

Truly a Radical Cure

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Abstract:

An introduction to the use of photoinitiators covering...

- Components of the photoinitiator “cocktail”
- Different photoinitiator mechanisms
- Different photoinitiator chemistries
- Selection criteria and factors affecting performance

Photoinitiators can be of a variety of types, split by chemistry and the mechanism by which they create radicals under the influence of UV light. They can also act in different ways in the curing of a UV-curable film. I would like to explore the performance characteristics of photoinitiators, along with some rationale used in selecting them, usually in a blend, for particular curing applications.

Introduction

A traditional ink of whatever sort will contain a resin, a solvent and, if it is a colored ink rather than an overprint varnish or lacquer, also a colorant, normally a pigment. When the ink dries, the solvent either evaporates, or can be absorbed into the substrate. In some cases the resin does more than just come out of solution and can cure by oxidation or coalescence. In all cases though, the unsolvated resin and the pigment are left as the dried ink film.

UV-curable inks are formulated differently. There is no solvent, and this brings a number of advantages; emissions are not an issue and thick ink films can be printed and cured with less problem. Gloss can be improved as the film often cures to give a smoother glossier surface. Also, inks stay “open” on press—i.e., they do not dry up or skin. This last point is a key advantage as it reduces cleanup and startup time on press and maximizes production time.

A UV ink will contain a pigment colorant in exactly the same way as a conventional ink but here the similarity ends. Solvent, typically around 70% of a conventional flexo ink formulation is no longer a component. The resin in a UV

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ink is an acrylated oligomer, i.e., a low-molecular-weight polymer, and this is thinned in viscosity using a monomer of related chemistry. When the ink cures, the monomer reacts along with the oligomer to form the finished ink film.

How is this achieved? Well, the curing reaction has to be induced and this can be done in two ways: either by firing an electron beam at the ink (a high-energy and somewhat costly affair) or, more commonly, by ultraviolet light. When UV light is used, we need something in the ink that can absorb at the appropriate ultraviolet wavelength and set off a chain reaction to cure the ink. This is the photoinitiator, and without these the UV industry would not have progressed to anywhere near the level that it has. The photoinitiator typically accounts for between 2–10% of a final ink formulation; there are a number of types on the market and they are normally used in blends or “cocktails” to achieve the best cure in any given situation.

Components of the Photoinitiator “Cocktail” and Their Mechanisms

What of photoinitiators then and how have they developed? In the beginning there was benzophenone and there was UV light. The new photoinitiator allowed new ink formulations to be dried instantly by UV curing—and printers saw that it was good.

Benzophenone was really the first photoinitiator used in the market. It is an example of a Norrish type II photoinitiator and is today still very much used in cocktails to promote cure. It has a number of attractive features and a number of limitations that we can explore.

How is a photoinitiator cocktail formulated? If we leave the other components of the ink aside, let us consider the different types of component that can be used in a photoinitiator package. They would consist of...

- The photoinitiator itself, very often used in blends
- Often an amine synergist
- Often a photosensitizer

Some detail then on each of these, starting with the nature of the photoinitiators used for free radical type polymerization. In these systems, the photoinitiator generates radicals under the influence of UV light, and there are two mechanisms by which this can be done.

Norrish type I photoinitiators cleave at the alpha bond under the influence of UV light to create radicals without the need for proton donation from a secondary source. This category constitutes the largest number of photoinitiators in the

market, including alpha hydroxy ketones, alpha amino ketones, and phosphine oxides. We will describe these in a little more detail in a minute.

Norrish type II products generate radicals by an intermolecular process whereby an electron is transferred from a neighboring molecule followed by hydrogen abstraction. For this reason they are used in conjunction with an amine synergist that aids the process by donating the necessary proton.

Examples of Type II photoinitiators are benzophenone or Isopropyl Thioxanthone, commonly referred to as ITX.

A common amine synergist that would be used along with these types is EDB—i.e., Ethyl-4-Dimethyl amino Benzoate. This can have a dramatic effect on the performance of benzophenone—e.g., for given curing conditions it can increase the print speed of an ink by around a factor of three.

There are a number of different types of amine synergists and these can be powder, as EDB, or liquid as with slightly longer chain varieties. There are also oligomeric amine synergists on the market and amine modified acrylates which are used as synergists but also have the dual function of acting as flow improvers in some systems.

