

Performance Solvents—What are They, Why are They Important?

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Introduction

In the golden age of paint formulation, when nearly all formulations were solvent based, the efficiency with which the solvents left the applied film was far more critical to the formulator than the degree to which the binder system was dissolved by the solvent. Today's formulation criteria increase emphasis on reduced VOCs, and therefore efficient vehicle systems with the lowest possible viscosity and the highest solids loading have become as important as being able to actually apply the coating in a defect free film.

It is necessary for the modern formulator to wring the best application properties that they can from a reduced volume of sometimes sub-optimal solvents. This solvent or solvent blend must be efficient at dissolving the binder system of the coating. This makes modern solvent systems more complex, usually made up of a combination of solvents that in some way synergistically provide resin solvency, while fulfilling the coating's viscosity or application needs.

For these and other reasons, we as formulators are finding it increasingly beneficial to quit thinking of solvents as one large group. The easiest method of distinguishing between "old world" or commodity solvents and these new purpose-intended "tune-up" solvents is to come up with a whole new classification for the new products, hence the name Performance Solvents.

The Relationship of Solvent and Resin Dissolution

Obviously, the resin or binder portion of a paint formulation must be dissolved in a vehicle of some kind to allow further processing and final application. A resin, by definition, is an amorphous polymeric mass of molecular chains, which are entangled and held in place by secondary valency attractions between sites on adjacent polymer chains. Kinetic energy (provided, for instance, by a high-speed disperser) can partially overcome these valency attractions. This causes the polymer mass to stretch and move, allowing the relatively small solvent molecules to invade the polymer. If the inter-molecular forces acting between the polymer chains are stronger than those between the solvent molecules and the polymer chains, dissolution will not occur. In this case, the "solvent" introduced is a non-solvent for that polymer.

However, if the solvent has a stronger attraction to the polymer chain than it has for its neighboring chain, the secondary valency bonds break under the application of kinetic energy, and the invading solvent displaces each polymer chain from the next. Recombination of the polymer chains is unlikely, because the solvent molecules are populating the bonding sites. This process continues to act on the entire polymer or resin mass, until the polymer chains are separated and detangled, the resin chains float

The degree to which the molecules of this dissolved “resin soup” interact with each other and other components of the formulation (including pigments, fillers and modifiers,) establishes the viscosity of the final formulation. Viscosity is critical at many levels in formulation, from downstream processability, to application of the film to a substrate and the number of flaws experienced in the finished dry coating film.

Our Love-Hate Relationship with Solvents

Today, due to legislation and the economy, solvents have taken on a negative aura mostly because of their flaws as physical substances. They are expensive. They are free flowing and invasive, and difficult to clean up. Most are flammable to one extent or another, and can pose an explosion risk. Some are toxicological hazards. They are the single largest contributor to right-to-know, hazard and storage paperwork in a modern paint plant. Globally, their use causes a depletion of our scarce petroleum resources, and they can even do more harm than good to a coating if improperly used. Rising costs in the 1990s, tilted even further skyward since the fall of 2000 and the advent of VOC legislation have, caused formulators to reexamine their relationship with solvents on a large scale. As formulators, we hate them, but we need them. On the other hand, the minimization of their use challenges us intellectually and creates niche markets for our employers to exploit, insuring us future employment.

Classes of Solvents—Where Performance Solvents Fit

There are 10 classes of solvents falling into three categories. The first category of solvents are the hydrocarbons, which are generally mixtures of materials of different molecular weight, and are classified by boiling point rather than chemical structure. Members of this category are:

- Aliphatic hydrocarbons
- Aromatic hydrocarbons
- Chlorinated hydrocarbons
- Terpenes

The second and most important category is that of oxygenated solvents, where most of our Performance Solvent category resides. These pure chemicals have an occurrence of oxygen in the molecule at some point, and have greater solvency for most resin types used in coatings. Members of this group include:

- Alcohols
- Glycol Ethers
- Esters
- Ketones
- Nitroparaffins



And finally, in a class all by itself, is that strange little molecule, the “universal solvent”, water. Water is a category unto itself primarily due to its molecular structure, which is at once very good and very bad for coatings applications. In water, we have two active (exposed) hydrogen ions and one electronegative atom (oxygen). Instead of forming linear chains as (similarly structured) alcohols do, water molecules associate in three-dimensional arrays similar to cross-linked polymers. When associated with each other in this way, the strength of their secondary bonds is greater (more resistant to cleavage) than alcohols. Much higher amounts of energy are needed to dissociate the molecules and bond them with other materials than alcohols. This means that while water is an efficient solvent for many resin materials, it suffers from high specific energy and high boiling point. Unlike most solvents, the evaporation rate of water is greatly influenced by the ambient relative humidity at application and by air flow across the wet film. Finally, the same unique molecular structure that defines the low vapor pressure of water also dictates its high surface tension. This directly affects the formulation's ability to wet and stick to a substrate. This high surface energy, provided by the hydrogen ions, account for water's difficulty in wetting and obtaining a good adhesive bond to lower surface energy substrates. It is here that most Performance Solvents come to the fore; by essentially “fixing” water's bad contact angle parameters while leaving its positive capabilities intact.

In most waterborne systems of the emulsion and solution types, the addition of Performance Solvents is necessary. They are known to the industry by many names, but a general category name of co-solvents has been used in the industry for years. Co-solvents may comprise as much as 20% of a waterborne's formulation, and the amount necessary varies by the type of system being formulated. These materials are used for numerous purposes.

In emulsions, they may serve as coalescing agents, freeze-thaw stabilizers, and leveling and wet edge aids. In solution alkyds and acrylics, they can help solubilize vehicles of lower volatility, speed up water release, adjust drying rate, improve flow and leveling and control foaming. Many co-solvents are used to assist in pulling pigment dispersions. Others act as couplers, turning immiscible mixtures of water and resin into stable dispersions.

Performance Solvents as Coalescents

Because of the way emulsion coatings cure, it is always a concern that the small droplets of polymer suspended in the vehicle are allowed to coalesce into a contiguous film. Latex coatings, for instance, must be applied within a narrow range of temperatures, because the T_g (or glass transition temperature,) must be below ambient temperature, or heat must be applied to make the film coalesce. In this case, Performance Solvents do the work of copolymerization. Small amounts of these solvent materials can act as external plasticizers. The solvent molecules remain between the resin globules as the water in the coating evaporates. After the water evaporates, it migrates into the latex resin droplets and swells them, in effect forcing them to coalesce into a contiguous film.

Performance Solvents as Dispersants

Some dispersants have a negative effect on the water and corrosion resistance of a dry film. Formulators often try to reduce these effects with Performance Solvents, which can act as dispersing aids. They have an advantage over some surfactants because they evaporate completely from the film during the drying process and do not remain as water-attractants.

Performance Solvents as Defoamers

The materials can act as defoamers in certain systems because they are not soluble in water, but can impart low surface tension to the foam cell wall. They are employed in very small amounts, and again, have the benefit of leaving the formulation upon curing, causing no dry film complications.

Performance Solvents as Film Modifiers

Formulators often use these materials to prolong wet film mobility, allowing a slower recovery of rheology, in turn improving leveling. Certain fast drying coatings require a wet-edge modifier to eliminate material buildup in lapped areas. Some of these materials allow lapped areas to flow back, eliminating lap marks.

Performance Solvents in Solution Waterbornes

Some Performance Solvents are used in solution waterbornes as coupling solvents to improve binder solubility. In order for this to work properly, the solvent and water must leave the film at the same time. These materials assure this by forming azeotropes with the water in the formulation. An azeotrope is a mixture of multiple solvents which associate together and have a lower fixed boiling point than any of the solvents standing alone—a benefit of the formation of hydrogen bonds between the solvents.

