# Investigation of a System Capable of Photoinitiating Radical Polymerizations in Thick Pigmented Media

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**ABSTRACT:** A new system consisting of a xanthenic dye, a ferrocenium salt, a hydroperoxide, and an amine, capable of photoinitiating the radical polymerization of thick and pigmented films exhibiting a thickness of ca. 100 microns was studied. This is a one-step process, with a working speed of 10 m min$^{-1}$, involving four 80-W cm$^{-1}$ lamps. This is one present-day system capable of working under industrial conditions. The photolysis investigation in solvent medium of its various components is a first approach to discuss the photochemical mechanism involved in this four-component system. Thus, one can assume that both mechanisms could occur through charge transfer : dye/amine interaction and dye/ferrocenium salt interaction, the latter one being presumably the most efficient. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1911–1923, 2001

## INTRODUCTION

The technique of UV-visible radiation polymerization has considerably expanded for several years in the coating field.[1–10] In particular, many industrial substrates of the paper, wood, plastic, and metal type can be coated with varnishes or very thin pigmented layers (inks). The manufacture of UV paints capable of polymerizing a hundred micron deep is, currently, still extremely difficult. The pigments behave like an internal filter, so that the UV radiation cannot easily penetrate inside the coating. A novel initiating mixture that allows the polymerization of a pigmented formulation designed for the furniture marked[11,12] has been recently developed. It becomes possible to realize under industrial conditions 100 micron-thick pigmented films. These new UV-curable paints meet the following conditions: a sufficient covering power provided by the amount of pigment inside the film, or the thickness deposited on the substrate; a short exposure time to the UV radiation; a significant pot life; a resistance of coatings to photoaging; physical and chemical properties meeting the specifications.

The authors will present results of photopolymerization experiments and a photolysis investigation in a model medium solvent of the various components of the initiating system, which is a first approach to discuss the photochemical mechanism involved in the initiation step.

## EXPERIMENTAL

### Photoinitiating Systems

The initiating system consists of:[11] (a) a ferrocenium salt: ($\eta^5$-2,4-cyclopentadien-1-yl) [(1,2,3,4,5,6,$\eta$)-(1-methylethyl)benzene]-iron (II) hexafluorophosphate (Ferrocenium salt from Ciba Geigy Company, Switzerland). Abbreviation CpFe$^+$Aren denotes the cationic part of this salt (Cp = C$_5$H$_5$, Aren = C$_6$H$_6$); (b) a peroxydic compound: cumene hydroperoxide (Aldrich); (c) a dye of the xanthenic type or belonging to the thiazine family: Rose Bengal

(Aldrich), thionine (Aldrich); and (d) a tertiary amine: *N*-methyldiethanolamine (Aldrich), abbreviated to MDEA.

A hydroxy alkyl acetophenone (Darocure 1173) is added to this four-component system to favor the surface curing of the paint.

To understand the mechanisms that are involved in solution and the effect of each component, photolyses were carried out successively on systems consisting of one, two, . . . as many compounds as are included in the full mixture. All the photolyses were carried out in acetonitrile. The role played by oxygen was also taken into account. To perform photolyses in the absence of oxygen, as a preliminary step, nitrogen was bubbled into the solution for 10 min.

### Irradiation Conditions in Solution

The solutions were illuminated by a HPK 125W (Philips) medium-pressure mercury vapor lamp. By using a high-pass filter, visible lines of the emission source can be chosen, in particular at 550 and 580 nm. Two filters were favored: the one transmits light from 350 nm onward, for solutions with no dye; the other from 535 nm onward, so as to demonstrate the sensitizing role of the dye. Special attention was given to photolysis of the system under visible light. Indeed, according to experiments carried out in a pigmented filformer, the reactivity of the initiating mixture is largely due to absorption of visible light, because pigments absorb the UV radiation.

### UV Curable Formulations

Photosensitive formulations consist of an oligomer, a monomer acting as a diluent, a pigment base, and an initiating system.

#### *Functionalized Oligomers*

As photopolymerizable acrylic resins made great strides in recent years, our investigations were focused on two representative materials in each class of oligomers used in the varnish industry: an unsaturated polyester in styrene (Exter PL 2100 from the Coim SPA Corporation): PL 2100; an urethane–aliphatic acrylate (Ebecryl 264 from the UCB Corporation): E264; an epoxy–acrylate derivative: (Actilane 70 from the SNPE Corporation) A 70, and (Laromer 8765 from the BASF Corporation) LF 8765.

