

UV-Curable Paints & Coatings: A Practical Application of Quantum Mechanics

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Most manufacturing operations require a paint or coating treatment of some type (i.e., protective, identification, decorative). This is especially true for metal finishing where in many cases acceptance of the part by the customer is predicated upon the appearance of the part. Compliance with ever tightening environmental legislation will sooner or later be an issue for most all manufacturers who incorporate a coating operation. Consequently, manufacturers must seek and implement new technology that will not only provide them with a competitive advantage but will also comply with environmental legislation, simplify production, and enhance product quality. One coating technology that professes such a win-win scenario is ultraviolet (UV) coating technology. This article will, in addition to providing an overview of typical features and benefits of UV coatings, touch upon basic quantum mechanical theory behind the technology in order to understand how such performance, features, and benefits are possible.

NO TIME FOR INCOMPATIBILITIES

Properly formulated, UV-cured coatings are capable of a minimal dwell time (the time between application and cure) on parts. As truly zero VOC, UV coatings require no flash-off time and UV cure can be near instantaneous, the potential for incompatibilities to manifest (between the coating and substrate) is minimized. For example, microscopic evaluation of metallic flake pigments in nitrocellulose basecoat films have shown that such paints may be clearcoated and cured without detrimental effect or disruption of the metal flake cluster patterns or cluster distribution. Though UV-curable resins may act as a "solvent" on some substrates generally the time required to solubilize the substrate is longer than the combined dwell and

cure time typical of UV coatings. Once cured the UV-curable coating is an extremely durable and stable polymeric system. UV-cured coatings will not revert to liquid form by solvent attack and generally are resistant to chemical attack.

The inherent stability and wide range of commercially available raw materials provide the basis for a wide latitude of formulation parameters capable of producing engineered, final properties in the cured coating. An example of the "formulation universe" for engineering such properties will be touched upon further in this article.

WHY UV WAVE LENGTHS?

To understand how UV-curable paints and coatings eliminate the drying process fundamental quantum mechanics need to be reviewed.

The realm of quantum mechanics differs from the realm of classical mechanics. Classical mechanics is a deterministic tool allowing us to accurately define and predict the behavior of macroscopic entities in a nonrelativistic system. Put simply, in cases where the subject system is not moving at high velocities the subject can be easily measured, quantified, and defined with such properties fully predictable at some time in the future.

Quantum mechanics takes into account the actual wavelike behavior microscopic and atomic particles take on as they gain speed toward relativistic levels (i.e., the speed of light). The faster a particle moves the more wavelike its nature becomes. The particle becomes hard to observe, the edges become fuzzy, outlines become more indistinct until it effectively disappears altogether per the time independent Schrödinger equation (Erwin Schrödinger, 1887-1961). The mathematical arguments behind the Schrödinger equation (a basic postulate of quantum mechanics—and unprovable), are beyond the scope of this paper.

The relativistic nature of the parti-

cle-turned-wave is such that its position in time and space cannot be defined with any certainty, rather only the probabilities of its various possible future locations can be calculated. The concept is rather simple in that if visible light energy is used to "observe" a relativistic particle then, by the time the light reflects off the observed object and travels to the mechanism making the observation, the particle under observation has moved in that time interval and is no longer at the observed coordinates. This uncertainty is the basis of the Heisenberg Uncertainty principle.

From this point predicting the location and behavior of a particle in the mathematical model of a one-dimensional box yields the concept of probability densities. Whereas classically, finding the particle at any given position within the box is equally likely for all possible positions within the box, quantum mechanically, the probability density of the particle exhibits "oscillations." The higher the energy in such a system the greater the frequency of the oscillations, with the upper limit of oscillations yielding the classical model of equal probability distribution throughout the box. (Imagine a ball bounding around in a box at light speed, it's everywhere at the same time!)

