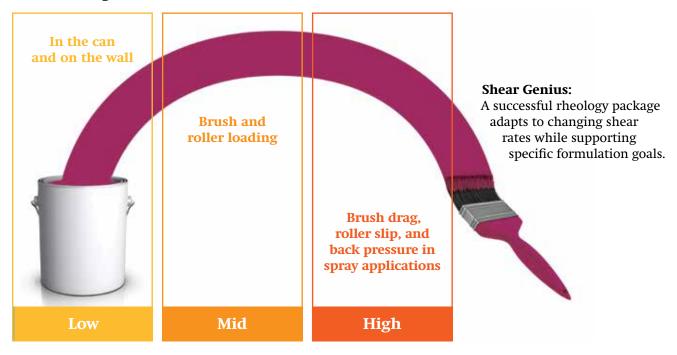
Dow Coating Materials

ACRYSOL[™] Rheology Modifiers

Product Solutions Guide



Shear Rate Regions



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 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 lowshear 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 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 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.

Key Terms

1

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/cm²] is the force per unit area used to move a material. It is defined as force divided by area.

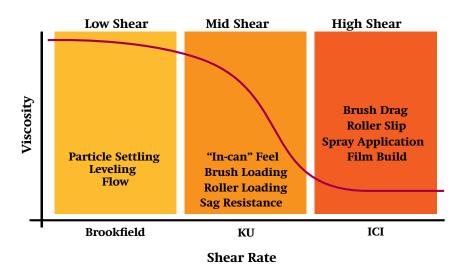
$$\tau = \frac{F(force)}{A(area)}$$

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 lowshear flow and is indicative of paint viscosity when it is in the can and after it has been applied to the wall.
- <u>KU viscosity</u> 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.
- <u>ICI viscosity</u> is a measure of highshear flow and is indicative of paint viscosity when it is being rolled or brushed onto the wall.

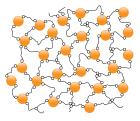
All three shear rate regions should be considered when building an optimum rheology profile.

How Rheology Modifiers Thicken



Volume Exclusion Thickeners 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 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.

<u>Key Terms</u>

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.

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.

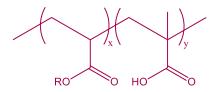


Figure 1. Alkali soluble/swellable emulsions (ASE) contain copolymer chains of methacrylic acid and acrylate ester in a ratio at or near 50:50.

Next-generation ASE thickeners are copolymers of methacrylic acid and ethyl acrylate ester (Figure 1.). 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. 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), and so ASEs are well suited to building high viscosity at very low shear rates.

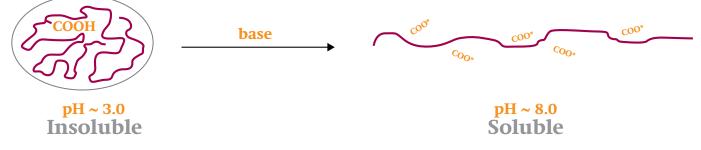


Figure 2. pH-triggered thickeners are insoluble at low pH and soluble at high pH. ASE and HASE rheology modifiers are pH-triggered thickeners.

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 shear-thinning 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.

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 3.), which is water soluble and makes up the majority of the polymer structure.

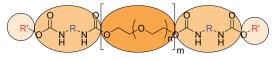


Figure 3. HEUR morphology features repeating polyethylene glycol units at the center and hydrophobic groups on either end. Isocyanate linkers on either side of the polyethylene oxide connect the polymer backbone to hydrophobic end groups.

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.

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.

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 4.). 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.

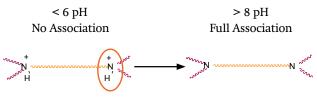


Figure 4. ACID SUPPRESSION Technology employs pH-triggered association and thickening in HEURs.