#### *Acrylic Monomers*

To the above prepolymers, a low molecular weight monomer carrying one or several acrylate func-

tions is added. This solventless formulation should have a viscosity between 100 and 500 m mla.s to be used in industrial applications. Among the monomers commonly used in photocurable resins, 1,6-hexanediol diacrylate (HDDA) was chosen.

#### *Concentrated Pigment Bases*

To estimate the polymerization characteristics of pigmented coatings, several concentrated pigment pastes were prepared by dispersing the components in a deflocculator and then grinding in a glass bead mill several pigments to obtain the required tint. The dispersing agent consists of cellulose acetatebutyrate (CAB 552 001) (Eastman Kodak Corporation) to which HDDA was added. As a general rule, the amount of monomer, oligomer, and pigment paste involved in the composition of the formulation was specified for all the systems described. The concentration of photoinitiators was indicated in weight percentages of the previously described formulation. Medium wood panels covered with a white UV primer were used as a substrate. The paint film was produced by means of a calibrated draw-down device to form a coating with uniform thickness. Generally, the thickness was fixed at 100 microns.

The maximum thickness of the polymerized layer of a formulation for a given illumination time is calculated as follows: if the thickness of the polymerized layer was less than or on the order of 150 microns, various calibrated drawdown devices are used. Films of increasing thickness are successively applied and peeled off after proper treatment, until the time when either the side facing the substrate is not sticky or trace amounts of the unpolymerized formulation are not found on the substrate. The thickness is measured with a micrometer. If the thickness of the polymerized layer is greater than 150 microns, a different procedure is used. Cupels are filled with the formulation up to a level not in excess of 5 mm and subjected to illumination. The film resulting from the surface polymerization is withdrawn. The surface of the side in contact with the unpolymerized liquid is washed with acetone and dried, and the thickness of the film is measured by using a micrometer.

The illumination time required for the polymerization of a layer whose thickness was fixed beforehand is estimated according to the following procedure: after the conveyor speed has been fixed, the illumination time is determined from

the number of passes under the lamp needed for a complete polymerization. This estimation is performed according to three criteria: the outer surface of the coating should be tackfree (test 1); an adequate polymerization of the core, i.e., the inner surface of the coating (facing the substrate) should not be sticky, no trace amount of the unpolymerized formulation should be found on the substrate (test 2): a "good adhesion" to the substrate, i.e., the coating should offer a good resistance to the peeling produced by means of a coin (a few tens of minutes following illumination).

Three drying units were used. Unless otherwise stated, the UV source used was a laboratory device: a medium pressure mercury vapor lamp with a linear power of 80 W/cm, located on a curing device consisting of a conveying belt and a semielliptic reflector (IST system).

A preindustrial UV drying unit was also used: it gives the possibility to use conventional Hg lamp and doped lamps.

In the industrial UV drying unit, the coating curing part includes a precuring tunnel (fitted with a 10-m long debubbling area at 40°C), a UV precuring area equipped with TL 03 and TL 05 low-pressure Hg lamps. Finally, the particle board passes through the curing tunnel (which contains on an average three 80-W/cm medium pressure mercury lamps and a doped lamp emitting at 420 nm) and is, then, conveyed through a cooling area. The passing rate of the conveyor ranges between 8 and 10 m/min.

## RESULTS AND DISCUSSIONS

### The Newly Developed Photoinitiating System: Effectiveness in Pigmented Media

#### On the Laboratory Scale

To estimate the properties of the developed system, its performances were compared with those achieved when using a pair of conventional initiators known as efficient for photopolymerization reactions in pigmented media [see, e.g., in refs. 1 and 2]: acylphosphine oxide TPO, 1 wt %; Darocure 1173, 3 wt %.

