A Novel Photoinitiator for U.V. Curable Digital Applications

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Abstract

Interest in inks and related surface coatings that can be cured by ultra-violet radiation is enlarging in the field of digital printing. The well-known and equally well-accepted advantages that U.V. curable printed inks and varnishes offer in traditional printing techniques are in most part directly applicable to non-impact printing technologies. Fast throughput from rapid "drying' and ink formulations with no volatile organic content are two examples. As a new technology or market evolves, however, it is generally accompanied by a need to develop, or at least adapt, existing raw materials and engineering designs to meet new or revised requirements. Chemical raw materials used in ink and surface coating formulations for digital printing are no exception. With this in mind, this paper introduces a new and novel photoinitiator, a chemical raw material integral to most U.V. curable inks and surface coatings, with an emphasis on digital printing applications. The chemical structure of this new photoinitiator differs from others that are commercially available and it is demonstrated how the new photoinitiator can enhance aspects such as the surface characteristics of plastics surfaces and the adhesion of U.V. curable inks to "difficult" substrates. Additionally other relevant features of this photoinitiator are explained. The photoinitiator can be described as "multi-functional" in that the molecule contains more than one reactive functional group capable of initiating free-radicals, it can also be incorporated into water-based formulations. Founded on experimental evidence, it is proposed that the new photoinitiator will be particularly suitable in surface coatings used to create digitally printed flexible packaging. But due to its versatility, other, more diverse applications are presented.

Introduction

If the term "photoinitiator' is mentioned, what immediately springs to mind? To those familiar with the formulation of U.V. curable inks and surface coatings the term is synonymous with the molecular compound that initiates the polymerization and cross linking of monomers and pre-polymers upon exposure to ultra-violet light. If the layman is asked the same question, then a response may be deduced by breaking the term, photo-initiator, into more manageable components. An educated definition could then be proposed - something which initiates something upon irradiation with light. Both explanations are correct and differ only in that one is more general than the other.

In recent years, exploring the possibilities of the more general definition has been a subject of fundamental research within Ciba Specialty Chemicals. New compounds are being developed that produce a detectable effect upon exposure to light; for distinction purposes these new chemical compounds are classified as "photolatent". Examples are chemicals that go from a colorless to a highly colored form, chemicals which produce strong acids or bases to produce a pH change, even chemicals that release a pleasant recognizable scent; all effects that are only noticeable upon exposure to light [1,2]. In keeping with these "photoinitiator" developments is a new compound that increases the adhesion of surface coatings and inks to many plastic surfaces when exposed to ultra-violet light. Although this photoinitiator has chemical similarities to those commonly used to cure acrylated monomers and pre-polymers, it has some unique characteristics that distinguish it. In general, it can be described as a "photo-curable surface active agent". This new liquid photoinitiator, named LE-PG2, is the subject of this paper and its unique properties are portrayed using application examples relevant to the digital printing industry.

Experimentation, Results and Discussion

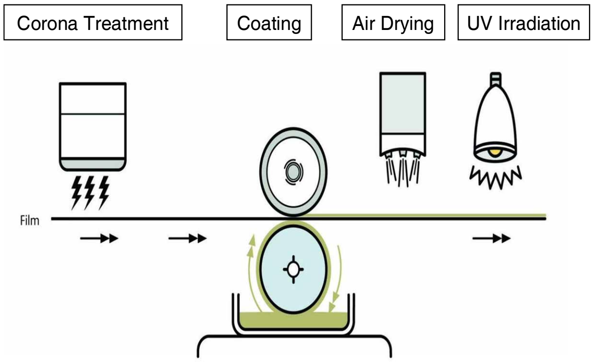
Experiment 1. Adhesion of U.V. Curable Inks

Coating mixtures, incorporating LE-PG2 and a reactive monomer were used to prepare thin film surface modifications onto various commercially available bi-axially orientated polypropylenes; according to the procedure illustrated in Figure 1. The coating mixtures contained 2.0% non-volatile content, the remaining 98% being distilled water or solvent. Hence, after applying the coating, an air drying step was necessary to evaporate the water or solvent before the pretreatment could be U.V. cured to form a stable and transparent coating.

***Figure 1**. Preparation of U.V. Curable Adhesion Promoter.*

Example Coating Formulation:

LE-PG2	*1.20 parts*
Reactive Acrylate Monomer	*0.70 parts*
Flow Aid	*0.10 parts*
Distilled Water	*98.0 parts*



The surface tension of each polypropylene substrate was measured before and after application of the U.V. curable pretreatment, the results are shown in Table 2.

