油漆和涂料**流变控制**添加剂

Additives to **Control the Rheology** of Paints and Coatings

配制油漆和涂料以提供恰到好处的性能平衡是一项复杂的工作。
获得正确的流变特性只是配方设计师待办事项清单上的一项重要任务，
但它对于涂层的最终成功至关重要。

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流变特性影响涂层在其整个生命周期中的特性，从制造、储存、混合和应用到最终的涂层特性。为了控制和优化液体涂料的流变性，配方设计师通常依赖添加剂，通常称为流变改性剂、增稠剂和触变剂。在本文中，将回顾流变学和流变添加剂的一些基础知识。

流变学基础

流变学被定义为检查材料流动和变形的科学。在考虑液体油漆和涂料等流体时，最常讨论的流变学方面是粘度。流体的粘度是衡量其在给定应力下抗变形能力的指标，是我们将涂层与「厚」或「薄」联系起来的一种材料特性。要了解粘度及其对涂料的重要性，快速回顾一下这些原理是有帮助的。

正如以撒牛顿多年前所做的那样，考虑两个板之间的流体，如**图 1** 所示，其中底板是静态的，而顶板由于施加的力 (F) 特定速度 (v) 移动。当对液体施加力时，液体将发生流动以减轻力的应变。剪切应力 (τ) 定义为导致液体流动的每单位面积 (A) 的剪切力 (F) ，单位为帕斯卡 (1 帕斯卡 = 1 牛顿 / 平方米) 或达因 / 平方厘米。剪切应变 (γ) 描述了流体的变形，定义为水平位移 (ΔL) 与高度 (h) 的比率。靠近顶板的流体层的速度将高于靠近底部静态板的流体层的速度。剪切速率 ($\dot{\gamma}$) 描述速度梯度，或剪切板之间单位高度的液体速度变化，

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Formulating paints and coatings to provide just the right balance of properties is a complex undertaking. Getting the rheology profile correct is just one important task on the formulator's to-do list, but it is crucial to the ultimate success of the coating. The rheology profile influences properties of the coating throughout its lifetime, from manufacture, storage, mixing, and application, to the resulting film properties. To control and optimise the rheology of liquid coatings, the formulator typically relies on additives, often referred to as rheology modifiers, thickeners and thixotropes. In this article, some of the basics of rheology and rheological additives will be reviewed.

Basics of rheology

Rheology is defined as the science examining the flow and deformation of materials. When considering fluids such as liquid paints and coatings, the aspect of rheology discussed most often is viscosity. The viscosity of a fluid is a measure of its resistance to deformation under a given stress, and is a material property which we associate with the coating as being either "thick" or "thin". To understand viscosity and its importance for coatings, a quick review of the principles is helpful.

As Isaac Newton did many years ago, consider a fluid between two plates as in **Figure 1**, where the bottom plate is static, and the top plate is moving at a certain velocity (v)

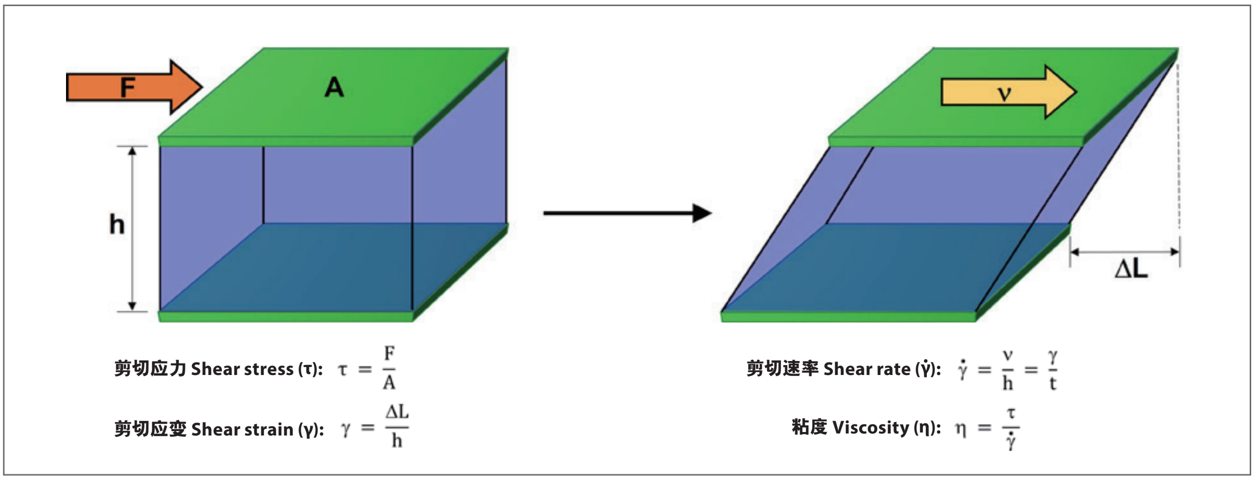
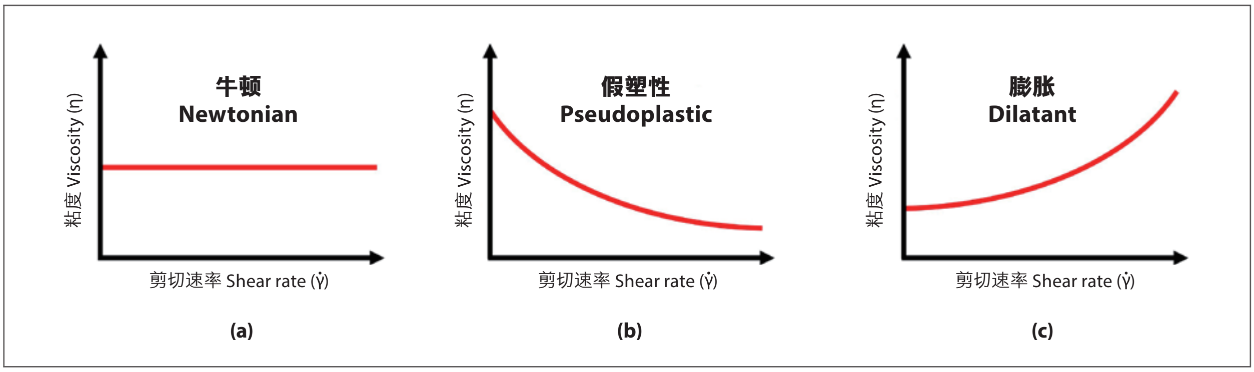