Pigmented formulations were intended to prepare paints containing in general 20% of inorganic pigments and 5% of organic pigments, to achieve sufficient opacity. These values were modified according to the nature of the pigment. A certain amount of photoinitiator or photoinitiating system was added. The illumination condi-
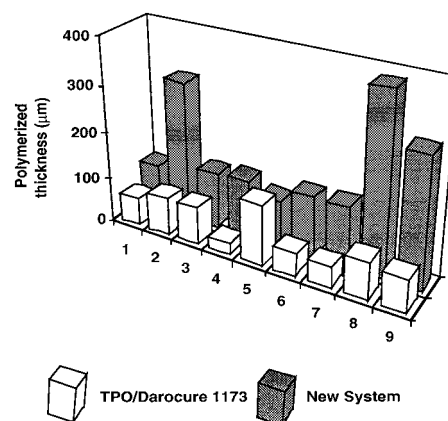


**Figure 1** UV curing of thick pigmented coatings of multifunctional monomer and oligomer acrylates/pigment paste/mixture of photoinitiators (% pigment is selected according to the requirements of the paint industry). Hg lamp: 80 W/cm; 1 lamp; cure speed: 3.3 m/mn: 1—$TiO_2$ rutile, 20%; 2—$TiO_2$ rutile, 10%; 3—Carbon black, 1%; 4—Cr yellow, 20%; 5—Prussian blue, 3%; 6—beige, 10%; 7—green (yellow 9%, blue 0.3%); 8—rose ($TiO_2$ 9.9%, red 0.02%); 9—sky blue ($TiO_2$ 9.85%, blue 0.045%); (1) Mixture of benzoylphosphine oxide (TPO) and hydroxyalkylphenyl acetophenone (Darocure 1173): 1%/3%; (2) new system.

tions of the laboratory were favored, i.e., just one 80-W/cm medium pressure mercury lamp.

Because the major difficulty about pigmented media was concerned with the polymerization of the inner layers of the coating, we took as a criterion of comparison the maximum hardened thickness after three passings under the lamp at a rate of 10 m/min.

The most attractive performances were achieved (Fig. 1) for yellow- and white-coloured coatings. At high pigment concentrations, the system remained five times more performing, and made it possible to produce 120 micron-thick opacifying films containing 20% of inorganic pigments. This effectiveness may be accounted for the existence of a spectral window from 450 nm onwards, in yellow pigments. This wavelength area corresponds both to the maximum absorption area of the photosensitive area and one of the main emission lines of the radiation source. The same holds true in respect to white pigments transmitting light for wavelengths over 420 nm. For black coatings, the effectiveness remained sufficient to produce a hundred micron-thick covering films. Red paints are, at the present time, the most difficult to produce when it comes to form full tints (this type of pigments transmit mainly from 600 nm onwards).

On the other hand, the production of a pink paint does not present any difficulty. Indeed, the general shape of the absorption curve of the pigment mixture is almost identical to that of rutile titanium dioxide. Other pastel tints with a blue cast were also tested. In a similar way to the case of the pink tint, the new system was more effective than that of prior art. In contrast with the TPO/D1173 initiators, whose reactivity depended mainly on the titanium dioxide concentration, the performances of the new formulations were governed by the amount of blue pigments. It is also possible to manufacture paints whose tints result from the mixture of several pigments, within the absorption limits of the new coloring. Green and beige tints have, thus, been produced by means of Chrome yellow in larger proportion than Prussian blue, Arylamide red, and carbon black.

### On the Industrial Scale

Red, blue, yellow, and beige paints have been cured in the preindustrial UV drying unit (Fig. 2). For marketing purposes, a beige formulation with a pigment concentration of 10% was favored for testing under real industrial conditions. The application of the product was satisfactory. With a working speed of 10 m/min (in an industrial UV drying unit), under three mercury lamps and a lamp doped with gallium-indium at 420 nm, a
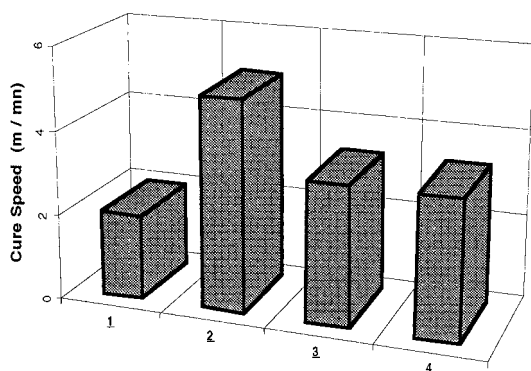


