# **UV Pigmented Coatings for Three Dimensional Metal Applications**

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#### **Abstract**

In the past, UV curing of coatings for three dimensional parts has presented a challenge to the formulator and end user alike. The same can be said of pigmented opaque coatings at higher film builds. When metal substrates are thrown into the mix, another degree of complexity is encountered. This paper will address the processing and formulation requirements involved with curing pigmented opaque coatings at high film builds on three dimensional metal parts.

#### Introduction

Formulation and application go hand in hand. The end requirements of the coating - adhesion, gloss, opacity, and weathering - are crucial in determining which raw materials can be used successfully. This paper will focus on a coating that is: opaque white; spray applied at 100% non volatiles; adheres to stainless steel; high gloss (>85 at 60°); and minimal weathering (6 to 9 months).

At the same time, application method will also influence the raw materials utilized. For example, spray applied coatings will not use the same raw materials as a roll coated coating simply due to the differences in the viscosity needed to apply each. With so many possibilities, where does a formulator start? Start at the end and work your way back.

# **Application Method**

Many ways exist to apply a UV curable coating to a substrate: spray, roll, dip, flow, gravure, vacuum coat, just to name a few. Part geometry, amount of production floor space, and the coating's solid content are just a few parameters that will influence the application method. Since the coating of interest will be spray applied, the other application methods will not be addressed.

In order to successfully spray a coating, viscosity and rheology are key factors. A coating must have a low enough viscosity so it can be properly atomized before hitting the substrate. However, to prevent runs and sags on the finished product, the coating must have a rheology that allows the coating to recover quickly and not run down the part. This balance can either be achieved in the formulation or by manipulating the coating by physical means during the application process.

The quickest way to lower the viscosity of a coating is to cut it with an organic solvent. However, if solvent is used, a separate processing step must be added in order to ensure its removal prior to UV cure. This step will not only take up production floor space and require additional capital investment, it will also decrease through put by increasing overall process time. The coating under discussion does not contain solvents, so other methods will be used to ensure that it is at the proper spray viscosity.

A highly viscous coating can be modified for spraying simply by heating the coating prior to application. Heat is a very efficient method to lower viscosity; however, it must be applied uniformly and not excessively to retain the integrity of the coating. Each formulation will vary, but in general, UV curable coatings should not be heated above  $120^{\circ} - 140^{\circ}$ F for extended amounts of time.

There is no absolute viscosity that will give the best performance. Optimum performance will vary depending on the thixotropy of the coating, part geometry and other processing variables. However, the viscosity can influence which spray method to use. Conventional spray guns, High Volume-Low Pressure (HVLP) guns, air assisted airless guns, and rotary atomizing units can all be used successfully. However, some formulations are better suited for specific application types.

# **Conventional Spray Guns**

Conventional spray guns are the simplest to use and have been around the longest. Simply stated, the coating is drawn through the gun nozzle. Compressed air is introduced to the coating; the air surrounds the coating breaking it into fine droplets. These droplets are then propelled towards the substrate. Once they hit the substrate, they will flow together giving a smooth continuous coating layer. Lower viscosity coatings (22 seconds, Zahn 1 up to 25 seconds Zahn 2) should work well with conventional spray guns.

#### **HVLP Guns**

HVLP guns are similar to conventional spray guns with the exception that they operate with lower atomization pressure. This will give higher transfer efficiency over conventional spray guns due to the decreased amount of overspray. The lower atomization pressure will greatly reduce the coating "cloud" seen with conventional guns. In some cases, orange peel can increase compared to a conventional spray gun. The viscosity range of conventional guns applies here as well.

#### **Air Assisted Airless Guns**

Air assisted airless can allow for better atomization over conventional and HVLP guns. Atomization air pressures are lower, but fluid pressures are higher, (200 – 1200 psi). Also, transfer efficiency is higher with the air assisted airless. This will allow the coating to build faster on the part over conventional and HVLP guns. If higher film builds are required, air assisted airless guns may be a better choice. A coating with a 28 second viscosity Zahn 3 sprays well with this set up.

## **Rotary Atomization**

Rotary atomizing units operate on a different principle. Instead of using air to atomize the coating, the units use centrifugal force. The faster the rotational speed, the finer the atomization. The rotary atomization can break the coating into finer particles which allows for a smoother laydown at lower film builds. Rotary atomization also works very well for high viscosity coatings. Coatings with a viscosity as high as 45 seconds on a Zahn 3 have been sprayed successfully in a commercial environment.