图1：剪切下液体的一些关键流变参数的定义
Figure 1: Definition of some key rheological parameters for a liquid under shear



(a)
(b)
(c)

图2：显示的液体流变曲线类型
Figure 2: Types of rheology profile displayed by liquids

定义为v/h，其中v=ΔL/t，t为顶板移动距离ΔL所用的时间。剪切速率的单位是秒的倒数（s^{-1}）。我们已经注意到粘度是衡量流体抗变形能力的指标，它是剪切应力（τ）与剪切速率（$\dot{\gamma}$）的比值，以帕斯卡•秒或达因•秒/平方厘米为单位（其中1达因•秒/平方厘米 = 1泊（P），1泊等于0.1帕斯卡•秒。

当流体的粘度在不同的剪切速率下保持恒定时，会表现出理想或牛顿粘度（**图2a**）。牛顿流体包括简单的流体，如水、溶剂和油。然而，大多数液体材料，包括油漆和涂料，本质上是非牛顿流体，并且具有随剪切速率变化的粘度。油漆和涂料的粘度通常随着剪切速率的增加而降低，也称为剪切稀化或假塑性行为（**图2b**）。剪切涂层会破坏液体内的结构，并导致与涂层静止和未受干扰时相比较低的粘度。一些流体，例如高固体分散体，会随着剪切速率的增加而显示粘度增加，也称为剪切增稠或膨胀行为（**图2c**）。通常，不希望形成膨胀流体，因为它会在制造过程中以及在混合和泵送等过程中引起问题。

剪切速率和物理过程

油漆和涂料经受物理过程，其特徵在于各种剪切速率。例如，由于重力导致的颜料沉降是一个非常低的剪切速率过

due to an applied force (F). When a force is applied to the liquid, flow of the liquid will occur to relieve the strain from the force. The shear stress (τ) is defined as the shear force (F) per unit area (A) that results in flow of the liquid, and has units of Pascals (1 Pa = 1 N/m^2) or dyne/cm^2. The shear strain (γ) describes the deformation of the fluid and is defined as the ratio of the horizontal displacement (ΔL) to the height (h). The velocity of a fluid layer near the top plate will be higher than the velocity of a fluid layer near the bottom static plate. Shear rate ($\dot{\gamma}$) describes the velocity gradient, or the change in liquid velocity per unit height between the shear plates, and is defined as v/h, where v = ΔL/t, and t is the time it takes the top plate to move over the distance ΔL. Shear rate has units of reciprocal seconds (s^{-1}). Viscosity, which we already noted is a measure of the resistance of the fluid to deformation, is the ratio of shear stress (τ) to shear rate ($\dot{\gamma}$), and is reported in units of Pa·s or dyne·s/cm^2 (where 1 dyne·s/cm^2 = 1 Poise (P), and 1 Poise equals 0.1 Pa·s.

When the viscosity of a fluid is constant at varying shear rates, it is said to exhibit ideal or Newtonian viscosity (**Figure 2a**). Newtonian fluids include simple fluids like water, solvents and oils. However, most liquid materials, including paints and coatings, are non-Newtonian in nature, and have a viscosity that changes with shear rate. The viscosity of paints and coatings generally decreases with increasing shear rate, also known as shear-thinning or pseudoplastic behaviour

程。应用于墙壁的建筑涂料的流挂是在低剪切下发生的另一个过程。手动或使用低速高架混合器混合涂料是一种中等剪切过程，而分散颜料并使用高速 Cowles 分散器混合是一种高剪切速率过程。应用方法跨越剪切速率的范围。通过浸涂或流涂机施加的涂料经历低到中等的剪切速率，而通过刷涂或无气喷涂施加的涂料受到高剪切。通过反向辊涂机应用卷材涂料是非常高剪切速率工艺的另一个例子。**图 3** 描述了在油漆和涂料的制造、储存和应用过程中的各种过程中涉及的剪切速率的大致范围。

图 3 还显示了一些用于测量油漆和涂料粘度的常用仪器所涵盖的剪切速率范围的描述。克雷布斯 - 史托摩尔型粘度计是涂料实验室中非常常见的设备，用于测量涂料（如建筑和工业维护涂料）的粘度（以 Krebs 单位或 KU 报告）。它采用以 200rpm 恒定转速旋转的桨式转子，粘度较高的涂料需要施加更大的力以按设定的速度使转子旋转。因为它在大约 60 s^{-1} 的固定剪切速率下运行，所以 Stormer 粘度计为比较不同的油漆提供了一致的标准。然而，基于**图 3**，虽然在优化混合和浇注等中等剪切过程时使用它是一种很好的工具，但在喷涂或刷涂过程中尝试优化低剪切过程（如抗流挂性或高剪切性）时，它显然不适合使用。

为了将涂料粘度与低剪切速率过程相关联，布鲁克菲尔德粘度计是涂料实验室中常用的仪器。它是一种旋转粘度

(**Figure 2b**). Shearing the coating will break down structure within the liquid, and lead to a lower viscosity versus when the coating is at rest and unperturbed. Some fluids, such as high solids dispersions, can show an increase in viscosity with increasing shear rate, also known as shear-thickening or dilatant behaviour (**Figure 2c**). Generally, dilatant flow is not desired, as it can cause problems during manufacture and in processes such as mixing and pumping.