Table 2. *Effect on Surface Tension.*

Substrate / Surface Tension	***Surface Tension of Substrate as Supplied /Dyne cm^{-2}***	***Surface Tension After Corona Treatment Dyne cm^{-2}***	***After U.V. Curing Applied Pre-treatment /Dyne cm^{-2}***
BOPP 1	36	52	50
BOPP 2	32	50	44
BOPP 3	40	54	50

To each pretreated film a U.V. curable ink was applied using a conventional printing method. The ink was applied and U.V. cured in compliance with the manufacturer's recommendations. The final print was tested for adhesion using a tape test and the results are displayed in Table 3.

Table 3. *Adhesion of U.V. Cured Ink*

Substrate / Adhesion of U.V. Ink	***Substrate as Supplied***	***Corona Treated Substrate***	***U.V. Cured Pre-treated Substrate***
BOPP 1	5	4	0
BOPP 2	4	3	0
BOPP 3	5	3	0

Key: 0= 0% removal. 1=10% removal, 2=20% removal, 3=40% removal, 4+40% removal 5 <50% removal

From this experiment, two significant outcomes are worth highlighting. Firstly, it is apparent that although corona discharge treating the polypropylene substrate yields a measurable increase in the substrate's surface tension, subsequent application of the U.V. cured pretreatment produces no further change; in fact, in one case, a slight decrease is seen. Secondly, the U.V. cured pretreatment affords immaculate adhesion to a U.V. cured ink. Both points are significant to digital printing, more specifically, U.V. curable ink-jet printing. It is known from the literature that a primer layer for porous and non-porous substrates is advantageous when printing U.V. curable jet inks [3]. In the same literature, good results were reported using a surfactant as a primer layer for non-porous substrates (by first applying a surfactant to a surface before jetting an ink, dot gain and ink spreading can be successfully controlled). It is suggested that by applying a U.V/ curable primer to a non-porous substrate not only can ink spreading be adequately controlled due to surface tension differences, but improvements in adhesion can be attained onto a multitude of "difficult" substrates. This approach for adhesion promotion is repeatable, regardless of the substrate's source, implying this much wider applicability.

Experiment 2. Adhesion of Water-Based Coatings

An additional benefit of the LE-PG2 photoinitiator is its water solubility; Table 4 profiles its solvency in this vehicle against other commercial photoinitiators.

Table 4. *Water Solubility of LE-PG2 and Commercial Photoinitiators at 25^{0}C.*

Conc^{n} / PI	***1% (wt:wt)***	***2% (wt:wt)***	***5% (wt:wt)***	***10% (wt:wt)***
DAROCUR® 1173	Soluble	Insoluble-forms stable dispersion	Insoluble-unstable dispersion	Insoluble-unstable dispersion
IRGACURE® 2959	Soluble	Insoluble-forms stable dispersion	Insoluble-unstable dispersion	Insoluble-unstable dispersion
LE-PG 1	Soluble	Insoluble-unstable dispersion	Insoluble-unstable dispersion	Insoluble-unstable dispersion
LE-PG2	Soluble	Soluble	Insoluble-forms stable dispersion	Insoluble-forms stable dispersion

To establish if LE-PG2 could be used as a photo-curable adhesion promoter in water-based coatings, the water-soluble polymer polyvinyl alcohol was chosen for a set of experiments. Polyvinyl alcohol is widely used in the surface coating and packaging industries because it has many useful properties; for example, it is a good oxygen and aroma barrier, it is also effective in ink-jet media coatings. It is known however, that this polymer suffers from poor adhesion to many plastic surfaces [4]. On this basis, a series of water-based mixtures were coated onto polyester film, then dried and U.V. cured; essentially repeating the process already outlined in Figure 1. The coating mixtures used and the results obtained are shown in Table 5.

Table 5. *Adhesion of U.V. Cured Polyvinyl Alcohol Films.*

Formulation (parts by weight)				***Adhesion to PET (after Drying / U.V. Curing)***
Polyvinyl Alcohol	LE-PG2	EtOTMPTA (20mol)	Distilled Water	
10	---------	---------	90	5
10	0.30	0.20	89.50	4
10	0.60	0.40	89.0	1
10	0.90	0.60	88.50	0

Clearly, the adhesion results are favorable for the hybrid, water-based, U.V. curable mixtures and it can be concluded that photo-curing polyvinyl alcohol in the presence of LE-PG2 and 20 mol EtOTMPTA can produce a coating with perfect adhesion to polyester film. Furthermore, due to the complete water solubility of the U.V. reactive mixture used, all films exhibited a high degree of clarity and transparency with no residual odor.