The amine synergist can also help with incorporation of other photoinitiators into the system, for instance EDB (a powder) is a solvent for ITX and thus, with a little bit of heat up to around 50°C, this provides the interesting phenomenon of being able to mix two powders to make a liquid.

A photosensitizer acts to transfer energy to another photoinitiator so boosting the overall efficiency. As an example, the most common photosensitizer is ITX or Isopropyl Thioxanthone. This is itself a photoinitiator, but also acts as a photosensitizer in conjunction with other products and is commonly used with certain alpha amino ketone initiators. In simple terms, the ITX absorbs UV light more effectively than the alpha amino ketone over the range 360–400nm and transfers this energy to it, boosting radical formation and cure. A key part of the deal is that ITX absorbs at 250nm and 370–380nm, which coincides with the emission from a medium-pressure mercury lamp. This maximizes the use of the light available.

Adding ITX to some alpha amino ketones can boost cure speed by as much as 150%.

Different Photoinitiator Chemistries

These then are the major components of the photoinitiator cocktail, but clearly some more detail is required on the photoinitiators types. Aside from the two mechanisms for radical generation, photoinitiators can be split by chemistry.

As an overview...

- Alpha hydroxy ketones are used extensively in overprint varnishes, or OPVs. They are used as co-initiators with other photoinitiator types and are essential to gain the best surface cure in a system.
- Alpha amino ketones are used more in colored inks to gain through cure and adhesion to the substrate.
- Mono and bis acyl phosphine oxides are used extensively in whites and pale shades to gain through cure and adhesion.

In a little more detail, alpha hydroxy ketones create radicals using a Norrish type I mechanism and absorb at 240–280nm depending on species. This is a relatively short wavelength, and it is the reason why these species are associated with surface cure of ink and overprint varnish films.

Why is this the case? Just as a red light penetrates through fog better than white light, it takes light of longer wavelength to penetrate through a pigmented UV film to provide proper through cure. Light of the short wavelength absorbed by the alpha hydroxy ketones simply doesn't penetrate far enough into a pigmented ink film and for this reason, they are very often used in conjunction with a second initiator chemistry.

Alpha amino ketones also tend to be Norrish type I initiators, however they absorb light at longer wavelength.

Earlier versions have an absorption peak at around 305nm, but more newly introduced types have the advantage of absorption at a slightly longer wavelength around 320nm. Light of these wavelengths is far better able to penetrate the UV film and so the alpha amino ketones are associated with through cure and adhesion of the ink film onto the substrate. This is especially important for curing darker colors like phthalo blues and greens, where overlap with the absorption of the pigment itself can be a factor.

Phosphine oxides constitute a third key chemistry for photoinitiators.

A key product here is Mono Acyl Phosphine Oxide known as a MAPO or more commonly as TPO. This product absorbs across the UV range from around 220nm tailing off at around 420nm. This means that TPO is a powerful through cure initiator and is generally used for systems like opaque whites where

absorption and scattering of the incident UV light is a huge factor and through cure is difficult.

The second and newer phosphine oxide type on the market is Bis Acyl Phosphine Oxide known as BAPO. This type of chemistry has the added advantage over TPO in that the absorption tails off at an even longer wavelength around 440nm meaning that through cure is yet more efficient.

These are not the only types used for free radical systems. There are substituted benzophenones on the market—e.g., diethyl amino benzophenone—that can be used for through cure. Another category is Benzoin ethers used as surface cure agents—e.g., for overprint varnish applications. The absorption of this type is also at relatively short wavelength, in the same region as the alpha amino ketones.

Another important and completely separate category is photoinitiators used for cationically cured systems. This type of system uses a completely different mechanism to cure involving protonation of an epoxide ring followed by propagation by a cationic species. The resins are also different, normally using a cyclo aliphatic epoxide or vinyl ether.

There are a number of pros and cons with the cationic system.

A key advantage is that they can give a better combination of adhesion and film flexibility than free radical systems. The resin system generally cures to give a more 2D structure than the very highly cross-linked radical systems and this allows the cured film to flex. There is also less shrinkage on cure. The cationic cure system is self-propagating meaning that UV is only required to initiate the reaction after which the reaction will run until completion. There is no oxygen inhibition, no residual unreacted material after cure and applications like food packaging can be less of an issue. Cationic overlacquers have FDA approval in some cases.

