Viscosity Control of Spray Applied Coatings - Balancing Environmental Compliance and Performance

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Abstract

Solvent free, UV curable coatings can be the first choice for many finishers looking to simplify their regulation processes. However, other options may be available for UV curable, spray applied coatings that can maximize process windows and still keep costs and regulatory issues manageable.

Introduction

In order to avoid complicated and expensive air permitting, many finishers turn to UV curable coating technology. A 100% solids formulation will not emit environmentally damaging solvents into the atmosphere. This technology can be successfully employed in many market segments. However, when lower viscosity formulations are needed, there can be added costs due to higher priced / specialty raw materials, narrowed processing windows, and /or specialty application equipment.

Formulation

Typical UV curable coatings can contain: oligomer(s), reactive diluent(s), photoiniator(s) additives, and sometimes pigments.

Oligomers

For free radically cured formulas, a variety of acrylated oligomers exist to provide the proper coating properties. Urethane acrylates provide the best exterior durable properties. Polyester acrylates make excellent pigment wetters. Epoxy acrylates can make some of the most abrasion and heat resistant coatings. Oligomers will provide the bulk of the coating properties; however, they are also the component that can have the largest effect on viscosity. Some urethane and epoxy acrylates' viscosities are so high that they must be cut in reactive diluents just to get them out of the reactor. Even then, they may require the addition of heat to allow for handling. Some typical viscosities are listed in Table 1.

Table 1: Acrylated Oligomer Viscosities

Chemistry	Viscosity (20C)
Di-functional Urethane Acrylate	43,930 cPs
Hexafunctional Urethane Acrylate	35,000 cPs
Epoxy Acrylate	25,000 cPs (cut 20% in reactive diluent
Polyester Acrylate	40,000 cPs

Reactive Diluents

Reactive diluents will vary by structure (linear or cyclic) and functionality (one to six acrylate groups being the most common). Reactive diluents can greatly enhance the coating's properties. They are also the best means to control the viscosity. Unfortunately, some can also be strong skin and/or eye irritants. Irritancy can be rated on the Draize scale; the higher the number, the more irritating the material. Common reactive diluents and their ratings are listed in Table 2. Hexane diol diacrylate (HDDA) is one of the most efficient viscosity reducers; however, it also has one of the highest Draize ratings for skin irritancy. Pentaerythritol Triacrylate (PETA) is excellent for abrasion resistance, but is categorized as a severe eye irritant. Formulators can be challenged to find the right balance of properties and minimize irritancy concerns for solvent free coating systems.

Table 2: Irritation of Reactive Diluents - Draize

Reactive Diluent	Skin Irritation (8 max)	Eye Irritation (110 max)
IBOA (Isobornyl Acrylate)	2.5 (minimal)	20 (minimal)
TPGDA (Tripropylene Glycol Diacrylate)	2.5 (minimal)	57 (moderate)
PETA (Pentaerythritol Triacrylate)	4.6 (moderate)	109.2 (severe)
TMPTA (Trimetholpropane Triacrylate)	5 (moderate)	46 (moderate)
HDDA (Hexane Diol Diacrylate)	6.2(severe)	16 (mild)

Photoiniators

Photoiniators are the chemicals necessary to start the curing mechanism. They can be liquid or solid. When the photoiniator is a solid, solvency in a 100% solids coating formulation needs to be addressed. Again, reactive diluents are called upon to achieve this task.

Additives

Typically, additives can be used for: flow and leveling, slip and mar, enhanced adhesion, protection from exterior degradation, pigment orientation, and/or prevention of pigment settlement. For some additives, compatibility can be an issue. Polarity of the system may come into play. To help control polarity, choice of reactive diluents is once more key. Also, some additives, such as UV Absorbers (UVAs) and Hindered Amine Light Stabilizers (HALs) can be solids, again relying on solvency of the reactive diluents.

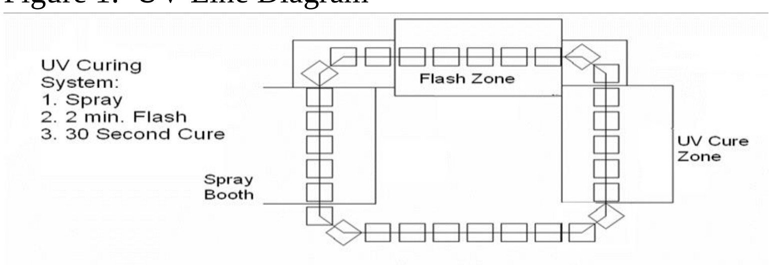
Pigments

Pigments are used to provide color or special effects to a coating. For an opaque white, high levels of titanium dioxide are typically used. As a rule, the higher concentration of pigment, the higher the viscosity. In addition, matting additives, typically, but not always silica, can be used to lower the gloss of a coating. This can be problematic in solvent free coatings in two ways: viscosity increase and flat orientation. The majority of fillers that are used to lower gloss tend to cause a dramatic increase in viscosity. Also, in order for the particles to be effective, they must orient at the surface of the coating. If the viscosity is too high, these particles will be trapped in the interior of the coating and will not have the intended effect of lowering the gloss.