Shear rate and physical processes

Paints and coatings are subjected to physical processes that are characterised by a wide variety of shear rates. The settling of pigments due to the force of gravity, for example, is a very low shear rate process. The sagging of an architectural paint applied to a wall is another process that occurs under low shear. Mixing a paint by hand or with a low-speed overhead mixer is a medium shear process, while dispersing pigments and mixing with a high-speed Cowles disperser is a high shear rate process. Application methods span the range of shear rate. Coatings applied by dip or flow coater application experience a low to medium shear rate, while paints applied by brush or airless spray are subjected to high shear. Application of coil coatings by reverse roll coaters is another example of a very high shear rate process. **Figure 3** describes the approximate ranges of shear rate that are involved in various processes during the manufacture, storage, and application of paints and coatings.

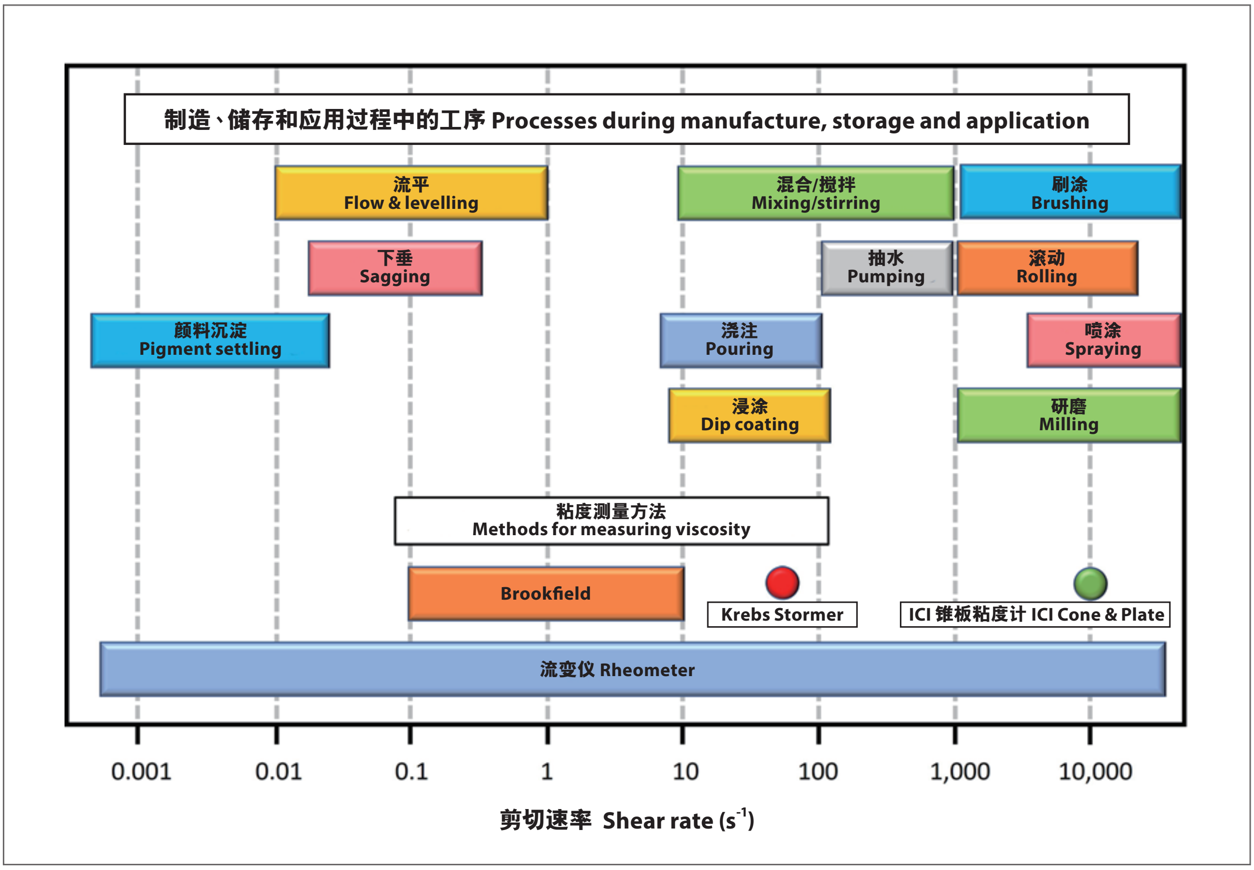


图3：油漆和涂料行业中使用的各种工艺的剪切速率示例，以及一些测量粘度的常用方法。
Figure 3: Examples of shear rates for various processes used in the paint a& coatings industry, and for some common methods of measuring viscosity.

计，它可以使用几个不同的圆柱形和圆盘形转子以及不同的转速来测量低到中等剪切速率范围内的粘度（通常以厘泊或cP为单位报告）。对于高剪切速率下的粘度，ICI锥板粘度计是一种常用设备。剪切速率约为10,000 s^{-1}，对于试图优化属于该高剪切范围的刷涂、辊涂和喷涂应用的粘度的配方设计师来说非常有用。ICI粘度通常以泊（P）为单位报告。为刷涂而设计的标准水性建筑涂料的ICI粘度约为1.0–1.5 P。粘度太低会导致涂膜效果不佳，而值太高会导致涂刷阻力过大。

装备精良的油漆实验室可以使用已经提到的三种粘度计——Brookfield、Krebs Stormer和ICI锥板粘度计，以适中的价格评估低、中和高剪切条件下的粘度。众所周知，这些仪器将仅提供少数值或小范围剪切速率下的粘度数据。然而，为了更全面地了解涂层的流变特性，油漆化学家可以求助于更昂贵、更先进的流变仪，它可以在很宽的剪切范围内进行测量。当然，在实际应用中评估涂层是对涂层流变学是否得到优化的最终检验。在使用记录建筑涂料滚涂过程中施加的位置和力的仪器的测试方法开发文献中也有报导，试图将流变学的标准化测试与实际应用和最终用户偏好相关联[1]。