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[™] HASE Rheology Modifiers

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*	Actives	Brookfield	KU	ICI	Benefits
TT-615	30.0%	***	*		Strongly shear-thinning rheology. Recommended for high sag resistance/film build in interior formulations.
DR-72	30.0%	***	*		Excellent for sag resistance, particularly in high film-build applications.
TT-935	30.0%	**	***	*	Efficient KU builder recommended for flat through sheen paints.
DR-110	30.0%	***	***	**	Efficient KU builder that is recommended as a replacement for HMHEC in interior premium formulations.
DR-73	30.0%	**	**	***	Good ICI efficiency with notable KU build. Sole-thickening candidate.
RM-7	30.0%	*	*	***	Excellent ICI efficiency. Recommended for PVA and lower efficiency acrylics.
DR-6600	30.0%		**	***	ICI efficient. Recommended in semi-gloss and gloss paints.
DR-5500	30.0%		*	***	ICI efficient. Recommended in semi-gloss and gloss paints.

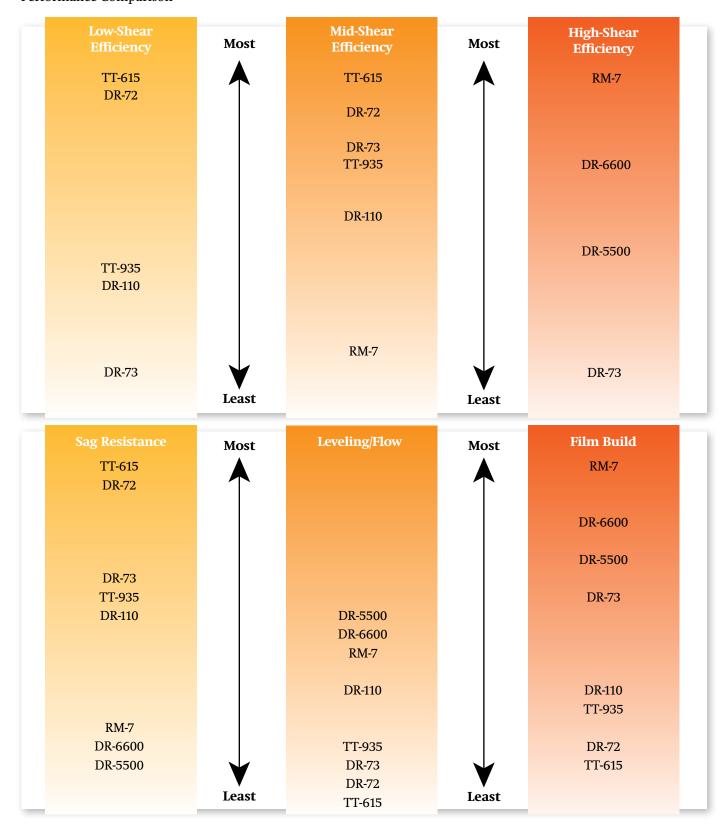
* Manufactured without added solvent or APEO surfactant

* Good ** Better *** Best

Dispersant Recommendations

TAMOL*	Salt	Solids	Use Level (on pigment)	Benefits		
Polyacid Disper	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.		
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.		
SG-1	NH ₄	35%	0.7 - 1.0%	Excellent gloss potential, low-foam generator. Can give thixotropy. Imparts lower rheology modifier demand.		

ACRYSOL™ HASE Rheology Modifiers Performance Comparison



ACRYSOL™ HEUR Rheology Modifiers

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).