Also, most solution systems do not decrease in viscosity linearly when water is added as a thinner—viscosity may actually increase when the attempt is made. The addition of certain performance solvents can reduce this effect and improve the efficiency of viscosity reduction.



Regulation, HAPs, VOCs, MIRs

Understanding the governmental regulation alphabet soup requires the ability to couple these solvents together in a formulation in a way that optimizes a formulator's control parameter, whether it be overall VOC content, hazardous air pollutant content or lower reactivity. A HAP is a hazardous air pollutant; one of 188 chemical compounds which EPA has determined presents, or may present, through inhalation or other routes of exposure, a threat of adverse health effects.

EPA as any compound of carbon, excluding carbon monoxide, carbon dioxide, generally defines a VOC, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions with NO_x, in the presence of sunlight, to create ozone, a major ingredient of smog. They are regulated in coatings according to the coating type and the volume of VOC in the formulation. A number of solvents, which have been determined by EPA to have negligible contribution to ozone creation, are exempt from regulation as VOCs in the US. These VOC exempt solvents can be useful in formulating to low VOC limits.

In addition, for many consumer product categories, EPA and California have determined that low volatility compounds may also be exempted from regulation as VOCs. These are generally solvents that:

- Having a VP < 0.1mm Hg at 20C; or
- Consist of more than 12 carbon atoms, if the VP is unknown; or
- Having a MP > 20C and which does not sublime (i.e., does not change directly from a solid into a gas without melting), if the VP is unknown.

Formulating to low MIR (maximum incremental reactivity) is a practice fairly new to the coatings industry and was instituted because not all VOCs are equally reactive with the atmosphere in forming ozone.

A concept, known as “incremental reactivity (IR),” was developed to assess relative atmospheric reactivity differences in VOCs. These differences have been quantified (recognizing that uncertainties in the measurements and calculations of atmospheric reactivity exist) and are the foundation for a different methodology for controlling ground-level ozone formation. This approach is quite different from the present VOC policy that recognizes only two classes of VOCs: exempt and nonexempt, with ethane being the boundary line between the two classes.

The California Air Resources Board (ARB) established photochemical reactivity-based limits using the new approach for regulating ozone formation from general aerosol coatings, effective June 1, 2002, and for specialty aerosol coatings on Jan 1, 2003. Both regulations replace the traditional mass-based VOC emission guidelines.

The most common measure of incremental reactivity in the US—and the one used by ARB in their recent aerosol rule—is the MIR (Maximum Incremental Reactivity) scale. Using this methodology, each VOC is assigned an individual reactivity value. This MIR value enables the formulator to compare the photochemical reactivity differences of various solvents used in aerosol coatings. Higher values denote more reactive compounds, which have a greater propensity to create ground-level ozone, and the formulator can reduce the VOC content of the formulation by substituting low-MIR solvents for higher-MIR solvents.

The ARB is working on developing similar rules for AIM (Architectural, Industrial and Maintenance) coatings and General Purpose Solvents, and the EPA has recognized the validity of this method. It is anticipated that more and more VOC regulations across the US may adopt a similar methodology in the future.

Performance Solvents Allow Formulators to Meet Technical Challenges

As formulators, we are hit from all sides by conflicting needs every day on the job. Our company's customers expect incremental increases in the performance of the coatings we design, but at the same time have no idea that government regulations have effectively narrowed the choice of solvents used in paint formulations to an unprecedented extent. Our employers sometimes require that we provide far more complex formulations than before in far less time. And then there's money. Although the new coatings formulations brought about by VOC regulations have more components, more expensive raw materials and are more difficult to manufacture, consumers are not really willing to reward this innovation with a higher purchase price per gallon.

A solid knowledge judicious use of performance solvents can go a long way in ameliorating these internal conflicts, while providing formulations of which we can be justifiably proud.

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PS: Go to <http://www.performancesolvents.com> and see how Performance Solvents are changing the coatings topography today, and find out how you can easily profit from a fuller knowledge of them.