配制时以粘度曲线为目标

那么，配方设计师在设计涂料时应该以什么样的粘度为目标？由于涂料等假塑性流体的粘度随剪切速率而变化，这个问题当然变得复杂了。了解涂料在剪切速率范围内的粘度回应对于涂料配方设计师很重要，因为涂料会经历许多物理过程，如**图3**所示，这将有助于回答这个问题。在设计新涂料时，配方设计师将依靠流变添加剂来确定最佳流变特性，以在所有这些过程中发挥最佳性能。例如，为了防止储存过程中的沉淀和颜料凝固，在低剪切下以更高的粘度为目标更好。稠密的颜料和体质颜料更容易在布鲁克菲尔德粘度较低的涂料中沉淀。在低剪切速率下较高的粘度也有助于抗流挂。这必须与良好的流动性和流平性以及低剪切速率工艺的需要相平衡，但较低的粘度将有助于实现这一点。作为另一个例子，在喷涂应用中，当涂料离开喷枪时，涂料流体被分解成小液滴，并且这种雾化过程通常通过在喷涂中发生的高剪切条件下的较低粘度而增强。另一方面，如果配制用于刷涂应用，则需要在高剪切下具有更高的粘度以实现更大的成膜。如果粘度太低并形成涂膜，则可能会牺牲诸如遮盖或基材保护（例如腐蚀）等特性。

流变控制添加剂

在溶剂型涂料中，溶解的树脂会对粘度产生很大的影响。在给定的固体含量下，较高的树脂分子量和聚合物骨架刚度会导致较高的溶液粘度。聚合物设计和体积固体份是用于控制溶剂型涂料粘度的变数，而添加剂通常用于提高抗流挂性和颜料沉降。溶剂型体系中常用的触变剂包括有机改性粘土（有机粘土）、聚醯胺和蓖麻油衍生物。

水性涂料，尤其是基于乳胶聚合物的涂料，通常会依赖添加剂来控制流变性。由于乳胶聚合物是胶体颗粒且不溶于水，因此聚合物分子量和骨架刚度对粘度没有影响。

Also shown in **Figure 3** is a description of the shear rate ranges covered by some of the common instruments used to measure the viscosity of paints and coatings. The Krebs Stormer viscometer is a very common piece of equipment in paint laboratories for measuring viscosity (reported in Krebs units or KU) of coatings such as architectural and industrial maintenance paints. It utilises a paddle-type rotor that is rotated at a constant 200 rpm, with higher viscosity paints requiring a higher force to rotate the paddle at the set speed. Because it operates at a fixed shear rate of about 60 s^{-1}, the Stormer viscometer provides a consistent standard for comparing different paints. However, based on **Figure 3**, while it is a good instrument to use when optimising for medium-shear processes like mixing and pouring, it is clearly not the right one to use when trying to optimise low-shear processes like sag resistance or high-shear processes like spray application or brushing.

To correlate paint viscosity with low shear rate processes, the Brookfield viscometer is a common instrument used in paint labs. It is a rotational viscometer which can use several different cylindrical and disc-shaped spindles and different rotational speeds to measure viscosities (typically reported in units of centipoise or cP) over a range of low to medium shear rates. For viscosities at high shear rate, the ICI Cone and Plate viscometer is a common piece of equipment. With a shear rate of about 10,000 s^{-1}, it is useful to formulators trying to optimise viscosity for brush, roller and spray applications which fall in that high shear range. ICI viscosities are typically reported in units of Poise (P). A standard waterborne architectural paint designed for brush application will have an ICI viscosity of approximately 1.0–1.5 P. Much lower viscosities will lead to poor film build, and much higher values will lead to excessive brush drag.

A well-equipped paint laboratory can evaluate viscosity at low, medium and high shear conditions for a moderate price with the three viscometers already mentioned – Brookfield, Krebs Stormer and ICI Cone and Plate viscometers. It is recognised that these instruments will only provide viscosity data at a few values or small ranges of shear rate. However, for a more complete picture of the rheology profile of a coating, paint chemists can turn to a more expensive and more advanced rheometer which can make measurements across a wide shear range. Of course, evaluating a coating in the real-world application is the final test of whether the coating rheology has been optimised. There have also been reports in the literature of test method development using an instrument that records position and forces applied during the roller application of architectural paints, in the attempt to correlate standardised testing of rheology with real-world application and end-user preferences.[1]

Targeting a viscosity profile when formulating

So, what viscosity should a formulator target when designing a coating? This question is of course complicated by the fact that for pseudoplastic fluids such as coatings, viscosity changes with shear rate. Understanding the viscosity response of a coating across the range of shear rates is important for paint formulators because of the many physical processes which coatings experience, as illustrated in **Figure 3**, and will help in answering the question. When designing a new coating, formulators will rely on rheological

然而，细微性、细微性分布和体积分数（浓度）对胶乳的粘度有很大影响。当胶乳浓度接近理论最大体积分数时，小的变化会导致粘度大幅增加。出于这个原因，乳胶涂料通常以足够低的乳胶浓度配制以避免该问题，并且通常使用水溶性增稠剂来控制流变性。有多种水溶性有机流变改性剂和增稠剂用于水性体系，包括纤维素、碱溶（或溶胀）乳液（ASE）、疏水改性碱溶乳液（HASE）和各种类型的缔合流变改性剂，例如疏水改性的乙氧基化氨基甲酸酯（HEUR）和疏水改性的聚醚（HMPE）。无机流变改性剂也用于水性体系，通常用于抗沉降和抗流挂性能，包括粘土（例如凹凸棒土和膨润土粘土）和气相二氧化硅。下面将更详细地讨论这些流变改性剂化学品中的一些。

