“Quality is never an accident. It is the result of intelligent effort”

John Ruskin

Abstract

UV Curing is a photo-polymerization process, initiated by UltraViolet (UV) Energy. During the process, Electromagnetic Radiation transforms a liquid, applied to a substrate, to a solid cross linked polymer material. The process is extremely fast, which makes it very favorable for today’s manufacturing demands of high throughput (increased productivity) as well as higher product quality when compared to other coat and cure processes. UV curing is also considered an environmentally friendly (GREEN) solution as companies are looking for additional ways to reduce the use of solvents, hazardous air pollutants and VOC’s.

While this process has many established benefits, the push for lower film weights on various substrates and many new applications have made the use of inert atmosphere curing a must to allow more complete cross linking. In fact, without the exclusion of Oxygen (O₂) from the curing zone, some processes will not cure. The benefits of improved adhesion, chemical resistance and lower photo-initiator levels bring a higher need for inert atmosphere curing.

The termination of the reaction by hydroperoxides, causing the incomplete network formation at the surface and the remaining acrylate double bonds are commonly called the referred to as oxygen inhibition.

Introduction

Photo polymerization can be broadly divided into free radical and cationic systems. This discussion refers to Free Radical polymerization initiated by UV Energy in the form of radiation. With all the advantages of UV Curing over other manufacturing curing, there are still problems that face the system, such as oxygen inhibition. Exposed to a specific electromagnetic wavelength, the photo-initiator absorbs the UV energy and forms free radicals. These radicals combine with the reactive groups from the Oligimers and Monomers to start the polymerization reactions and to yield a highly cross linked polymer network with high molecular weight.
Radical type polymerization is known for high sensitivity toward molecular oxygen, which has a detrimental effect on the course of the reaction.[3] The UV curing process is slowed down, or even ceased, by the O₂ present in the atmospheric air. The free radical polymerization reaction is inhibited due to the high reactivity of molecular oxygen toward radical species. Oxygen reacts with the radicals generated from the photoinitiator to yield peroxide species and hydro-peroxides which are inefficient for the polymerization. [2] The efficiency of cross linking is due to the efficiency of the propagation step. In the presence of air, the oxygen diradical reacts much faster with the photoinitiator or propagating radical to form a relatively stable peroxy-radical, which does not initiate the polymerization, but rather acts as an inhibitor. This inhibition results in an induction period of the polymerization until all oxygen is consumed. This initial slow stage of chemical reaction can retard or terminate the polymerization by the presence of O₂.

No matter what the oxygen bonds to, it essentially stops the cross linking process needed to cure the coating. Long, cross-linked chains cannot, and will not, be formed. This leads to coatings that lose their properties, such as durability, hard finish, glossy finish, optical properties and scratch and heat resistance. Signs of oxygen inhibition include a tacky or sticky finish, drop in coating performance, longer cure times, and a decrease in coating thickness. A Complete Photo Polymerization process is shown in Figure 1.

Figure 1: UV Photopolymerization
Methods to Overcome Oxygen Inhibition

- There have been several methods used to overcome this effect of oxygen inhibition. Increased radiation can be an option. This can help to scavenge the molecular oxygen by increasing the number of radical species. The challenge is that it will have a direct effect on the energy consumption and life of system components.

- Another method is to add excess photo-initiators in order to consume the oxygen present on the surface of the coating. This method will increase the price of the coating and may lead to yellowing and increased odor of the coating.

- The UV curing process is a continuously operating process, taking place in atmospheric air. With atmospheric air having a concentration of 21% Oxygen, and 78% Nitrogen, reducing this concentration will have the best impact on complete polymerization of the UV coating. Reducing the oxygen from about 210,000 parts per million to below 50 parts per million is ideal to prevent oxygen inhibition from occurring. Displacing the Oxygen level in the curing area of UV Radiation can be accomplished by increasing Inert gases within the curing area. While many inert gases can be used, such as Carbon Dioxide, Argon and Nitrogen, the use of Nitrogen will be the discussed in this paper.

Inerted atmosphere curing is not a new process. In fact, it has been around for years. Today’s manufacturing challenges include working with thinner films and lower molecular weights for coatings. Faster speed can be obtained by inerting the cure area with Nitrogen gas. Using the same coated material in an inerted atmosphere, it is quite possible to increase through speed 2-4 times. Nitrogen inerted UV Curing has many advantages in the field of UV radiation curing. UV curing can be done faster and more completely in an O₂-free environment. The resultant cure will exhibit improved surface properties, in particular higher gloss and a better scratch resistance than coatings cured in the presence of atmospheric air.[3]

As with all technologies, advancements hold the key for improved performance and new possibilities that were not previously available. Depending upon the coat and cure application, may it be radial, linear or through a conveyor, systems have been improved to provide a nitrogen enriched chamber for the parts to cure at high performance levels. Below is an example of a nitrogen inerted conveyor system capable of operating continuously at Oxygen levels of less than 50PPM. See Figure 2.
Figure 2: Inert Atmosphere UV Curing

Other Inert atmosphere UV curing examples include Radial or Linear Light shields are shown below.