Processing

UV curable coatings have the advantage of much shorter processing and more compact line designs than conventional coatings. A typical process would be five to ten minutes in duration and include: spray, flash, cure. (See Figure 1 for a line schematic.)

Figure 1: UV Line Diagram



100% Solids

Without any solvent in the formulation, finishers do not have to be concerned with air permitting for volatile organic compounds. In addition, since there is no solvent to evacuate, flash time and temperatures can be shorter and lower. This is extremely important when dealing with heat sensitive substrates like PVC. The purpose of a flash zone in solvent free coatings would be for flow and leveling rather than solvent evacuation. However, depending on the properties desired, sprayable viscosities can be difficult or costly to achieve. Table 3 lists various type of spray guns and optimum viscosity ranges. In general, as the ability to spray higher viscosities increases, so does the cost of the equipment. This is important information to consider when applying 100% solids formulations. As previously mentioned, viscosities of acrylated oligomers can be on the high side. To control application viscosity as a formulator, some oligomers with optimum properties may be eliminated due to inability / expense of processing.

Table 3: Spray Equipment Comparison

Gun Type	Viscosity Range	Cost (Relative)
Conventional and HVLP	22 seconds (Zahn 1) – 25 seconds (Zahn 2)	$
Air Assisted Airless	Up to 28 seconds (Zahn 3)	$$
Rotary Atomization	Up to 45 seconds (Zahn 3)	$$$$$$

In order to bring the coating viscosity down, more reactive diluents may be required. Table 4 lists the same oligomer with various reactive diluent reductions. It quickly becomes apparent which diluent has the biggest effect on viscosity. As previously mentioned, the use of certain diluents can increase the chance of skin and/or eye irritancy. In addition, some diluents are considered "swelling monomers". This means that they can attack and etch certain substrates. HDDA, one of the best diluents but higher skin irritancy, is such an example. Polycarbonate and certain grades of ABS are examples of polymers that can be etched by too aggressive of diluents / solvents. A blend of diluents is usually employed to balance viscosity, irritancy, cost and performance.

Table 4: Oligomer Viscosities with Reactive Diluent Reductions

Oligomer	Viscosity	25% HDDA	25% TPGDA	25% IBOA	25% TMPTA
Di-functional Urethane Acrylate	43,930 cPs[1]	4,720 cPs[2]	8,233 cPs[3]	8,133 cPs[3]	18,200 cPs[1]

Brookfield DV 1 Viscometer; 60 rpm; 21.5C
1 spindle RV-7
2 spindle RV-5
3 spindle RV-6

Even lower viscosity coatings are critical when spraying low (5-7 microns) dfts. If the viscosity is too high, the coating will not have acceptable leveling, leading to orange peel and other surface defects. An extended or higher temperature flash may be required to achieve acceptable appearance; thus adding to process time.

Of course, there are mechanical ways to lower the viscosity. Coatings can be heated prior to spraying to lower the viscosity and improve flow and levelling. Some care is required to make sure that excessive heat is not used, nor that the coating be exposed to extended time at elevated temperatures. Doing so can cause degradation of stabilizers and lead to premature polymerization. These options will add cost to the line design. Basic heated coating systems can run $5-7000 to install.

Conventional Solvents

Conventional solvents can solve a lot of the previously mentioned issues. Much lower viscosities can be obtained with the same amount of organic solvent (Table 5). They are also much more efficient at lowering viscosities (Table 6). So, even if solvent free formulations are not an option, higher solid versions may be.

Table 5: Oligomer Viscosities with Reactive Diluent and Organic Solvents Reductions

Oligomer	Viscosity (cPs)	25% HDDA	25% TMPTA	25% Acetone	25% Butyl Acetate	25% IPA
Di-functional Urethane Acrylate	43,930[1]	4,720[2]	18,200 cPs[1]	460 cPs[3]	1,193 cPs[2]	1,333 cPs[2]

Brookfield DV 1 Viscometer; 60 rpm; 21.5C
1 spindle RV-7
2 spindle RV-5
3 spindle RV-4

Table 6: Oligomer Viscosities Varying Amount of Organic Solvent

Oligomer	Viscosity (cPs)	25% HDDA	10% Acetone	25% TMPTA	5% Acetone
Di-functional Urethane Acrylate	43,930[1]	4,720[2]	5,340[2]	18,200[1]	15,700[3]

Brookfield DV 1 Viscometer; 60 rpm; 21.5C
1 spindle RV-7
2 spindle RV-5
3 spindle RV-6

Although the cost of solvents will vary, the majority of solvents used in the coating industry are lower cost than most reactive diluents. This will in turn reduce the cost of the coating. In addition, organic solvents tend to have lower surface tensions than reactive diluents (Table 7). Having a lower coating surface tension can help wet out less than perfectly molded parts; consequently, widening the process window and decreasing scrap rates. In addition, for low gloss coatings, as the solvent evaporates, it carries the silica matting additives to the surface and improves the appearance of matte finishes.