The following table (**Table 1**) lists some typical transfer efficiencies for each spray method. These are guidelines and should not be considered absolute values. Actual transfer efficiencies will vary depending on part style, spray set up, painting style, and other factors.

**Table 1: Spray Technique Comparisons** 

Spray Technique	Typical Transfer Efficiency
Conventional Spray	20 - 50%
HVLP	30 – 55%
Air Assisted Airless	60 - 80%
Rotary Atomization	65 – 95%

With metal parts, electrostatic spraying is a natural option. Adding electrostatics to the spray application will increase transfer efficiency. However, depending on the geometry of the part, it may present more problems. If the parts have deep recessed areas, electrostatic spraying is not the best choice. Due to Faraday cages, the charged coating particles will not transfer to the recessed areas, but will accumulate on the side walls instead. This will lead to uneven film builds on the part and potential runs in the thickest areas.

The coating discussed in this paper can be sprayed via any of these techniques. The viscosity is low enough to be sprayed via conventional or HVLP guns; however, the DFT will be around 2.2 - 2.6 mils in order to get a smooth, continuous film. If either air assisted airless or rotary atomization is used, this minimum wetting film build range can be lowered to 1.6 - 2.0 mils.

After the coating has been applied to the substrate, it will remain in liquid form until it has been exposed to UV energy. This stage of the process is called curing.

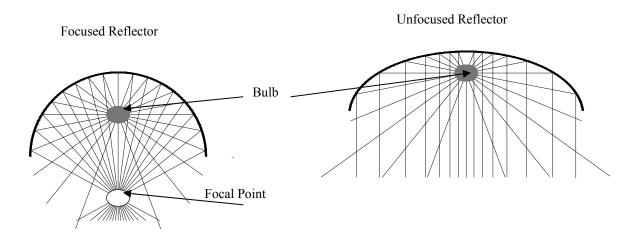
# Curing

UV cure is a line of sight process. This simply means that if the coating does not receive UV energy, it will not cure. This fact is crucial to successfully cure three dimensional parts. UV lamps must be placed in locations that allow for the energy to irradiate the coating. With complex three dimensional parts, the lamp placement can become quite creative to ensure that no shadowed areas are left underexposed.

Keep in mind that the lamp to part distance can make a vast difference in curing efficiency; the further the part is from the bulbs, the more the UV intensity will drop off. Lamps can be run in-focus or out of focus (**Illustration 1**). If the lamp to part distance is greater than the focal point of the lamp, it is better to run the lamps out of focus. This will ensure optimum UV intensity at the coating surface. Proper radiometry should be run to ensure that the optimum UV energy is reached.

There are two main types of lamps used to cure UV coatings: arc and microwave. These terms refer to the way in which the bulbs are powered. An arc system relies on an electric current to excite the gas molecules inside the bulb. A microwave bulb is powered by microwave energy exciting the gas molecules. The microwave systems are considered "instant on", whereas an arc system will need a few minutes initially to reach the optimum operating conditions. The start up time is but one difference between the two technologies. Others being: bulb size, bulb life, and heat produced. Despite these differences, once the systems are operating, there is little difference in the UV energy each emits.

**Illustration 1: Focused and Unfocused Reflectors** 



#### **Bulb size**

Arc lamps can utilize longer bulbs; microwave systems are generally six inches but can go up to ten inches. This does not mean that larger parts cannot be cured with microwave systems; multiple bulbs can be staggered to create the same curing area.

# **Heat production**

In general, arc lamps will produce more energy in the form of IR than a microwave system; however, there are ways to dissipate the heat emitted from an arc system – air or water cooled jackets – that could still make them a viable choice. If the parts being run are heat sensitive, microwave systems may be a better choice. In most instances, heat will not be a major concern with metal substrates. However, some instances when it could be a factor are in the immediate handling of parts after cure or if the parts contain flammable material.

#### **Bulb life**

An arc bulb will typically need to be replaced after 1500 - 3000 hours. Keep in mind that these bulbs will burn out from the ends to the center. The microwave bulbs have a longer life and generally do not need to be replaced until around 8000 hours. Both systems do require regular maintenance – reflector and bulb cleaning and rotation – to ensure proper UV output.