**Figure 2**   UV curing of lacquers in a preindustrial UV drying unit. The complete surface and body cure is achieved under the successive use of two kinds of lamps (A and B) (one-step process—wood finishing—polymerized thickness: 120 $\mu$m). The use of a doped lamp for the curing of the yellow lacquer has no effect. The figure shows the cure speed attained with 1 pass under lamp A and B. Lamp A is Ga in doped Hg lamp—$\lambda$ = 420 nm, 80 W/cm, 1 pass; Lamp B is medium pressure Hg lamp 80 W/cm, 1 pass. *1* red 3%; *2* blue 5%; *3* yellow 20%; *4* beige 10%.
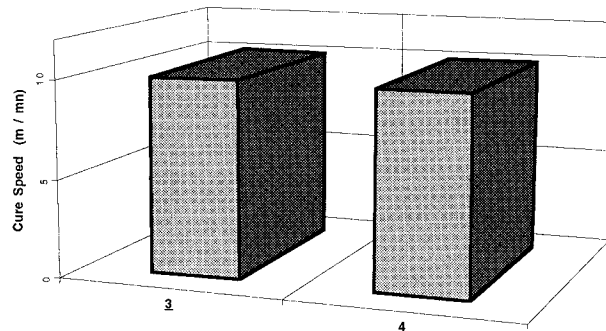


**Figure 3**   UV curing of lacquers in the industrial UV drying unit described in the experimental part: *3* yellow 20%; *4* beige 10%.

hundred micron-thick crosslinked, opacifying coatings, exhibiting a very good adhesion to the wooden substrate were produced (Fig. 3). In addition, the pot life of the formulation was checked for a quantity of 25 kg during the whole test, i.e., about 8 h. Using a doped lamp increased the feasibility of the reticulation of a red or blue paint in deeper tints (Fig. 2).

### Steady-State Photolysis of the Photoinitiating System in Solution
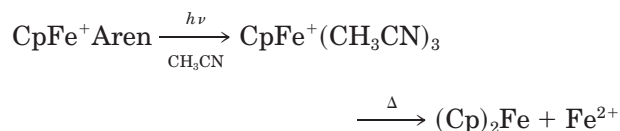
The present study is carried out on the four-component system mentioned in the experimental part: the fifth component (Darocure 1173) does not play a role in the core curing, and should not interact with the other components.

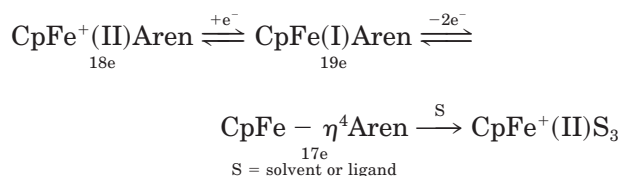### The Photolysis of the Ferrocenium Salt: CpFe⁺Aren

The photolysis reaction of ferrocenium salts was studied at great length.[13] According to this investigator, the balance sheet of the decomposition in various solvents in absence of $O_2$ amounts to a disproportionation leading to ferrocene and $Fe^{2+}$ ions:

$$2 \text{ CpFe}^+\text{Aren} \xrightarrow[\text{CH}_3\text{CN}]{h\nu} (\text{Cp})_2\text{Fe} + 2 \text{ Aren} + \text{Fe}^{2+}$$
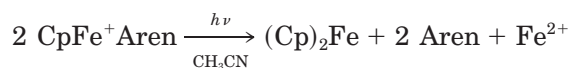
More recently, authors have suggested,[14] and, then, demonstrated[15] that the photolysis of CpFe⁺Aren in acetonitrile leads transitorily to a thermally unstable complex that decomposes according to:

$$\text{CpFe}^+\text{Aren} \xrightarrow[\text{CH}_3\text{CN}]{h\nu} \text{CpFe}^+(\text{CH}_3\text{CN})_3$$

$$\xrightarrow{\Delta} (\text{Cp})_2\text{Fe} + \text{Fe}^{2+}$$

Many electrochemical studies also deal with the cathodic behavior of $CpFe^+Aren$ complexes in various aqueous or organic media.[16a] These complexes may undergo a reversible electron transfer between the 18 electron cationic form $CpFe^+(II)Aren$ and the 19 electron neutral complex $CpFe^+(I)Aren$. In ref. 16b, attention has been given to the electrochemical mechanisms involved in the reduction of $CpFe^+Aren$ in acetonitrile, and in particular, to the neutral complex $CpFe(I)Aren$. The following stages were demonstrated:

$$CpFe^+(II)\underset{18e}{Aren} \underset{}{\overset{+e^-}{\rightleftharpoons}} CpFe^+(I)\underset{19e}{Aren} \overset{-2e^-}{\rightleftharpoons}$$

$$CpFe - \eta^4\underset{17e}{Aren} \overset{S}{\longrightarrow} CpFe^+(II)S_3$$
$$\text{S = solvent or ligand}$$