But how does this relate to UV energy? These principles, extended to the three-dimensional box model, define the orbitals of electrons in atoms. Orbitals are actually probability density plots of finding a given electron in a given energy state associated with a particular nucleus. When energized these electrons "jump" to higher energized states called excited electronic states. These energized electronic states are, however, unstable. The energized electron cannot return to its original state (ground state) while energized; hence, the electron's energy must be released, converted, or dissipated to return the electron to its original ground state. The way this energy

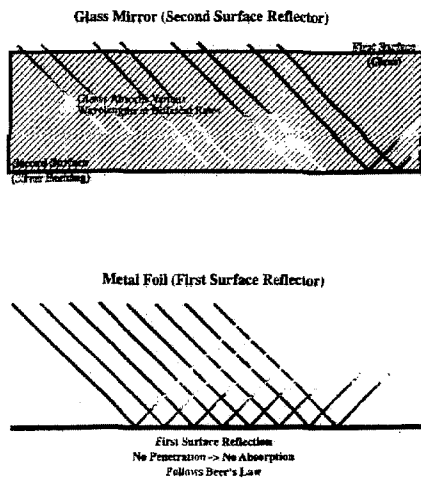


Figure 1. First order (surface) reflectors serve to distribute UV light throughout a coating chamber.

they required a direct "line-of-sight" exposure to high-intensity UV light sources in order to produce sufficient free radicals for the reaction to take place. Today highly efficient photoinitiator systems are commercially available. These systems can initiate UV cure with indirect exposure to UV light. In fact photoinitiators are commercially available that can use the natural UV found in sunlight to affect polymerization without introducing significant health considerations. Since this advance several retail, sunlight UV-curable products, which cure even on heavily overcast days and are non-irritants to the skin, are planned for market introduction within the next 12 months.

Though pigmented systems may require more UV light than nonpigmented systems the ability to "key" UV-curable paints to spectral outputs of lamps minimizes UV equipment requirements and expenditures. Also, the nature of and degree of pigment loading changes the cured physical properties of the pigmented coating from the clear coating. Pigments may detract from or add to physical properties, however, this factor is common to all paints and coatings.

Increased photoinitiator efficiency has resulted in elimination of line-of-sight-cure resulting in the ability to reflect UV light in a manner similar to reflective IR ovens. A method of distributing UV light throughout the curing chamber comes in the form of first order (surface) reflectors (Fig. 1). This concept and related techniques are

Table II. Reflective factors of various Substances at 254 nm

Material	% Reflectance ^a
Aluminum, etched	88
Aluminum, polished commercial	78
Aluminum, foil	73
Chromium	45
Nickel	38
Stainless Steel	20-30
Silver	22
Tin-plated steel	28
White-wall plaster	40-60
White paper	25
White cotton	30
White oil paints	5-10
White porcelain enamel	5
Glass	4
Water paints	10-30

^aValues obtained at normal incidence. The percentage reflectance increases rapidly at angles greater than 75%.

commonly used in IR drying systems and are used in UV curing systems as well.⁷ It is important to note that not all materials reflect UV with equal efficiency (especially at the critical wavelengths required for free radical generation). Table II contains data on UV reflectance ratings for various materials.⁸

FIRST VERSUS SECOND SURFACE REFLECTANCE: BEER'S LAW

The Beer-Lambert law relates the absorbance of light to the characteristics of the medium through which the light passes:

$$\log I_0/I = Ecl$$

where

E = extinction coefficient of the material
 c = concentration of the light-absorbing material

Table III. ASTM B 117 Salt Spray Test Results

Sample Identification	Scribe 96 hours	Field	Scribe 2,784 hours	Field
Phosphated Panels:				
A3	-	-	9	9
A4	-	-	6	9
B3	-	-	10	9
C2	-	-	10	9
D3	-	-	10	9
E3	-	-	10	9
Nonphosphated Panels:				
F3	0	0	-	-
G3	-	-	9	9
H2	-	-	9	9
I3	-	-	7	9
J3	-	-	6	9

l = length the light travels through the material

In general glass is opaque to UV and IR radiation; therefore, second surface reflectors such as silver-backed glass mirrors generally do not reflect UV light.⁹ This is due to the fact that UV light must pass through the glass layer (first surface), which absorbs a majority of UV energy before it even reaches the reflective silver backing (second surface); whereas first surface reflectors such as metal foils make excellent UV reflectors. It is vital to select reflective materials that reflect and not absorb critical UV wavelengths required to generate free radicals.

Given that critical curing wavelengths are known to the formulator and the appropriate reflective materials have been selected, reflectors may be used to facilitate non-line-of-sight UV cure. This is accomplished by positioning the reflective material to facilitate UV distribution or redistribution to non-line-of-sight areas on the target part. This implies that in properly designed UV chambers secondary and tertiary reflectance of UV energy can (and is) utilized in industrial curing processes.