#### **Doped bulbs**

The UV spectrum is divided into 4 regions: UVA (320 – 390 nm), UVB (280 – 320 nm), UVC (250 – 280 nm) and UVV (395 – 445 nm). For most clear UV curable coatings, UVA and UVB are the critical regions of energy. Regular mercury vapor bulbs will cover these regions adequately and will work well with most UV curable coatings (Chart 1). However, adding pigments or increasing film builds may require special bulbs called doped bulbs. A doped bulb refers to the addition of another metal to the mercury in the bulb. Both microwave and arc lamps can use these types of bulbs. The two common metals used are iron and gallium. The presence of these metals will reduce the life of the bulb by 15 - 20%, but they will shift the UV energy spectrum (Charts 2, 3). An iron doped bulb will give a broader intensity in the UVA region. While a gallium doped bulb will provide greater intensity in the UVV region. For white coatings at greater than two mils, a gallium doped bulb followed by a regular

mercury bulb can give optimum depth of cure with a balance of good surface cure. Blacks and darker blues may benefit from an iron doped bulb combination. Since the doped bulb will provide depth of cure, it is important to have it before the mercury bulb. Formulations with different photoinitiators and pigments may require different lamp set ups.

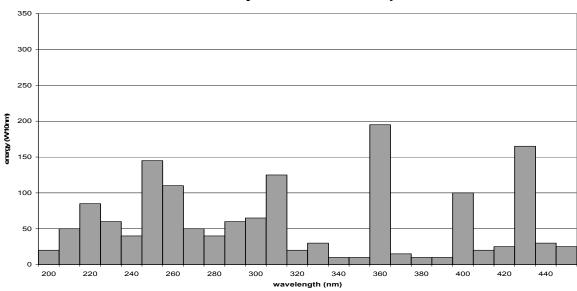
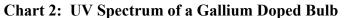
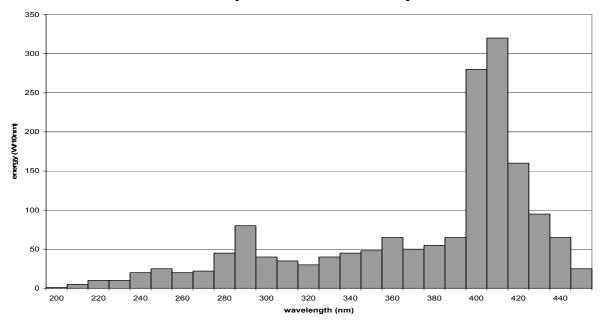


Chart 1: UV Spectrum of a Mercury Bulb





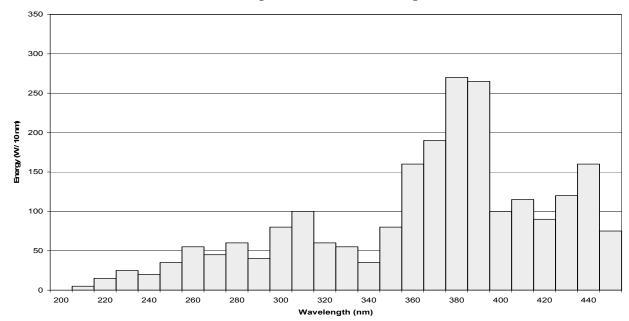


Chart 3: UV Spectrum of an Iron Doped Bulb

#### **Formulation**

Now that the ground rules are set for processing, formulation can begin. Based on the requirements set out in the beginning of the paper – high gloss, 100% NVM, and limited weathering – several raw material choices will be eliminated.

# **Oligomers**

The first choices to make in formulating are the oligomers. UV curable coatings can cure by either free radical or cationic mechanism. Many metal coatings utilize the cationic mechanism due to the lower shrinkage encountered. This lower shrinkage will generally provide better adhesion to metals. Since cationic cured coatings do not have great weathering characteristics, we will focus on a free radical formulation.

Free radical formulations are based on acrylate chemistry. The oligomers can be: urethane acrylates, epoxy acrylates, polyester acrylates, or acrylic acrylates. Each group has its positive attributes: urethanes weather well; epoxies cure quickly; polyesters wet pigments well; acrylics improve adhesion. Based on these general descriptions, any of these families could be used to formulate a coating for metal applications. Extensive screening must be done to find the best oligomers for the application. In most formulations, a blend of chemistries can optimize the performance characteristics.

#### **Reactive Diluents**

Once basic adhesion is obtained, the rest of the properties must be addressed. Since no solvent can be used to lower the spray viscosity of this coating, reactive diluents are necessary. Reactive diluents can best be described as lower molecular weight oligomers. It is due to this lower molecular weight that some reactive diluents can cause skin irritations. Not all reactive diluents are considered irritating, but individuals will react differently to each diluent, such as a bee sting allergy. Proper handling should be followed at all times.