水性涂料的有机流变改性剂可以根据它们如何增稠涂料进行分类。这些流变改性剂有两种基本的增稠机制——缔合性和非缔合性。非缔合增稠通过体积排阻机制起作用，其中通常是高分子量水溶性聚合物遇水膨胀并占据涂层中的流体力学体积（**图 4**）。例子包括 HEC 和 ASE 增稠剂，它们通过链缠结和颗粒絮凝（即空缺絮凝）产生粘度。缔合性增稠剂是含有疏水基团的水溶性聚合物，它们彼此相互作用（或缔合）并与涂料配方的其它成分，特别是乳胶颗粒，形成网络结构（**图 5**）。网络限制了乳胶颗粒的运动会导致粘度增加。缔合增稠剂的例子包括 HEUR 和 HMPE 流变改性剂。还有一些流变改性剂依赖于缔合和非缔合机制的组合进行增稠，包括 HASE 和疏水改性的 HEC，或 HMHEC 增稠剂。

非缔合流变改性剂是水溶性聚合物，可增稠涂料的水相。较高分子量的聚合物在溶液中往往具有较高的粘度，这适用于水溶性流变改性剂，如纤维素醚和 ASE 增稠剂。纤维素增稠剂源自天然产品纤维素。油漆和涂料中最常见的纤维素衍生物是羟乙基纤维素（HEC），它有各种分子量。HEC 增稠剂是非离子型的，可在很宽的 pH 范围内产生良好的粘度稳定性。作为天然产物的衍生物，HEC 容易受到微生物的侵袭。微生物产生的纤维素酶可以分解纤维素增稠剂并导致已经配制好的油漆粘度损失。制造商已经开发出经过改性以更能抵抗此类攻击的等级。HEC 增稠剂特别擅长在低剪切速率下产生粘度，因此具有良好的抗颜料沉降、抗流挂和抗脱水收缩能力。它们也不会受到表面活性剂存在的很大影响，因此与 HEUR 等缔合增稠剂相比，添加着色剂时粘度下降的问题较少。然而，HEC 增稠剂会对涂膜光泽产生负面影响。

与较低分子量级别的 HEC 相比，较高分子量级别的 HEC 具有更高的增稠效率，但由于链缠结在剪切时被破坏，因此剪切稀化程度也更高。为了在高剪切速率下获得高粘度，例如改善刷子阻力或成膜，配方设计师必须添加足量的 HEC。由于高分子量 HEC 含量高，涂料配方设计师可能会面临剪切粘度过低的风险，这将导致流动性和流平性差。对于低分子量的 HEC，风险在于需要使用过多的水溶性聚合物并且最终涂膜的耐水性较差。折衷方案通常是使用中等分子量等级。疏水改性的 HEC 或 HMHEC 增稠剂将疏水基团结合到聚合物中，这也通过缔合机制增加了粘度，并且在建立高剪切粘度方面也更有效。与未改性的 HEC 相比，MHEC 牌号还提高了辊涂的抗飞溅性，这一直是用 HEC 增稠的涂层

additives to target the optimal rheology profile to perform best across all these processes. For example, to prevent sedimentation and pigment setting during storage, targeting a higher viscosity at low shear is better. Dense pigments and extenders are more prone to settling in paints with low Brookfield viscosities. Resistance to sagging is also aided by a higher viscosity at low shear rate. This must be balanced with the need for good flow and leveling, also a low shear rate process, but which would be aided by a lower viscosity. As another example, in spray applications, a stream of paint is broken up into small droplets as the paint leaves the spray gun, and this atomisation process is generally enhanced by a lower viscosity at the high shear conditions that occur in spraying. On the other hand, if formulating for a brushing application, a higher viscosity at high shear will be desired to allow for greater film build. If viscosity is too low and a thin film results, properties such as hiding or substrate protection (e.g., corrosion) might be sacrificed.

Additives for rheology control

In solventborne coatings, the dissolved resin can have a strong influence on viscosity. At a given solids level, higher resin molecular weight and polymer backbone stiffness leads to higher solution viscosities. Polymer design and volume solids are variables used to control viscosity in solventborne coatings, and additives are often used to improve sag resistance and pigment settling. Common thixotropic agents used in solventborne systems include organically-modified clays (organoclays), polyamides and castor oil derivatives.

Waterborne coatings, especially ones based on latex polymers, will typically rely on additives to control rheology. Because latex polymers are colloidal particles and insoluble in water, the polymer molecular weight and backbone stiffness have no effect on viscosity. Particle size, particle size distribution and volume fraction (concentration) however have a strong effect on viscosity of the latex. As the latex concentration approaches the theoretical maximum volume fraction, small changes can lead to large increases in viscosity. For this reason, latex coatings are usually formulated at latex concentrations low enough to avoid the issue and typically use water-soluble thickeners to control rheology. There are a variety of water-soluble, organic rheology modifiers and thickeners used in waterborne systems, including cellulosics, alkali-soluble (or swellable) emulsions (ASE), hydrophobically-modified alkali-soluble emulsions (HASE) and various types of associative rheology modifiers such as hydrophobically-modified ethoxylated urethanes (HEUR) and hydrophobically-modified polyethers (HMPE). Inorganic rheology modifiers are also used in waterborne systems, typically for anti-settling and anti-sag properties, and include clays (e.g., attapulgite and bentonite clays) and fumed silicas. Some of these rheology modifier chemistries will be discussed in more detail below.