ACRYSOL*	Active Polymer	As Supplied Solids	Brookfield	KU	ICI	Benefits
RM-12W	19.0%	19.0%	****			Use to improve sag and/or stability.
RM-995	20.0%	23.5%	***	**		Excellent sag/level balance. Improved viscosity retention upon tinting.
RM-400	20.6%	18.0%	***	***	*	Good ICI contribution with improved sag/ leveling balance and viscosity loss upon tinting. Best when paired with acrylic binders.
SCT-275	17.5%	17.5%	**	***	**	Good KU/ICI efficiency. Can be used as a sole thickener. Contains solvent.
RM-825	25.0%	25.0%		**	*	Highly efficient KU builder. Contains solvent.
RM-8W	17.5%	21.0%		**	*	Broad utility low-shear.
RM-6000	17.5%	17.5%		**	***	To be used in PVA/VAE formulations in combination with HASE low shear.
RM-5000	18.5%	18.5%		*	***	Recommend with ACRYSOL [™] RM-995.
RM-3000	20.0%	20.0%			***	More efficient ACRYSOL™ RM-2020 NPR.
RM-2020 NPR	20.0%	20.0%			***	To be used in formulations sensitive for color float/syneresis or HMHEC.

Product Selector Guide for All Binder Systems

For Acrylic and Styrene Acrylic Binder Systems

Active As Supplied ACRYSOL* ICI Benefits Polymer Solids Used with styrene acrylics and very small RM-242 16% 18% * * * * particle sized acrylics. Similar efficiency and rheology to ACRYSOL™ RM-244 16% 18% * * * * RM-825 Rheology Modifier. Highly efficient KU-builder with utility in large particle acrylics or low-efficiency RM-845 25% 27% * * * \star formulations.

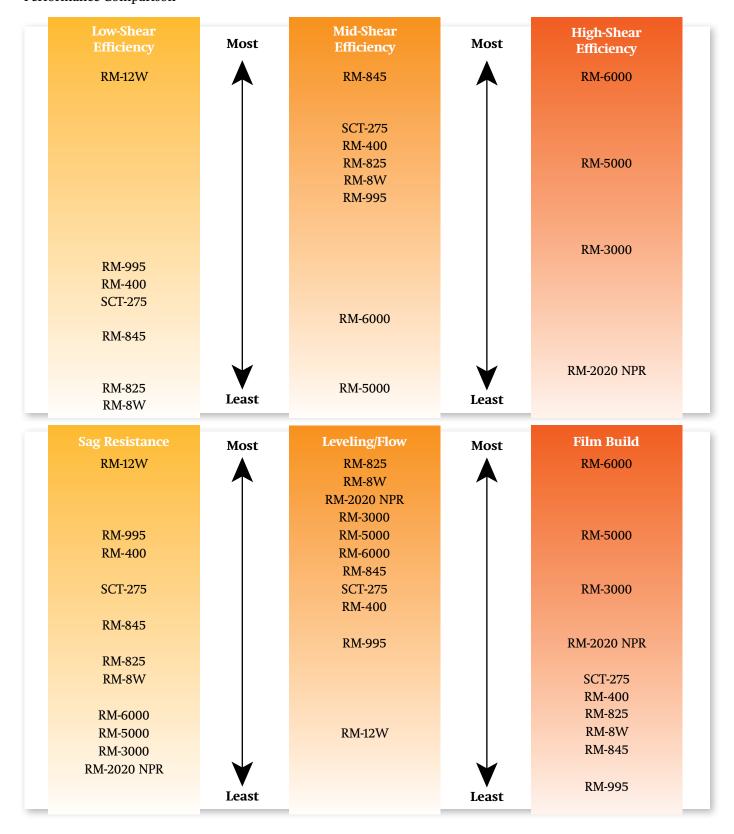
* Good ** Better *** Best

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* Manufactured without added solvent or APEO surfactant unless otherwise noted.

HEUR products range in solids from 17.5% to 35%. However, some products contain non-active ingredients designed to lower the product viscosity for ease of handling. As-Supplied Solids refers to the sum of all the solids in the product, whether active thickener or not. Active polymer reflects only the actual polymer that creates thickening in the formulation.