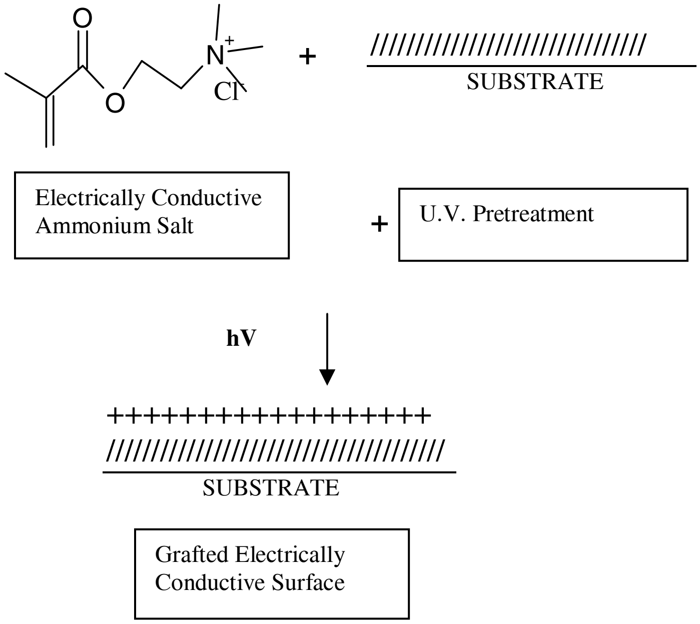
Again, similarly to the previous experiment, two immediately apparent benefits attributable to LE-PG2 are noteworthy. Firstly, and foremost, is its water solubility; secondly is the improvement in adhesion of the polyvinyl alcohol film. It is reported that a limitation for effectively U.V. curing water-based inks, including jet-inks, is the solubility parameters of commercially available photoinitiators [5]. Rather than change the chemical composition of the photoinitiator molecule to address this, most suppliers prefer to either change the physical form of the compound or its medium, to render known chemistries water-dispersible. This type of strategy has obvious technical and marketing motivation as U.V. curable inks, coatings and the like that contain no volatile component have market dominance. The results of this experiment is to demonstrate that U.V. curing has potential advantages beyond these types of "100% active" formulations and U.V. curing water-based formulations to improve adhesion may be one of them. LE-PG2 can be considered in this respect.

Experiment 3. Adhesion of Functional Surface Modifications.

In the area of digital printing, and particularly in the growth area of digital fabrication, it may be necessary to form mono-molecular or very thin surface modifications onto plastic surfaces. Examples of these types of "surface preparations" currently employed in the electronics field are thin film transistors, sputtered indium tin oxide, spin coated electrically conductive polymers and dielectric layers. Digital printing, as a method of making, such structures, may seem immediately appealing on the outset for reasons of perceived ease and for goals envisioning increased throughput and adaptability [6,7]. Nonetheless, adhesion and fixing functional material to surfaces with differing properties is still a continual study within the inks and coatings industry and it can not be assumed that these studies will disappear within the framework of digital fabrication. Consequently, this experiment describes how compounds can be fixed to a plastic surface utilizing a combination of the photoinitiator LE-PG2 and radiation curing- thus forming a robust, functional, thin-film surface modification.

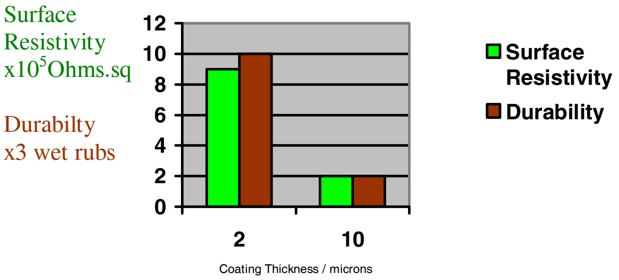
For this experiment the compound shown in Chart 6 was used, a methacrylated quaternary ammonium salt. (This unsaturated molecule can be used to make electrically conductive surface coatings [8] and in this context is considered as a 'functional material"). A U.V. cured surface modification was prepared in exactly the same manner as depicted in Figure 1 and a coating solution composed solely of the reactive functional material was applied over the pretreatment. The two layers were U.V. cured and Chart 6 shows diagrammatically the desired final construction. This construction was evaluated for performance.

***Chart 6.** Grafting U.V. Reactive Functional Materials and Proposed Coating Cross-Section*



Consistent with the diagram above is a set of results that indicate functional material can be successfully grafted to the U.V. pretreatment, unfortunately with a trade-off, as described in Chart 7.