Cationically cured inks are said to be easier to manufacture as gelling issues—e.g., caused by heat—are far less severe. Sensitization issues are less and inks are easy to use on conventional presses. Cationic systems are however more expensive than free radical.

How do you cure a cationic system? Well, a few years ago this issue almost eliminated this cure type from the market. Sulphonium salts were used as photoinitiators and in some cases small traces of benzene and diphenyl sulfide were found post-cure.

New systems have however come to the market, and it is now possible to cure cationic systems using an iodonium salt. This has meant somewhat of a resurrection for cationic systems although the market at the moment is recovering from rather a low level.

For cationic systems, curing of whites can be an issue as the rutile TiO₂ used as pigment absorbs up to around 380nm and also releases an electron pair that can inhibit the reaction. In fact the iodonium salt cationic initiator operates more efficiently when used with ITX sensitizer or even with some alpha hydroxy ketones. Curing problems have largely been overcome, and cationic white systems can offer advantages in metal decoration as the cured film is flexible enough to be printed and cured on flat metal before being formed into the required shape. A free radical ink, as far as I know, would not be able to achieve this.

Selection Criteria for Photoinitiators

So then we have quickly run through the players sheet, how would these be selected from the bench to assemble the best team for any occasion? Let us look at the rationale for photoinitiator blend selection...

Clear overprint varnishes:

Here there is no pigment in the system to absorb or scatter any of the incident light, and so through cure is not really an issue for thin layers. However, a key criterion in most cases is that yellowing of the OPV is minimal. An alpha hydroxy ketone is the normal choice for this market and there is some scope for choice; most offer efficient cure but cure speed can be compromised a little to gain lower yellowing or lower odor. FDA approval is also possible. Benzoin ether types yellow quite strongly and normally wouldn't be used for this type of application. There are also new photoinitiators coming on the market that are a step forward in terms of low yellowing and odor. Another point is that it is increasingly common to use UV absorbers in OPVs to extend the lifetime of the printed item—but this is a whole other story.

Benzophenone and amine synergists can be and are used in OPV systems partly because they lower the cost of the overall photoinitiator package. They do however cause yellowing to a greater extent than alpha hydroxy ketone and their use has to be restricted or eliminated depending on the tolerance for yellowing. Benzophenone also should not be used for any food contact applications.

For a pigmented system:

Here through cure becomes much more of an issue as the pigment will scatter the incident UV light as well as absorb according to color. As photoinitiators, a combination of alpha hydroxy ketone used along with alpha amino ketone is more likely. For darker systems the use of an alpha amino ketone is an absolute necessity, and, for the fastest curing speeds an initiator absorbing at the longest wavelength is best.

What if we have an offset system with a film thickness of 1–2 microns, versus a flexo system with probably a slightly thicker printed layer, or a screen ink at around 15 microns. What implications are there? In many cases the same types of photoinitiator are used, however the ratio of photoinitiators for surface and through cure has to be optimized accordingly. The overall level of photoinitiator may also be different depending on the required print speed. Issues can arise due to the solvency of the system for the photoinitiator. In general the photoinitiator is added to an ink system by first dissolving in monomer so that it is fully and uniformly incorporated into the system.

In a UV offset ink, viscosity is higher and the system will contain far less monomer which means that incorporation of the photoinitiator is less straightforward. Here raising the solvency of the photoinitiator cocktail becomes an issue. Usage of amine synergists and benzophenone can help this, however amines can affect the emulsification properties of an offset ink with fountain solution and negatively affect the printability.

Increasing the level of alpha amino ketone in an offset ink will raise the cost, however data suggests that by doing just this a more-than-compensatory advantage can be obtained in the print speed of the ink. It just depends what print speed is required and how “value in use” is assessed. To this avail, new alpha amino ketones with somewhat higher solvency have recently appeared in the market that can be incorporated at higher concentrations. Raising the level of such a species in an offset system from 3% to 4% can allow print speeds to be increased by around 50% where other, older alpha amino ketone types would either give problems of crystallizing out of the system or of odor.

What about a white ink?

