



# High-Solids Headspace

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This article addresses some of the key challenges associated with formulating resins at high solids levels and outlines the potential for Michael addition chemistry to raise coatings solids levels to new heights. This topic is relevant because reducing emissions (without increasing the CO<sub>2</sub> footprint) is a critical sustainability pillar for the coatings industry.

First, a bit of discussion as to the problems associated with high-solids coatings systems. Arguably, the three most relevant parameters are viscosity, solids and hardness. Viscosity is perhaps the simplest to address, as it is intuitive that adding solvent reduces the viscosity of paint and that to increase the solids of a paint one needs to reduce solvent content. All things being equal, reducing solvent content raises paint viscosity, leading directly to application issues (atomization, flow, leveling, etc.). It is difficult to apply paint that has the consistency of mud, isn't it? Leaving aside options like switching to lower-oil-absorbing pigments or stronger solvents, one immediately looks to the resin in the coating for an answer.

Expanding the discussion, an important comparison may be drawn by looking at some of the earliest resin systems — linseed oil and thermoplastic acrylics (TPAs). TPAs lacquer dry, while linseed oil oxidatively cures. In the case of good old linseed oil, initially, it's quite fluid and low in viscosity, but upon application and with a bit of time, it reacts with oxygen, crosslinks, and viscosity and network molecular weight rise, and hardness and resistance levels are ultimately achieved. TPAs on the other hand are quite static in that they don't crosslink and develop properties once solvent evaporates. Of course, the problem with TPA-based coatings is that they are quite high in viscosity, coming from their very high molecular weight. The point here is that in order to maximize the solids levels of any paint, as with linseed oil, the system needs to begin its life in a low-viscosity state, which enables application, and then react and build viscosity and hardness in order to deliver film hardness and performance.

## Challenges in Formulating High-Solids Acrylic Polyols for 2K Urethane Systems

Taking the discussion into the 21st century, it's hard not to think about two-component (2K) urethane systems as they represent the gold standard in providing most of the highest-solids, versatile and durable coatings in the market. If we look at these systems, like linseed oil, they start their lives in a low-viscosity, relatively high-solids state but react with isocyanate (as opposed to oxygen) to develop the bulk of their properties. Of course, some 2K urethane systems are made with alkyds and cure partly by both oxidation and crosslinking with isocyanate.

Applying the question of how to raise solids in 2K urethane systems from 65% (about 400 g/L) to 80 or 90% (about 150 g/L) is an important one, as although waterborne options can typically deliver low VOC levels, they tend to have a much lower application bandwidth. For simplicity then, let's focus on the resin and assume we're using the best solvent, the lowest oil absorption pigments imaginable and the fastest, lowest-viscosity isocyanate for crosslinking your system. What's left is the need for a resin, a polyol (a resin with hydroxyl or "OH" functionality) available for reaction with isocyanate, which has remarkably low viscosity, all primary hydroxyls as they react the fastest, enabling rapid hardness development. Of course, our polyol once reacted with isocyanate needs to stick like glue, have remarkable chemical resistance, hardness, flexibility and UV stability, and withstand large bullets fired from close range. We'll keep our focus only on solids.

The resin industry has determined ways to make polyols that are as low in molecular weight as allowed. "Allowed" meaning that the molecular weight is above 1,000 Daltons so that it qualifies as being "polymer exempt". In short, the EPA, ECA and many other regulatory authorities will grant product registration that officially enables a company to sell its material based mainly on molecular weight. If the resin or any other substance is not polymer exempt, then expensive product-substance registration is required in order to legally sell the product. The reason for this is that generally, smaller resins or molecules have higher potential for human and environmental toxicity. One could imagine that it's a lot easier for a small molecule to penetrate your skin and make trouble relative to a large one. If you do want to sell a new small molecule (<1,000 MW) then it's going to need a pretty solid business case with a bit of money, along with an appetite for risk, as you'll need to do a lot of expensive toxicity testing that may ultimately result in an MSDS that is so unattractive that no one will buy your latest miracle. So, we see another physical limitation to increasing solids in that we have a molecular weight floor of 1,000.

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The good news is that at a MW of around 1,000, viscosity is quite low and solids relatively high. The bad news is that small, low-MW polymers by definition have a low Tg and are generally soft, and at the synthesis level it is difficult to guarantee the presence of hydroxyls on them. If a polyol fraction does not have a hydroxyl then it doesn't react with isocyanate, and it just sits in the film and acts as a plasticizer or softener. To better understand the relationship between molecular weight and hardness or Tg, one may google or wiki search on the Flory Fox equation.