Organic rheology modifiers for waterborne coatings can be classified according to how they thicken the paint. There are two basic mechanisms of thickening utilised by these rheology modifiers – associative and non-associative. Non-associative thickening works via a volume exclusion mechanism, where typically high molecular weight water-soluble polymers swell with water and take up hydrodynamic volume in the coating (**Figure 4**). Examples include hydroxyethyl cellulose (HEC)

的历史问题。

开发了碱溶性乳液(ASE)增稠剂以模拟纤维素的流变性，但更易于使用。HEC 增稠剂以干粉形式提供，而 ASE 增稠剂以液体形式提供。ASE 增稠剂通常是丙烯酸乙酯 (EA) 和甲基丙烯酸 (MAA) 的共聚物，通过乳液聚合工艺制成。它们以易于使用的低粘度液体形式作为未中和的、低 pH 值、高固体含量的不溶性聚合物分散体提供。聚合物中 MAA 的重量百分比相当高，当中和到更高的 pH 值时，聚合物溶胀，变得更易溶于水，并开始展开。一旦展开，ASE 聚合物链就会通过体积排阻机制使涂层变厚。增稠程度取决于聚合物的分子量。因为中和是启动 ASE 增稠剂增稠能力的触发器，所以配方设计师可以依靠涂料配方中的氨或其它中和碱来启动增稠作用。需要调整中和剂的用量以保持合适的 pH 值。ASE 增稠剂擅长在低剪切下为具有良好抗沉降和抗流挂性能的涂料建立高粘度，并提供急剧剪切稀化的流变曲线。由于羧酸官能度高，ASE 增稠剂可以赋予涂膜一些水敏感性，并对建筑涂料的耐擦洗性或工业涂料的耐腐蚀性等性能产生负面影响。其它限制可能包括不理想的流平性和平整度。

如前所述，HASE 流变改性剂通过涉及体积排阻和疏水物缔合的双重机制产生粘度。HASE 增稠剂是利用 ASE 技术的丙烯酸聚合物，即它们含有足够的酸官能团以在中和时

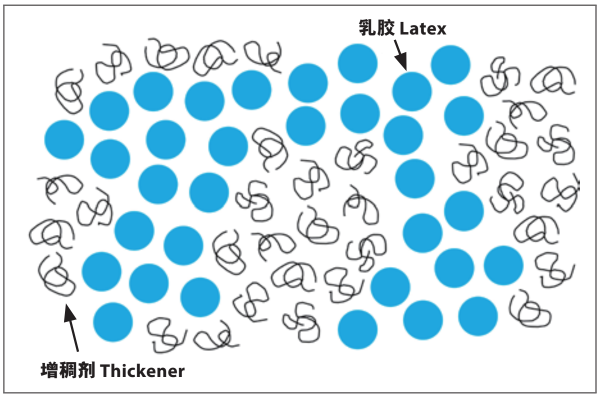


图4：非缔合流变改性剂的乳胶涂层的增稠机制。
Figure 4: Thickening mechanism for latex coatings with non-associative rheology modifiers.

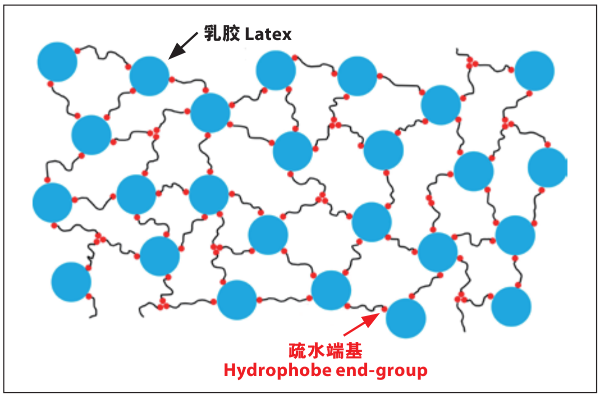


图5：缔合流变改性剂的乳胶涂料的增稠机制。
Figure 5: Thickening mechanism for latex coatings with associative rheology modifiers.

and ASE thickeners, which create viscosity through chain entanglements and particle flocculation (i.e., depletion flocculation). Associative thickeners are water-soluble polymers containing hydrophobic groups that interact (or associate) with one another and with other components of the coating formulation, particularly the latex particles, to create a network structure (**Figure 5**). An increase in viscosity results from the network restricting the motion of the latex particles. Examples of associative thickeners include HEUR and HMPE rheology modifiers. There are also rheology modifiers which rely on a combination of associative and non-associative mechanisms for thickening, including HASE and hydrophobically modified HEC, or HMHEC thickeners.

Non-associative rheology modifiers are water-soluble polymers that thicken the water phase of a coating. Higher molecular weight polymers tend to have a higher viscosity in a solution, and that holds for water-soluble rheology modifiers such as cellulosic ethers and ASE thickeners. Cellulosic thickeners are derived from a natural product, cellulose. The most common cellulosic derivative used in paints and coatings is hydroxyethyl cellulose (HEC), which is available in various molecular weights. HEC thickeners are non-ionic and yield good viscosity stability across a wide pH range. As a derivative of a natural product, HEC is susceptible to microbial attack. Cellulase enzyme produced by microbes can break down cellulose thickeners and lead to viscosity loss in an already formulated paint. Manufacturers have developed grades which are modified to be more resistant to such attack. HEC thickeners are particularly good at creating viscosity at low shear rate, and thus offer good resistance to pigment settling, sag and syneresis. They are also not affected greatly by the presence of surfactants, and therefore viscosity drop on addition of colourants is less of a concern than with associative thickeners such as HEURs. HEC thickeners can however have a negative impact on film gloss.