PROFOUND PERFORMANCE

Properly formulated UV-curable, zero VOC paints and coatings exhibit profoundly superior performance over conventional coating systems. It is generally accepted that UV-curable coatings exhibit a wide range of chemical and weather resistant properties. This is partly due to the ability to control cross-linking density within the polymer and partly due to careful se-

Table I. Energies of Specific Wavelengths

Wavelength (nm)	Energy per Photon (eV)
200 (UV)	6.2
400 (Violet)	3.1
700 (Red)	1.8
1,000 (IR)	1.2

is released determines if it can be used as "fuel" for a chemical reaction.

Several mechanisms exist by which the electron may deenergize and return to ground state. The pertinent mechanisms to UV curing are: 1. emission of radiation (UV, heat, light, etc.) and 2. free radical generation (molecules in appropriate vibrational energy levels that disassociate into free radicals)

Energy released as light can be expressed as:

$$E_p = h\nu$$

where

E_p = energy of a photon (quanta)

h = Planck's constant

ν = frequency of the light

A quanta of energy can be measured in terms of electron volts (eV). Defined, 1 eV. equals the energy acquired by an electron accelerated through a potential difference of one volt. This equates to $1 \text{ eV} = 1.6022 \times 10^{-19}$ Joules.

Usually at least 1.5 to 2 eV are required to put a molecule into an excited electronic state. Using the above, Levine calculated the energies of specific wavelengths as shown in Table I.

Experimentally, it has been observed that UV cure can be initiated with as little as $5.0 \times 10^{-2} \text{ J/cm}^2$ (average over 320–390 nm). This was done by the author by using a UVI-CURE Plus Radiometer. The significance of this reading is that it is the average natural sunlight UV dosage for Miami at noon.^{1,2}

Using the same radiometer, a flat-line industrial UV curing system imparts a UV dosage of 2.026 J/cm^2 with a line speed of 10 ft/min and a UV exposure "window" 4 in. wide. (Dosages of greater than 7.4 J/cm^2 have been observed and measured by the author on 3-dimensional systems in the field.)

With a 4-in. wide exposure "window" the time exposure at 10 ft/min is 2 sec; hence the UV energy imparted to the surface is $1.013 \text{ J/cm}^2/\text{sec}$. In

the 2 sec of exposure each square centimeter of the surface receives 2.026 J/cm^2 compared to the required $0.00000000000000000032044 \text{ J/molecule}$ required for photoinitiation!

Calculation of average molecular diameter to determine molecular density per square centimeter and thus arrive at the theoretical dosage of UV per molecule is a function of the particular formulation being evaluated. This calculation is particular to each individual formulation and is left as an exercise for the interested reader.

How does this relate to the 1.5 to 2.0 eV required to force an energy transition? According to the Stark-Einstein Law, there exists a one-to-one correlation between the number of photons absorbed to the number of molecule transitions to an excited electronic state. Thus, 200 nm photons (UV photons) individually carry three times the required energy (in eV) to force an absorbing molecule into an excited electronic state. Thus, UV photons have abundant energy to cause suitably absorbent chemical moieties to generate free radicals, whereas higher wavelengths, visible light, and IR photons do not.

Free radicals are extremely energetic molecules capable of producing extremely fast reactions. Such time frames range from as slow as 1 sec to as fast as 0.0000000001 second; however, free radical-based polymerization reactions are inhibited by the presence of oxygen.³ Post UV exposure curing was previously thought to be a universal phenomenon to UV acrylate chemistry and was appropriately dubbed the "dark cure." Recent spectroscopic investigations have shown that this phenomenon is linked to oxygen cure inhibition at the surface and not distributed homogeneously throughout the film thickness.⁴

The reaction rate of polymerization in the absence of oxygen has been reported to be 17.5 times faster than in the presence of oxygen. Zero VOC paint formulations can be tailored to take advantage of this effect or to resist it. In seeming defiance to the Stark-Einstein Law the efficiency of photoinitiator systems has advanced to the point that multiple free radicals can be generated from one molecule, given adequate energy is imparted to achieve a conducive vibrational energy state by

which the photoinitiator can disassociate into free radicals.⁵

This makes it abundantly clear why UV and lower wavelengths of visible light are used to initiate photochemical reactions while higher wavelengths of visible light and IR cannot be used. A simpler analogy of the photochemical reaction mechanism is the photoelectric effect—solar-powered paints and coatings!

Of special note, the energy mechanisms above are hampered by the presence of nonreactive molecular entities. In the case of zero VOC paints and coatings nonreactive diluents, such as solvents, alcohols, oils and water, decrease the effectiveness of the energy transfer mechanisms by absorbing activation energy and dissipating it through a nonreactive mechanism.