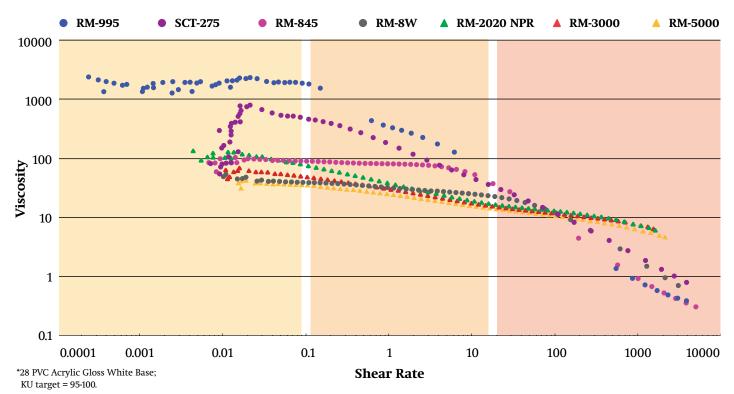
ACRYSOL™ HEUR Rheology Modifiers Performance Comparison



TAMOL*	Salt	Solids	Use Level (on pigment)	Benefits	
Hydrophobic Co	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%	3.0 - 5.0%	Maximizes gloss potential. Good stability in paints containing ZnO and other reactive pigments. Good corrosion resistance.	
2011	K	23%	3.0 - 5.0%	Low-odor, solvent-free* capability. Maximizes gloss potential. Good stability with ZnO. Good corrosion resistance.	
2002	n/a	42%	3.0 - 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.	
SG-1	NH ₄	35%	0.7 - 1.0%	High-gloss potential. Broad formulating latitude. Cost/performance balance. Low-foam generator.	

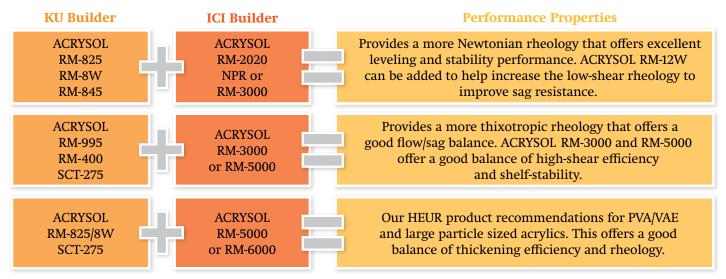
* Manufactured without added solvent.

Rheology Profiles* of ACRYSOL™ HEUR Rheology Modifiers



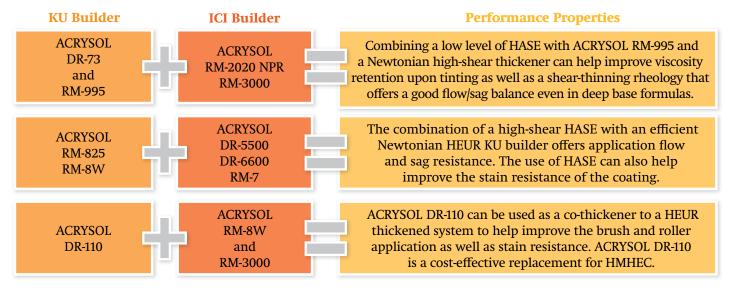
Starting Point Formulations

The Dow portfolio of the ACRYSOL[™] Rheology Modifiers has a tool for every formulation need. The following recommendations can get you started on finding the right solution for your formulation. In addition, the rheology experts at Dow are always available to assist in any of your formulating challenges.



Combining ACRYSOL HASE and HEUR products can offer distinct performance properties that neither chemistry family can provide alone. For example, adding a high-shear HEUR can improve the flow of a HASE base formulation. Combining HASE and HEUR products also can improve the stain resistance and sag resistance of HEUR-only coatings. Adding a HASE to a HEUR system in medium and deep base formulations also offers the benefit of improving viscosity retention upon tinting.

When formulating with HEUR and HASE thickeners try the following combinations:



For more information, contact Dow Coating Materials US Toll Free 800-447-4369 dow.com/coatingmaterials

Form No. 884-00334-1013-NAR-EN-GS

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