Higher molecular weight grades of HEC have greater thickening efficiency compared to lower molecular weight grades, but are also more shear thinning as chain entanglements are broken down on shearing. To achieve high viscosity at high shear rate, for example to improve brush drag or film build, a formulator must add an adequate amount of HEC. With high levels of a high molecular weight HEC, the paint formulator risks having an excessive low shear viscosity, which will lead to poor flow and leveling. With a low molecular weight HEC, the risk is needing to use too much water-soluble polymer and having poor water resistance in the final film. The compromise is often to use a medium molecular weight grade. Hydrophobically modified HEC or HMHEC thickeners incorporate hydrophobe groups into the polymer which also build viscosity through an associative mechanism, and are also more effective at building high shear viscosity. HMHEC grades also give improved spatter resistance in roller application versus unmodified HEC, which has been an historical problem for coatings thickened with HEC.

Alkali-soluble emulsion (ASE) thickeners were developed to mimic the rheology of cellulosics but with greater ease of use. While HEC thickeners are supplied as a dry powder, ASE thickeners are supplied in liquid form. ASE thickeners are typically copolymers of ethyl acrylate (EA) and methacrylic acid (MAA) and made by an emulsion polymerisation process. They are supplied as unneutralised, low pH, high solids dispersions of insoluble polymer in an easy-to-use, low viscosity liquid form. The weight percent of MAA in the

赋予溶解性并通过体积排阻增稠，如**图 4** 所示。然而，它们的分子量通常低于 ASE 增稠剂，并且还包含疏水性，一旦 HASE 溶解，它们就可以与彼此和乳胶颗粒结合，如**图 5** 所示。HASE 流变改性剂允许配制相对于 ASE 和 HEC 的各种流变特性，其中一些产品在低剪切下更有效地增加粘度，而其它产品在中高剪切率下更有效地建立粘度。它们通常比纤维素增稠剂提供更好的流动性和流平性，具有更好的光泽能力，并且适用于制备平光和高光泽配方。

相对于 HASE，疏水改性的乙氧基化氨基甲酸酯（HEUR）流变改性剂是非离子型、较低的分子量和较高的疏水基团密度。HEUR 是基于聚氨酯主链的水溶性聚合物，由聚乙二醇与异氰酸酯交联剂反应形成，并用疏水端基封端。HEUR 和相关缔合增稠剂（如 HMPE）通过三维缔合网络的发展产生粘度，如**图 5** 所示。疏水端基由于溶解性差和排除在乳胶表面上而被迫相互缔合水相。与 HEURs 相关的增稠程度高于 HASE 和 HMHEC。HEUR 以其出色的流动性和流平性、出色的防飞溅性以及良好的防水性和光泽潜力而闻名。生产中的变数，如分子量、疏水物尺寸和疏水物密度，使 HEUR 产品能够在剪切速率范围内进行定制，以提高效率。

缔合增稠的一个弱点是它容易被涂料配方中的其它含疏水物的物质中断，特别是被表面活性剂和与水混溶的成膜助剂和助溶剂中断。水溶性溶剂如乙二醇丁醚（Butyl CELLOSOLVE）或二甘醇丁醚（Butyl CARBITOL）可以增加疏水物在水相中的溶解度，从而中断它们相互间及与胶乳表面结合的驱动力。众所周知，含有大量溶剂（例如二甘醇丁醚）的工业涂料配方很难用缔合流变改性剂增稠。

表面活性剂与增稠剂竞争乳胶表面，并中断增稠剂分子上疏水物之间的结合。破坏三维网络会导致粘度降低。这种效果在中等至超深色调的底色中尤其成问题，其中大量含

polymer is fairly high, and upon neutralisation to a higher pH, the polymer swells, becomes more water-soluble, and starts to uncoil. Once uncoiled, the ASE polymer chains thicken the coating through the volume exclusion mechanism. The degree of thickening depends on the molecular weight of the polymer. Because neutralisation is the trigger that activates the thickening ability of ASE thickeners, formulators can rely on ammonia or other neutralising bases in the coating formulation to activate the thickening action. Adjustments in the amount of neutraliser will be needed to maintain a suitable pH. ASE thickeners are proficient at building high viscosity at low shear for coatings with good anti-settling and sag resistance properties, and give rheology profiles that are steeply shear thinning. Due to the high level of carboxylic acid functionality, ASE thickeners can impart some water sensitivity to films and negatively influence properties such as scrub resistance for architectural paints or corrosion resistance for industrial coatings. Other limitations can include flow and levelling that is not ideal.

As mentioned, HASE rheology modifiers create viscosity by a dual mechanism involving both volume exclusion and hydrophobe association. HASE thickeners are acrylic polymers that make use of the ASE technology, i.e., they contain enough acid functionality to impart solubility on neutralisation and thicken through volume exclusion as in **Figure 4**. However, they are typically lower molecular weight than ASE thickeners and also incorporate hydrophobic groups into the backbone, which are available for association with both each other and latex particles as in **Figure 5**, once the HASE is solubilised. HASE rheology modifiers allow for formulation of a wide range of rheology profiles relative to ASE and HEC, with some products being more effective at increasing viscosity at low shear and others more effective at building viscosity at mid and high shear rates. They generally provide better flow and leveling than cellulosic thickeners, have better gloss capability, and are suitable for flat through gloss formulations.

Relative to HASE, hydrophobically-modified ethoxylated urethane (HEUR) rheology modifiers are non-ionic, lower molecular weight and have a higher density of hydrophobe groups. HEURs are water-soluble polymers based on a polyurethane backbone formed by reacting polyethylene glycols with isocyanate crosslinkers, and capped with hydrophobic end-groups. HEURs and related associative thickeners such as HMPEs, create viscosity through the development of a three-dimensional associative network, as in **Figure 5**. The hydrophobic end-groups are driven to associate with one another and latex surfaces due to their poor solubility and exclusion from the aqueous phase. The degree of associative thickening with HEURs is higher than in HASE and HMHEC. HEURs are known for their excellent flow and leveling, excellent spatter resistance, and good water resistance and gloss potential. Variables in their production such as molecular weight, hydrophobe size and hydrophobe density have allowed HEUR products to be tailored for effectiveness across the range of shear rates.