For concentrations higher than $10^{-3}M$, ferrocenium salts exhibit a marked absorption in the visible range of the luminous spectrum (between 350 and 500 nm). Therefore, the photolyses were carried out by using a high-pass filter ($\lambda > 350$ nm) in the presence or the absence of oxygen [Fig. 4(a) and (b)].

In the presence of oxygen, the ferrocenium salt exhibits a high photolysis rate under visible light [Fig. 4(a)]. An increase in the absorption maxima of the initial product takes place. This result in a deepening of the orange-brown coloration of the original solution which is ascribed to Fe(III) has been already reported.[17a] According to research work previously performed in this matter,[13] $CpFe^+Aren$ liberates ferrocene and $Fe^{2+}$ ions. The abrupt increase in optical density between 350 and 500 nm is not due to the presence of ferrocene or $Fe^{2+}$, if one takes into account the absorptions of these compounds. Moreover, the photolysis of ferrocene and $Fe^{2+}$ ions alone did not reveal any increase in absorbance between 350 and 500 nm. This coloration, therefore, does not result from a photooxidation mechanism of Fe(II) to Fe(III). In the absence of oxygen [Fig. 4(b)] the photolysis is slower. The colored product that was observed in the previous photolysis (Fig. 3) does not form any longer. This confirms the effect of oxygen on the formation of Fe(III) during the photolysis of ferrocenium salts. Recently, interactions of oxygen with ferrocenium salts in a photopolymerizable matrix have been reported.[17b] The last-mentioned has also suggested the formation of Fe(III) containing chemical species that
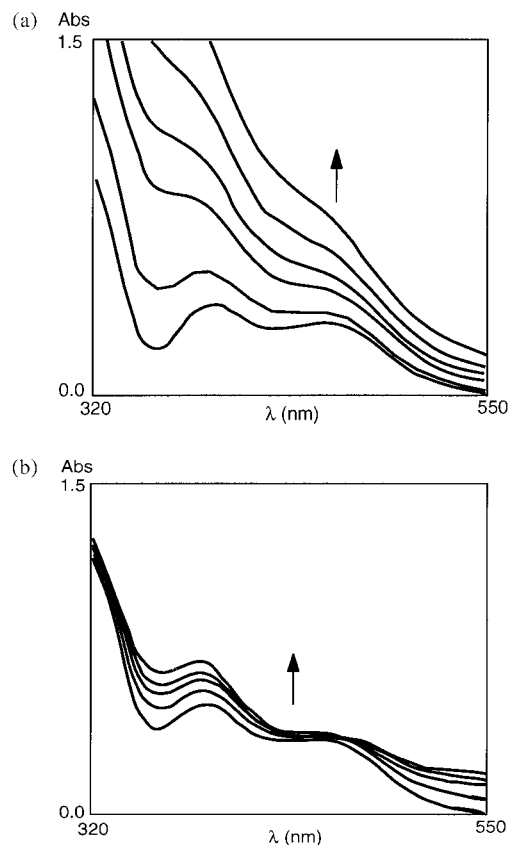


**Figure 4** (a) Photolysis of ferrocenium salt ($5 \times 10^{-3}M$) in $CH_3CN$, in the presence of $O_2$, at $t$: 0, 2, 5, 7, 10, and 15 min of illumination (350 nm high-pass filter). (b) Photolysis of ferrocenium salt ($5 \times 10^{-3}M$) in $CH_3CN$ in the absence of $O_2$ at $t$: 0, 2, 5, 10, and 15 min of illumination (350 nm high-pass filter).

can promote the formation of hydroxyl radicals through oxidation of organic compounds (the production of these radicals would then generate a radical process that is responsible for the polymerization of acrylate resins).