Radial designed application

Linear designed application
All inerted atmosphere UV curing processes, regardless of the application, share the same basic designs.

- Isolated UV Curing area which is inerted with Nitrogen to displace the Oxygen
- Properly designed Distribution network to efficiently displace the Oxygen
- Nitrogen gas and its many grades
- High Performance material properties for peak efficiencies and proper transmission of UV Energy
- Monitoring Controls which help to minimize waste of inert gases
- Instrumentation to accurately monitor the Oxygen level of the cure area

Other curing equipment components, such as heat and exhaust extraction are not covered in this discussion but are important parts of each UV curing system.

We will discuss updates to the points listed above to help bring a better understanding for the continued use of Inert Atmosphere UV Curing.

**Isolated UV Curing Area**

The main function of this isolated chamber is to provide a UV Cure zone that has displaced the Oxygen and maintains $O_2$ at the lowest levels possible to provide the highest efficiency cure at various speeds and conditions. The design of this is not a trivial matter. It is important to properly size the chamber to accommodate the substrate but provide a minimum containment area for efficient containment of the Nitrogen. This can only be accomplished through good engineering design considerations. Compact design will increase the efficiency of the chamber. Some thoughts to consider for the design include the ability to load and unload the part being transported through the inerted chamber. Some designs will incorporate Nitrogen recovery depending upon the location of the $N_2$ inerted chamber within the building. A quartz window is used to allow the transmission of UV radiation into the chamber. Proper sealing of the quartz is necessary to maintain the low $O_2$ level within this chamber. With the need to reduce the level of Oxygen to less than 50 ppm, high quality seals are necessary to prevent migration of atmospheric
air entering the cure zone. Improved materials of proper durometer, compression and elasticity will assure a complete seal time after time when the cure zone is opened for maintenance reasons. The best material is one that is compatible with Ozone, Heat, UV radiation and will form a tight seal to eliminate gas leakage from a breakdown of material or shape.

Using the example of inert atmospheric curing with a conveyor, proper selection of conveyor belt material needs to be considered. With the advancement of high performance composite materials, there are more possibilities of materials that will resist the heat and UV radiation as well as providing superior retention of the high concentration of Nitrogen within the chamber. High performance composite material selection from Saint Gobain and Advanced Flexible Composites (AFC) are just two examples of conveyor belting material suppliers. The performance of the material is critical to avoid micro cracks or pores which could leak nitrogen from the curing zone.

**Proper Design of Nitrogen Distribution Network**

The Nitrogen introduced in the chamber needs to be diffused quickly in the UV cure zone. Efficiency is the key consideration. Selecting the proper distribution manifolds sizing to the actual position of the manifold for a particular cure zone, a properly designed system will help to maintain the homogenous concentration of Nitrogen throughout the chamber. Manifolds need to be designed to distribute the Nitrogen to the entire cure chamber. Without a uniform composition of concentrated Nitrogen mixture in every area, the cure will be adversely affected. Once the $N_2$ is distributed, retaining the gas is necessary to maintain efficiencies of the system. The use of air knives is an efficient way to retard the leakage of $N_2$ from the chamber. Positioning the knife at the entrance will help to prevent the ingestion of high levels of Oxygen into the chamber. The pressurized Nitrogen exits the air knife in a laminar flow which forms a curtain, which can help to keep the Nitrogen within the cure area.

**Nitrogen gas and its many grades**

Inerting a chamber to any level is only as good as the grade of inert gas used. It is important to have a good source of nitrogen which has a low level of Oxygen. Industrial Nitrogen is commonly used in systems. Nitrogen purity is generally expressed as a percent, such as 99% Nitrogen (which means 1% Oxygen with the balance of nitrogen and other inert gases)[4]. For low volume systems, the use of a Nitrogen dewar or bottled Nitrogen can be adequate. These vessels will assure low water content within the gas. For medium to high volume needs, an on-
site nitrogen generator can assure long term supply stability with possible cost savings. Shown below are different purity grades of Nitrogen.

**High Performance materials**

In every inerted UV curing chamber, there is a need to allow the UV radiation to pass to the substrate and also isolate the inerted cure chamber to atmospheric air. Quartz is used for this purpose due to its high transmission of the UV radiation across the entire UV spectrum but not all quartz is created equal. In fact there are different grades of quartz that will allow improved transmission of the UV radiation from the lamphead bulb to the substrate. High purity quartz is essential to high transmission of UV radiation.

**Natural Fused Quartz vs. Synthetic Quartz**

While natural fused quartz is a popular choice in many applications, the use of synthetic quartz is increasing due to the improved transmission of energy throughout the entire UV spectrum.[5] As seen in the graph below, synthetic quartz has a much higher transmission percentage of the entire
UV spectrum than natural fused quartz. From quartz plates used in inert atmosphere chambers to bulb envelopes, increased short wave transmission through the quartz provides an advantage over previous technologies. Premium synthetic materials will provide advantages in UV output and transmission of the UV spectrum. The higher the quality of quartz used, the higher the UV spectrum transmission.