Use of nonreactive diluents or solvents in UV-curable systems confound the near instantaneous mechanism of UV cure by requiring a flash-off time to eliminate the nonreactive diluent or solvent prior to cure. Any such moieties, which do not flash-off and remain in the system, will cause at least one of the following:

1. Retarded/inhibited cure rates
2. Film flaws due to solvent boil-off/evaporation during cure
3. Autoignition of solvent (UV lamp surfaces operate at 250°C and hotter, well above the autoignition temperature of most solvents).

Rather than using nonreactive diluents as viscosity controls, novel methods have been developed that control viscosity without significantly hampering energy transitions vital to the UV cure mechanism while allowing for sprayability.⁶ This novel technology also provides for superior film properties over conventional paint and coating technology.

ONCE UPON A TIME: LINE-OF-SIGHT

Combined advances in photoinitiators and UV curing equipment have made non-line-of-sight curing of three-dimensional parts a reality using both pigmented and clear coatings.

Early photoinitiators were very inefficient. These early photoinitiator systems required so much UV energy that

Table IV. Key to Scribe Rating in Table III (per ASTM D 1654)

Rating Number	Representative Mean Creepage (in.) from Scribe
10	0
9	0-1/64
8	1/64-1/32
7	1/32-1/16
6	1/16-1/8
5	1/8-3/16
4	3/16-1/4
3	1/4-3/8
2	3/8-1/2
1	1/2-5/8
0	5/8 or more

lection of raw materials.¹⁰⁻¹² The wide range of commercially available raw materials and their related properties, which impact the final physical properties of the coating, can be organized into a "formulation universe." One such scheme of desired properties is given as an example in Tables III to IV. Different properties may be substituted into the various axis as a visual aid to the formulating chemist.

There exist UV-curable coatings capable of resisting concentrated hydrochloric acid, concentrated nitric acid, and concentrated sulfuric acid (and mixtures thereof) for observed periods of 5 minutes with no adverse effect on

Table V. Key to Field Rating in Table III (per ASTM D 714)

Rating Number	Field Blistering
10	None
9	Pinpoint to slight
8	Size 8, few
7	Size 6, few
6	Size 4, few
5	Size 8, medium
4	Size 2, few; Size 6, medium
3	Size 2, medium
2	Size 4, medium dense; Size 6 to 8 medium dense
1	Size 2 medium dense; Size 4 dense
0	Complete failure

the film properties. In fact little, if any, impact is noticed on gloss.

There also exist UV-curable coatings, which are capable of resisting the saponification effects of strong alkalies on the ester linkage of the acrylate polymer. Resistance to alkalines confounds the expected susceptibility to saponification of the acrylic polymer. Saponification of the acrylic ester linkage is a catalyzed hydrolysis of the ester linkage by alkalines. Careful formulation of UV-curable coatings result in saponification resistance even to standing pools of aqueous NaOH (50% by weight) for several weeks.

Additionally, this author has experienced at least one UV coating that exhibits excellent chemical resistance to both strong acids and strong alkalis.

Evaluation of several UV-curable metal coatings have been evaluated and published on behalf of the U.S. Navy by Hughes Aircraft in a previous joint research effort with this author. Details of the research remain confidential; however, evaluations by Hughes found UV-curable coatings to be the most promising means of achieving VOC compliant, anticorrosive protection for aluminum (including application directly onto aluminum without pretreatment), and other metals in marine environments. This has prompted the U.S. Navy and Air Force to reevaluate the need to pretreat aluminum with chromium prior to UV coating in order to achieve 500+ hour salt spray resistance. Humidity chamber tests over 2,500 hours have been observed on metal substrates coated with UV coatings.

CONCLUSION

The past 50 years have experienced a remarkable leap in human knowledge and technology. As knowledge builds on knowledge, the learning curve that humanity rides is skyrocketing to dizzying heights. With this, mankind is

developing new technologies that are harmonious with our environment and safer for future generations. Zero VOC, UV-curable paints and coatings hold the promise of a technologically fostered win-win scenario promising a cleaner, safer, healthier environment while simultaneously improving manufacturing capability, profitability, and product quality. Simply put, 40,000 years of advancements in paint technology have resulted in reducing theoretical quantum mechanics to practical applications—quantum mechanics in a paint can. About time, isn't it?

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