Titanium dioxide absorbs up to around 380nm and so only longer wavelength UV light will penetrate adequately into the film. This is where the correspondingly long wavelength absorptions of the TPO and BAPO are required to gain proper through cure and adhesion.

Both TPO and BAPO should be used with a co-initiator, normally alpha hydroxy ketone, to achieve surface cure at the same time. The bis acyl BAPO

type is more active than TPO and can be used to achieve through cure at higher print speeds.

In white screen inks the situation is even more challenging as the ink film is generally thicker and can be loaded with up to 50% TiO₂. In these cases BAPO demonstrates faster cure than TPO when used in conjunction with alpha hydroxy ketone. An issue arising here is that both TPO and BAPO are powders and proper incorporation into the ink system is difficult without subsequent recrystallization and loss of performance. Use of benzophenone is not a solution as TPO and BAPO are not suitable for use with amine synergists that would be present in such a system. As a remedy, some liquid BAPO blends have recently been introduced to the market that can be simply incorporated and overcome the issue.

What about yellowing of the cured UV film?

This can be an issue and is most acute with some alpha amino ketones, however these tend to be used for strong colors like phthalocyanine blue when a little yellowing will not cause a perceptible difference. I have mentioned already that benzophenone can introduce yellowing into a system.

BAPO and MAPO types also yellow a little, which is unsurprising as their absorptions stray into the visible region. A bonus here is that after cure the degradation products from the photoinitiators are themselves broken down by visible light in a process known as photo bleaching. This means that yellow seen immediately after cure dissipates almost entirely a few minutes later. The problem is that the effect is hard to quantify if colors are measured directly in-line on press.

A new category of photoinitiator has also recently been introduced to the market for inks with very stringent non-yellowing requirements. Phenyl glyoxylate is used as co-initiator, replacing benzophenone or other alpha hydroxy ketones and allows better nonyellowing and low-odor cocktails to be developed.

Another potential dilemma is with odor coming from the ink film. UV inks simply smell different from other ink types but not necessarily in a bad way. The issue comes when certain alpha amino ketones are used which contain sulfur groups and can give a somewhat fishy smell on cure.

In response to this, newer-generation, lower-odor through-cure products are now available and the situation has become interesting with patent expiry of the older, high-odor types. How bad is the odor? It has been described as smelling at around 10 US dollars per pound of photoinitiator, however this does not tell the whole story. Tolerances on odor I believe are tightening, especially when it is realized that new-generation products can overcome the issue. Also, the newer

products give advantages in through-cure performance or in solvency for easier and higher incorporation, which can more than compensate for a higher price on the tag.

Some alpha hydroxies can also give less severe odor issues, which can be all but eliminated using a new phenyl glyoxylate co-initiator.

Summary

I hope that this has given some flavor of photoinitiator types and usage. Clearly photoinitiators have to be tailored by ink color and application rather than just curing ability.

We've been through the players and how the team may be assembled, however, we should not forget the keeper.

There has been some publicity recently for UV stabilizers and anti-skin agents used in the industry. These have historically used nitroso chemistries, and there are some queries over toxicological issues.

Very recently new, so-called "in-can stabilizers" have come onto the market that overcome these issues and perform outstandingly well in preventing gelling in UV- and electron-beam-cured inks. What is more, curing on press is not negatively affected. This is a step forward as gelling was an issue for all types of systems and avoiding it required careful formulating, not only of photoinitiators, but also of oligomers and monomers used in the ink. The new in-can stabilizers react with radicals to avoid early polymerization, give shelf lives of up to one year, don't give toxicological issues and give low yellowing. They mop up radicals very effectively during storage but don't hinder the curing during printing when they are overwhelmed by radical numbers coming from the initiator. Typical usage of the in-can stabilizer would be at or below 0.2% of formulation, which gives adequate shelf life for most needs. Data does exist however showing extended stability at usage of 0.5% on formulation.

So, great strides have been taken...benzophenone, benzoin ethers, alpha hydroxy ketones for surface cure, alpha amino ketones for through cure, phosphine oxides for whites and thicker film inks, phenyl glyoxylate for the lowest odor and yellowing, liquid BAPO blends for easy incorporation, and higher solvency alpha amino ketones.

For the future, the market will undoubtedly continue to bring new challenges for UV curing. However, I do believe that the progress made in recent years is set to continue, and I am confident that when issues arise we will be able to cure them.