Reactive diluents are classified by their functionality. They can be mono, di, tri, or multiacrylated. In general, the lower the functionality, the slower the cure rate and the more flexible the raw material will be. For example, isobornyl acrylate (IBOA) will require more energy to cure than trimethylpropyl triacrylate (TMPTA), but the IBOA will give much more flexibility and lower shrinkage than the TMPTA to the finished coating.

#### **Additives**

To enhance adhesion to metals, acidic adhesion promoters can be used. Although adhesion can be improved with these additives, care must be taken to ensure that they are compatible with the rest of the formulation. Components with basic functionality should not be used if an acidic adhesion promoter is in the formulation. Signs of incompatibility are: cloudiness, precipitates, rapid increase in viscosity or a dull appearance when cured. These additives should be used at lower addition levels.

Flow additives are used to improve the leveling and appearance of the coating. Again there are many choices on the market – silicone, fluorinated, and polymeric just to name a few. Although more efficient, silicone and fluorinated additives should be avoided if the coating will need to be recoated or decorated. These additives lower the surface energy of the cured coating so that if another coating is applied directly over the first layer, the liquid coating will reticulate and not form a uniform coat.

# **Pigments**

Of course pigments must be added to obtain the coloring. If an acidic adhesion promoter is being utilized in the system, it is wise to use pigments that do not have a basic surface treatment. There are many grades of each available on the market. Ease of dispersibility and undertone are characteristics that will determine which grade to use for a particular application.

Pigmented coatings add another degree of difficulty in curing UV coatings. Unlike thermal cured systems, pigments can interfere with the curing process. If the UV energy output of the bulb is compared to the absorbance of a white pigment, this becomes obvious (**Chart 4**). Below 400 nm, the absorption of titanium dioxide is so strong, that it can interfere with most of the energy output of the mercury bulb. A simple fix to this problem is to switch to a doped bulb (**Chart 5**). With a Gallium doped bulb emitting more energy in the longer wavelengths (greater than 400 nm), there is less interference with the pigment.

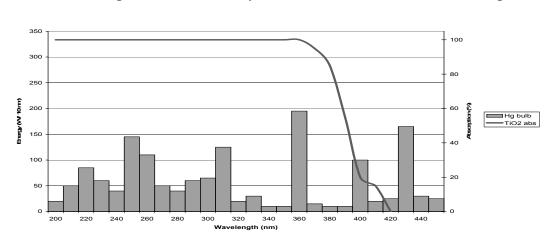
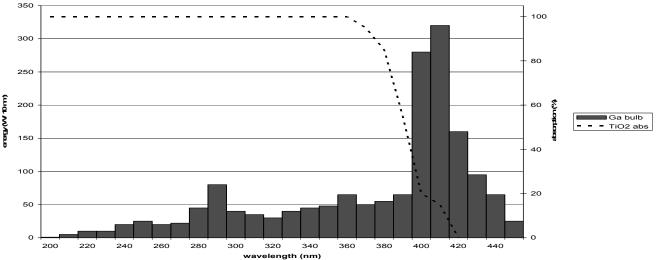


Chart 4: UV Spectrum of Mercury Bulb with Titanium Dioxide Absorption

Chart 5: UV Spectrum of Gallium Doped Bulb With Titanium Dioxide Absorption



Black coatings are difficult to cure because they absorb UV and IR energy. The absorption of IR in the form of heat can be a problem with heat sensitive substrates; the absorption of UV energy is a problem with cure. The pigment will be competing with the photoinitiator for the UV energy. This can lead to slower line speeds in order to obtain adequate cure, and with slower line speeds the substrate will absorb more heat.

While not absorbing UV energy, yellows are difficult to cure because they will filter the UV energy. This filtering will cause the photoinitiators to be less efficient, leading to slower line speeds.

The large amount of titanium dioxide required for opacity presents difficulty in curing white coatings. Pigment amounts will vary depending on the desired DFT of the coating and the amount of opacity needed. For applications where low film builds are called for, it is not uncommon for a formula to contain up to 45% titanium dioxide. If the film builds can be higher, less pigment is needed.

Although these colors are more difficult to cure, it does not mean that they are impossible. By proper bulb and photoinitiator selection, all colors can be successfully cured in a UV system.

## **Photoinitiators**

After oligomer selection, perhaps the most crucial formulating choice is the photoinitiator (PI). It is this component that makes the UV curing possible. Photoinitiators can either be for surface cure or through cure. Those that absorb energy at the longer wavelengths (>340 nm) are better suited for through cure of pigmented coatings. This is due to the fact that there is less interference with the pigment and the photoinitiator (Chart 6).