So, with such a small molecule, how does one maximize the hardness of the polyol so that the resultant polymer and coating film are also hard? The simple answer is to use harder (higher Tg) monomers to make the polyol. Easy, right? The general problem is that once again, just like increasing molecular weight, higher-Tg monomers in a polymer backbone generate higher viscosities. So again, another headwind for high solids at the monomer Tg level.

There are monomers and there are monomers. Special monomers finding utility in reducing viscosity while keeping solids and hardness levels high are referred to as "bulky monomers". Bulky monomers are relatively large and nonlinear, but importantly they allow for more polymer in a smaller space or volume. The resultant molecular density (more polymer in the same or less volume) directly leads to increased hardness at a given viscosity. Use of bulky monomers is relatively well known and remains an important resin-formulating tool, enabling the highest-solids, highest-performance acrylic polyols in use in 2K urethanes today.

There is one last formulating tool worth mentioning. To keep resin viscosities as low as possible, one may optimize the synthesis procedure such that the "polydispersity" of the resin is as low as possible. Polydispersity is a measure of uniformity of molecular weights in a polymer sample. Low polydispersity means that the distribution of molecular weights in the sample is narrow, with few low- and high-molecular-weight molecules present. To clarify, resins are polymer strings of generally the same composition and size (molecular weight), however, relative to the average size or molecular weight of the resin, some molecules are higher and some lower. In general, the resin formulator tries to minimize the amount of larger, undesirable, higher-molecular-weight resin fractions in the polymer solution. It is interesting to note that in many cases the number of larger, undesirable polymers is nearly equal to the number of smaller fractions, which are also undesirable... so one might assume that the viscosity impact of overly large and small fractions from a viscosity standpoint balance each other out, but in fact they don't. The larger, higher-MW polymers contribute more to viscosity than the smaller chains can counteract. So, yet another challenge for the resin chemist in keeping viscosity down is to control and reduce the polydispersity to the highest degree possible.

At this point hopefully a basic appreciation of the challenges in formulating high-solids acrylic polyols for 2K urethane-based systems is understood and appreciated. Many of these principles also apply to polyester polyols. It's hard to predict if new acrylic synthesis routes or new monomers will arrive that will enable appreciably higher-solids, lower-viscosity polyols for use in 2K systems. New monomers as referenced above are below 1,000 Daltons and as such carry business risk and very expensive registration costs, so to expect new monomers to save the day would be optimistic.

At the synthesis level, traditional acrylic synthesis is done by addition reaction across double bonds (initiated with peroxides). Non-traditional synthesis routes including ATRP (Atom Transfer Radical Polymerization) and RAFT (Reversible Fragmentation Chain Transfer) are being explored and predicted to deliver performance improvements because hydroxyl functionality can be placed precisely where it is needed along the chain and polydispersities can be very low. Commercial implementation is a ways off, and solids improvements of much greater than 50 g/L would also seem optimistic.

Based on the issues mentioned including molecular weight, Tg, polydispersity and others, it's generally agreed that the available head space to raise the solids of acrylic polyols is minimal, including the use of the existing tricks of the trade and future isocyanate iterations. So what do we do when we're stuck in a box? We jump out of it and move to a different chemistry!

## A New Chemistry Based on Michael Addition

Allnex has developed a chemistry based on Michael addition that delivers appreciably higher solids and much faster cure that does not rely on isocyanate. This novel chemistry is referred to as ACURE™ and it leverages Michael addition's speed and kinetics with a CO<sub>2</sub> blocked base catalyst. Kinetic control agents are used to manage open time and appearance. The simplest ACURE binder systems use a malonate functional polyester with a very low molecular weight, and acrylate functional monomers that are often well below 1,000 MW and include materials like diTMPTA. Using two very low-molecular-weight resins at the onset enables remarkably high paint solids levels of 80-95% with low viscosity and excellent application properties. The blocked catalyst enables hours of pot life.

There is little doubt that the key attributes of Michael addition chemistry are appealing, stemming from its ultra-high-solids capabilities and significant curing energy reduction potential. As mentioned previously, reduced emissions (with reduced CO<sub>2</sub> footprints) must be a key sustainability pillar for our industry. Additional benefits with this type of chemistry are also quite profound and include being isocyanate and tin free, and some versions of ACURE have bio contents of over 50%.

## Conclusion

In conclusion, raising solids in traditional 2K urethane-based systems is a critical challenge for the industry and its pursuit of sustainability. It is difficult to imagine that breakthrough innovations will arrive with traditional urethane chemistry due to the inherent challenges mentioned in this article. Arguably, those with a vested interest in these systems need to be open to exploring and investing in new technologies. ACURE and Michael addition are hard to ignore in this respect. One thing is certain, if we're serious about sustainability, we must not only think differently but consider and develop new options. Perhaps relevant: The definition of insanity = doing the same thing over and over again and expecting a different result.