Table 7: Surface Tensions of Organic Solvents and Reactive Diluents

Solvent / Reactive Diluent	Surface Tension (dynes / cm^2)
Isopropyl Alcohol	21.3
t-butyl acetate	22.4
Butyl Acetate	25.1
Methyl Amyl Ketone	26.1
Acetone	26.4
Dimethyl Carbonate	28.5
IBOA	30.5
TPGDA	32.7
HDDA	35
TMPTA	36.2
PETA	~39

As the name suggests, organic solvents are also beneficial when needing to dissolve solid raw materials, like photoiniators and UVA / HALs.

Although organic solvents offer multiple benefits, they are considered destructive to the environment and may require cumbersome permitting and regulations. In addition, there are some solvents that are considered Hazardous Air Pollutants (HAPs). These are solvents that are known to cause cancer and other serious health impacts. Even stricter regulations are required for these materials. A list of some common HAP solvents are in Table 8.

Table 8: HAP Listed Solvents

Benzene	Methyl Ethyl Ketone
Diethanolamine	Methyl Isobutyl Ketone
Ethylene glycol	Toluene
Hexane	Xylene
Methanol	

As per the Clean Air Act Amendment of 1990

Like aggressive reactive diluents, certain solvents can attack sensitive substrates. This likelihood increases as flash time / temperature increases. Slower evaporating solvents will greatly improve flow and levelling; however, the slower the evaporation, the longer the dwell time in the flash oven. Which, consequently, lengthens processing time and can potentially lead to substrate attack.

Water

Water reducible UV coatings can also address several of these issues. Water is not under regulation by the EPA and is not a skin or eye irritant. Many finishers are finding success with aqueous UV curable coatings.

Like all options, there are drawbacks. If the substrate is non-porous, flash times can be longer to ensure the evacuation of all the water. Additionally, some co-solvents, which can be subject to regulations, may still be necessary to assist in water evacuation. Although improving, water reducible oligomer choices are limited, especially if needing exterior durability. In addition, there are limited number of photoiniators and additives that are compatible in an aqueous UV coating. As a result, the materials that are available, tend to be higher cost.

Since the coatings contain water, storage and shipping conditions are critical in the winter months. If stored or shipped at below freezing temperatures, the coating can freeze and must be thawed prior to using. In some instances, this can negatively affect the stability of the formulation. Finally, some aqueous UV coatings can be susceptible to moisture after curing. Formulators must be diligent in raw material selections and finishers must process properly to avoid this problem.

Volatile Organic Compound (VOC) Exempt Solvents

By definition, a solvent is considered VOC exempt if it has reactivity levels lower than or equal to ethane. Such solvents are not considered to increase ground level ozone concentrations. These materials do not requiring permitting for emissions; acetone being the most common VOC exempt solvent.

By using VOC exempt solvents, finishers can get the benefits of adding solvent to a coating (lower viscosity, lower cost, improved silica orientation, solvency to solid formula components, polarity control and lower surface tension) without the burden of the regulations.

But nothing is a panacea. Since they are still solvents, they will require a heated flash zone. Duration and temperature will vary based on solvent selection. Most VOC Exempt solvents, like traditional solvents, will still be classified as Flammable (Flash point below 38C). Table 9 lists flash points of several solvents and reactive diluents. All flammable materials require proper safety precautions to prevent sparking, fires, and/or explosions. There are not as many choices of VOC exempt solvents as other organic solvents. Acetone has a very high evaporation rate; which can lead to issues during application. Other VOC exempt solvents may be considered to have an offensive odor.

Table 9: Flash Points of Organic Solvents and Reactive Diluents

Solvent / Reactive Diluent	**Flash Point (C)**
Acetone	-17
t-butyl acetate	4
Isopropyl Alcohol	11
Butyl Acetate	25
Methyl Amyl Ketone	37
HDDA	93
TMPTA	100
TPGDA	100
IBOA	108
PETA	110

Conclusion

There is no perfect solution for low viscosity spray applied coatings, but there are multiple options. By balancing performance needs, capital investment, and regulatory issues, a choice can be made that will optimize output and minimize costs. When one's priorities are addressed, a UV curable coating and process can be realized that is profitable to the finisher while minimizing negative impacts on the environment.