One weakness of associative thickening is its susceptibility to be interrupted by other hydrophobe-containing species in the paint formulation, in particular by surfactants and water-miscible coalescents and solvents. Water-miscible solvents such as ethylene glycol butyl ether (Butyl CELLOSOLVE) or diethylene glycol butyl ether (Butyl CARBITOL) can increase the solubility of the hydrophobes in the aqueous phase, and thus interrupt the driving force for their association with each other and the latex surface.

有表面活性剂的着色剂被添加到预增稠的色调底色中[2]。添加着色剂会显著降低粘度，同时对涂层性能（例如抗流挂性和刷涂量）产生负面影响。涂料制造商可以尝试通过过度增稠着色基料来补偿粘度下降，但这会导致更高的成本、更高粘度基料的处理问题以及基于添加的着色剂的类型和数量的着色涂料的不同粘度。另一种方法是使用非缔合增稠剂（如 HEC）代替缔合增稠剂，但这会导致流动性变差。

在过去几年中，推出了一些 HEUR 产品，解决了添加着色剂时粘度下降的问题。该技术使用疏水基团，基团结合力更强，不太可能被表面活性剂破坏[3]。这种方法依赖于一种使用 pH 值触发的新型溶液，该溶液可防止增稠剂疏水物与所提供的纯增稠剂自身强烈结合，否则可能导致无法使用的高粘度。疏水性胺基团并入 HEUR 主链中，在低 pH 值下，胺被质子化，由此产生的电荷排斥可防止疏水物缔合，否则会产生高粘度。一旦在较高的 pH 值下添加到配制的涂料中，胺就会去质子化，然后疏水基团可用于缔合。

影响 HEUR 增稠剂效率的一些其它因素包括乳胶聚合物表面的乳胶细微性和疏水性。由于可用于与疏水物结合的表面积更大，HEUR 对较小粒径的胶乳更有效。当两种相似的胶乳聚合物以相同体积的固体和颜料体积浓度 配制时，粒径较小的胶乳将需要较少的 HEUR 增稠剂以达到目标粘度。然而，乳胶聚合物组合物也会对 HEUR 效率产生很大影响，更多疏水性主链组合物需要更少的 HEUR 来达到粘度目标。例如，与纯丙烯酸树脂相比，HEUR 对苯乙烯 - 丙烯酸乳液通常更有效地增加粘度，而后者又比醋酸乙烯酯 - 丙烯酸共聚物更有效。

结论

本文仅简要介绍了流变学和流变学改性剂的一些重要方面，如果继续了解有关涂料配方这一关键方面的更多资讯，将对配方设计师有所帮助。流变学在涂层的生命周期内影响许多特性，包括在其制造、储存和应用过程中。流变特性还会影响最终的涂膜性能，以及最终使用者对特定涂料和品牌的态度。大量文献可以进一步促进这种持续学习，与此同时，流变改性剂的制造商继续研究和开发新的添加剂产品，以使配方设计师的任务变得更简单。

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Industrial coating formulations that contain high levels of solvents such as Butyl CELLOSOLVE are notoriously difficult to thicken with associative rheology modifiers.

Surfactants compete with thickener for the latex surface, as well as interrupt associations between hydrophobes on thickener molecules. Disrupting the three-dimensional network results in a lower viscosity. This effect is particularly problematic in medium to ultra-deep tint bases, where high levels of colourants containing surfactants are added to pre-thickened tint bases.[2] Viscosity drops on colourant addition can be significant, with a simultaneous negative effect on coating properties such as sag resistance and brush loading. Paint manufacturers can try to compensate for the viscosity drop by over-thickening the tint base, but that leads to higher cost, handling issues for the higher viscosity bases, and differing viscosities in tinted coatings based on the type and amount of colourant added. Another approach is to use non-associative thickeners such as HEC, in the place of associative thickeners, but this results in worse flow.

In the past several years, there have been some HEUR products introduced which address the issue of viscosity drop on colourant addition. One technology uses a hydrophobe group that associates more strongly and is less likely to be disrupted by surfactant.[3] This approach relies on a novel solution using a pH trigger that prevents the thickener hydrophobes from strongly associating with themselves in the as-supplied neat thickener, which could otherwise lead to unusable high viscosities. A hydrophobic amine group is incorporated into the HEUR backbone. At low pH, the amine is protonated and the resulting charge repulsion prevents the hydrophobe association which would otherwise create high viscosity. Once added to a formulated paint at higher pH, the amine is deprotonated, and the hydrophobe groups are then available for association.

Some other factors that affect the efficiency of HEUR thickeners include the latex particle size and hydrophobicity of the latex polymer surface. HEURs are more efficient with smaller particle size latexes due to the higher surface area available for association with the hydrophobes. When two similar latex polymers are formulated at equal volume solids and PVC, the latex with smaller particle size will require less HEUR thickener to reach a target viscosity. However, latex polymer composition can also have a large effect on HEUR efficiency, with more hydrophobic backbone compositions requiring less HEUR to reach viscosity targets. For example, HEURs are generally more efficient at building viscosity with styrene-acrylic latexes compared to all-acrylics, which in turn are more efficient than vinyl acetate-acrylic copolymers.

Conclusions

This article only touches upon a brief introduction to some of the important aspects of rheology and rheology modifiers, and formulators would be well served by continuing to learn more about this critical aspect of paint formulation. Rheology influences many properties during the life of a coating, including during its manufacture, storage, and application. The rheology profile can also affect both the ultimate film performance, as well as the end-user attitudes towards a particular paint and brand. A large body of literature exists to further that continued learning, and in the meantime manufacturers of rheology modifiers continue their research and development of new additive products to make the formulator's task less complex.