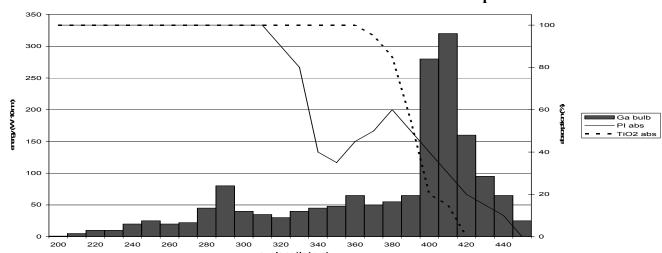


Chart 6: UV Spectrum of Gallium Doped Bulb With Titanium Dioxide and Photoinitiator Absorption

For white formulations, not only must the photoinitiator absorb in the longer wavelengths, it must also not cause yellowing. Efficient photoinitiators are on the market, but they must only be used in darker colors due to the negative effect they can have on the color of a white coating.

It is always important to balance through cure with surface cure. As stated earlier, UV coatings cure by line of sight. This means that they will cure from the surface of the coating down to the substrate interface. Usually, a photoinitiator package (two or more PI) is utilized that will cure both at the surface and at the substrate interface. If the surface cures too quickly, it will inhibit the amount of UV energy that is allowed to penetrate to the substrate. This will result in a wrinkled or "pinched" appearance. In severe cases, the surface may be completely tack free, but there will be wet coating underneath that has not had a chance to cure. This is more common as film builds increase to the 4 mil or greater range. This is also when proper bulb selection will make processing much easier. If a gallium doped bulb, which emits in the longer wavelength region, is utilized first, the UV energy will be allowed to penetrate deeper into the coating. If it is then followed up with a standard mercury bulb, the shorter wavelength UV energy can finish the curing at the surface. This is a prime example of formulating and application working together to optimize the cure process.

Conversely, if an insufficient amount of surface cure photoinitiators is used, the surface of the coating will be tacky (or even wet) and the gloss will be lower, but the substrate interface will be cured. Going back to bulb selection, as the film builds increase, it becomes more important to use two types of bulbs. The thicker the coating, the deeper the UV energy has to penetrate to cure all the way to the substrate. A white coating at greater than 3 mils will have a very difficult time curing tack free at the surface with only a gallium doped bulb.

The following table (**Table 2**) shows some comparisons between bulb combinations, film builds, and the effects on cure and appearance on a white coating. UV energy was measured with a Power Puck radiometer. Although all bulb combinations gave adequate cure responses at a DFT of 2 mils, the appearance of those cured with only a standard mercury bulb or an iron doped bulb was not acceptable.

The bigger differences arise when the coating was sprayed at 5 mils DFT. Based on cure response and appearance, the gallium doped bulb followed with a standard mercury bulb was the only combination to give acceptable results. The gallium doped bulb could not provide adequate surface cure by itself. The other bulb combinations could not cure the coating all the way to the substrate. The ability to be able to cure at a variety of film builds is crucial when coating three dimensional parts. Spraying recessed or shadowed areas can present difficulties in maintaining a consistent film build over the entire part. Coating will build quicker on flat open areas than in these problem sections.

Table 2: Effects of Bulb Selection on Curing of a White Coating

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Bulbs	UVA (320 – 390 nm)	UVV (395 - 445 nm)	DFT (mils)	Gloss (60°)	Cure	Appearance
Gallium /	2	2	2	97	good	good
Mercury	1736 mJ/cm <sup>2</sup>	2215 mJ/cm <sup>2</sup>				
iviercury			5	94	good	good
Gallium	1308	3492	2	97	good	good
			5	94	surface slightly soft	good
Iron / Mercury	2955	1468	2	96	good	good
			5	81	lacks through cure	wrinkled
Iron			2	92	good	okay
	2697	1347	5	83	lacks through cure	poor
Mercury	3742	1692	2	91	good	poor
			5	74	lacks through cure	poor

## Conclusion

The difficulties in UV curing an opaque coating on three dimensional metal parts are numerous. However, with the proper balance of application, curing and formulation this can be done successfully. Coating requirements will dictate much of the formulation; however, processing of the coating cannot be ignored. By optimizing all three areas, the end result will be a commercial success.

# Acknowledgments

Spectral distributions for the UV lamps are based on data from Fusion UV Systems. Photoinitiator absorption data is based on information provided by Ciba Speciality Chemicals Corporation.