UV Bulbs, within the lampheads, can also benefit from the use of synthetic quartz. Increased output in the UVC range (200-280nm) will benefit material cure and enhanced material performance if the spectral sensitivity of the coating is within the short UV wavelengths.

Bulb manufacturing techniques have also improved over the years for increased life with electrodeless bulbs. The ability to minimize contamination during manufacturing and eliminate manufacturer defects lead to increased bulb life over previous generations on the market.

UV Transmission through Natural and Synthetic Quartz

UV Transmission Graph courtesy of Baldwin UV
**Monitoring controls and Oxygen analyzers**

Controls design enables the end user to accurately control the volume of inert gas required to provide the benefits of Oxygen depletion within the cure area. Whether the system is a manual, automatic or even semi automatic, volume control valves gives the process controller a visual indication of volume used in each distribution zone. Improvements in manual valve controls as well as I/P and E/P flow regulators provide fine adjustments to control the inert gases.

With the cure chamber properly designed for distribution and containment of the inert gas, less than 50ppm $O_2$, an Oxygen analyzer is important to accurately monitor the level of Oxygen. Whether the system is open (manual) or closed loop (automatic), the placement and type of instrument used will determine the amount of inert gas within the chamber; which ultimately determines the quality of cure.

Recent improvements in the design of oxygen sensors, as well as the associated electronics, have led to improved measurement accuracy and reliability, and in certain cases, lower prices. Not every oxygen measuring technique is suitable for use in the UV curing environment and that is why caution should be exercised before an oxygen analyzer type is selected. The following is a brief review of the commercially available oxygen measuring techniques, as well as their potential suitability for use within the UV curing environment. The review can be used in conjunction with performance specifications from the oxygen analyzer manufacturer, before a final product selection is made.

**Electrochemical Percent and Trace Oxygen Analyzers**

Electrochemical sensors, often referred to as galvanic sensors, are a popular choice for UV curing applications. They can be used for low parts per million (PPM) oxygen measurements as well as for high percent oxygen. Most manufacturers of electrochemical oxygen analyzers offer two types of sensors, one specifically designed for trace measurements and the other for percent oxygen. Simply stated, the electrochemical sensors produce an electrical current proportional to the oxygen concentration in the sample. As oxygen molecules diffuse through the sensor’s semi-permeable gas membrane, the oxygen molecules are reduced at the cathode to form a positively charged hydroxyl ion. The hydroxyl ion migrates to the negatively charged sensor anode where the completion of the oxidation-reduction reaction takes place. This results in the generation of an electrical current (electron flow) proportional to the oxygen concentration in the sample gas. The current generated is both measured and conditioned with external electronics and displayed on a digital panel meter either in percent or parts per million concentrations. With the advance in the mechanical design of sensors, refinements in electrode materials, and enhanced electrolyte formulations, some manufacturers suggest sensor life of at least five years.
When electrochemical sensors need replacement, the sensor replacement price is usually quite modest and replacement is easily done in the field. Below are examples of two oxygen analyzers, one for percent measurement and the other for trace oxygen measurement.

**Percent Oxygen Analyer**

**Trace Oxygen Analyzer**

### Zirconium Oxide Oxygen Analyzer

Zirconium oxide sensors are occasionally referred to as a “high temperature” electrochemical sensor and is based on the Nernst principle. Zirconium oxide sensors use a solid state electrolyte typically fabricated from zirconium oxide stabilized with yttrium oxide. The zirconium oxide probe is plated on opposing sides with platinum which serves as the sensor electrodes. For a zirconium oxide sensor to operate properly, it must be heated to approximately 650 degrees Centigrade. A major limitation of the zirconium oxide oxygen analyzer in the UV curing application is that the sensor should not be used in the presence of volatile organics generated from the various product coatings. At operating temperatures of 650 degrees Centigrade, the organic species reacts with the oxygen in the inert gas to form water vapor. Depending on the concentration of organics vapors, a significant measurement error can take place due to the oxygen being reacted before it is measured. In such cases, the oxygen readings can be much lower than actual. This measuring technique is excellent to validate the purity of an inert gas prior to the UV curing process. Below is shown a zirconium oxide oxygen analyzer.
Other oxygen analyzer types are under development and in some cases, being used for specific applications. They include, but are not limited to, luminescence polarization, opto-chemical sensors, and laser gas sensors. As these techniques are further developed and prices fall in line with competing techniques, each may represent a viable alternative to the existing oxygen sensing technologies used for UV Curing.

Conclusion

The most efficient way to overcome oxygen inhibition in free radical polymerization is by performing UV curing in an inert atmosphere. There are a number of variables that play a key role in determining the quality and added benefits of UV curing in a Nitrogen inerted atmosphere. The quality of your end product starts with the quality equipment used during the design of the UV curing process. Technical advancements can provide an improved process gaining efficiencies which translate to higher quality control during the manufacturing process. A commitment to doing it right will assure great results. It is important to work with quality material and equipment suppliers who understand the process and who can work with you to meet your quality initiatives.

“Quality means doing it right when no one else is looking”

   Henry Ford

References:

[5] Baldwin UV, Ltd.: UV Transmission through Natural and Synthetic Quartz