***Chart 7.** Surface Resistivity and Coating Durability*



The chart shows that as the surface resistivity decreases (conductivity improves), the coating's durability degrades. In other words, because the "anchoring" layer lies beneath the functional layer it has limited binding capacity and the ratio between the two coating thicknesses may have to be optimized for sufficient grafting. Nevertheless, in certain instances an abundance of functional material at one interface is preferable and grafting has occurred at the lower film thickness of 2 microns. It is still suggested that this two-layer method is a technically viable alternative for making electrically conductive inks or coatings; it avoids formulating the active conductive material with non-conductive binders that may impede electron transport.

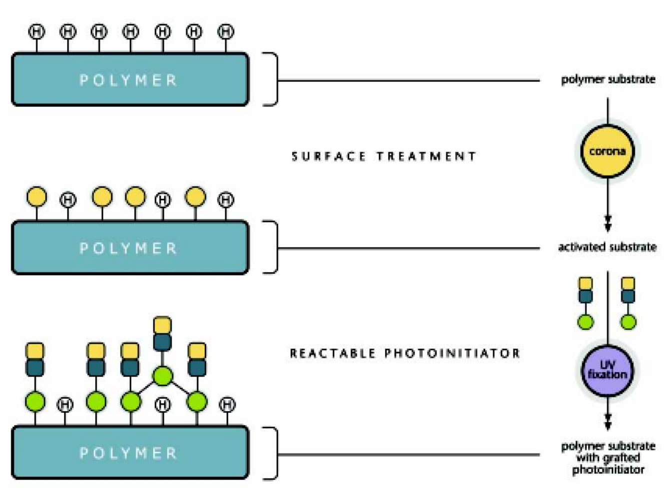
Summary and Conclusion

The new compound LE-PG2 has been represented in a way that promotes a new way of thinking about photoinitiators. It has been demonstrated that this compound is U.V. reactive and can promote adhesion of inks to plastic surfaces and has identical advantages in water-based coating formulations. The paper also endeavors to show that this compound can be used to graft U.V. reactive functional material to an interface, providing a technique for preserving the material's function when formulation may not.

An explanation of the utility of LE-PG2 can be found with insight into its chemistry. It is multi-functional, more than one functional groups per molecule that can initiate free-radicals, and it has a higher molecular weight than commonly associated with radical producing photoinitiators. Additionally, it has hydrophilic/lipophilic character, much like a surface active agent. These factors combined result in a molecule that lends itself well to the applications described above. Furthermore, its higher molecular weight makes it suitable for the formation of semi-interpenetrating networks; it is shown how LE-PG2 can be used to effectively encapsulate polymers within a U.V. cured matrix.

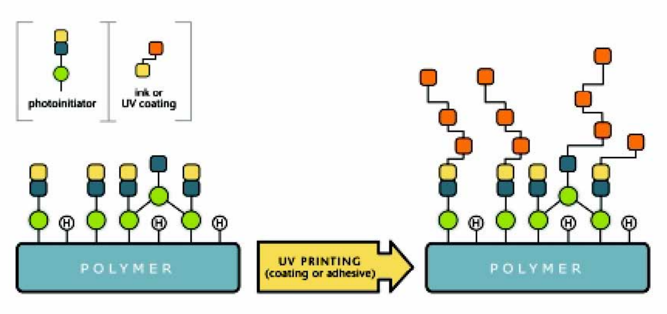
Much research has been done on the mechanism by which certain photoinitiators chemically graft unsaturated compounds to a surface or substrate, Figures 8 and 9 illustrate one theory.

Figure 8. *Mechanism for Forming Reactive Sites on the Surface of a Polymeric Surface or Substrate*



The theory proposes that corona or plasma treating a surface is not only useful for increasing the surface tension of a polymeric substrate to improve wetability and therefore adhesion, but it also generates an ideal topography for certain types of photoinitiators [9]. A photoinitiator, with surfactant-like properties, has a propensity to orientate itself on the discharge treated surface so that reactive sites are perfectly positioned to chemically graft other reactive materials [10]-see Figure 9.

Figure 9. *Mechanism for Grafting Reactive Materials to a Surface*



For reasons presented in this paper, it is evident that by developing photoinitiators with this type of grafting mechanism in mind, new compounds are emerging that have broader utility than may have been originally foreseen.

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Biography

Andrew Naisby is a Scientist in the Applications Laboratory of Ciba Specialty Chemicals Corporation in Newport, DE (USA). Supervising Ciba's digital media laboratory his primary line of work is developing novel polymers and additives. He has over ten years experience in the formulation of media coatings and printing inks and holds several patents in this area. Mr. Naisby holds an Honours Degree in pure and applied chemistry from the University in Bristol, England.