### The Photolysis of a Ferrocenium Salt in the Presence of an Oxidizing Agent: Cumene Hydroperoxide

In the presence of air and hydroperoxide, the rate of formation of the photolysis products decreases [Fig. 5(a)] in comparison with the results obtained when $CpFe^+Aren$ alone undergoes degradation [Fig. 4(a)]. In the absence of oxygen [Fig. 5(b)], a substantial formation of Fe(III) takes place. The amount of Fe(III) that was produced remains higher than that obtained in the absence of $O_2$ during the photodegradation of $CpFe^+Aren$ alone. This seems to prove that the hydroperoxide, as an
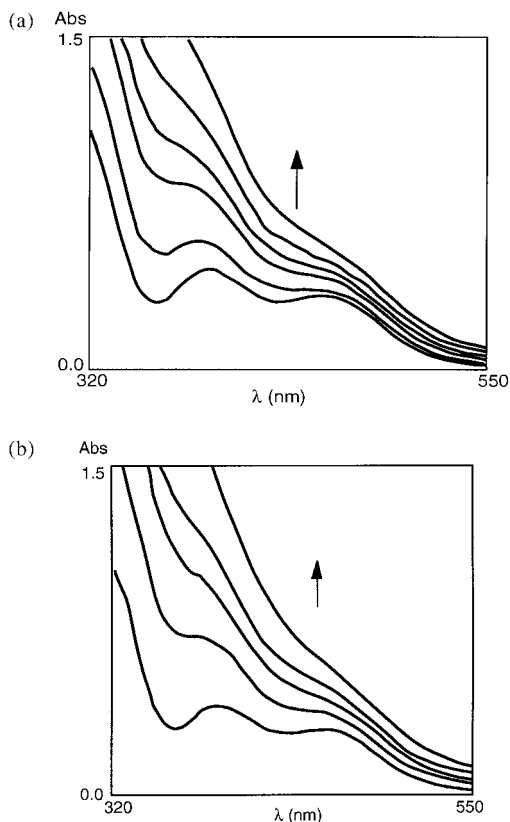
**Figure 5** (a) Photolysis in the presence of $O_2$ of system ferrocenium salt ($5 \times 10^{-3}M$) and cumene hydroperoxide ($5 \times 10^{-3}M$) at $t$: 0, 2, 5, 7, 10, and 15 min (350 nm high-pass filter). (b) Photolysis of system ferrocenium salt ($5 \times 10^{-3}M$) and cumene hydroperoxide in the absence of $O_2$, at $t$: 0, 5, 10, and 30 min (350 nm high-pass filter).

oxidizing agent, participates in the mechanism of photooxidation of Fe(II) to Fe(III). Indeed, $H_2O_2$ plays the role of an electron acceptor in the photooxidation of $Fe(CH_2)_nCO_2$ type ferrocene derivatives:[18]

$$H_2O_2 + Fe(CH_2)_nCO_2^- \xrightarrow{h\nu} Fe^+(CH_2)_nCO_2^- + OH^- + OH^\bullet$$
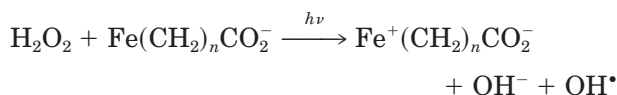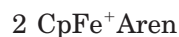
Other investigators have taken great interest in this reaction, that had been first reported in ref. 19a towards the close of the XIXth century. The last-mentioned showed that the association of Fe(II) with hydroperoxide forms a most effective oxidizing couple for many organic compounds. Forty years later, the formation of a hydroxyl radical in the oxidation mechanism was suggested.[19b] At the present time, the two major

reactions that are known to take place between metal complexes and alkyl hydroperoxides are:[19c,19d] reduction: $RO_2H + M^{(n-1)+} \to RO^\bullet + M^{n+} + OH^-$; oxidation: $RO_2H + M^{n+} \to RO_2^\bullet + M^{(n-1)+} + H^+$.
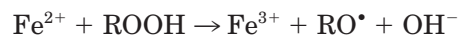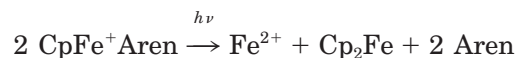
In inert solvents, these two reactions can be followed by a radical chain decomposition of the hydroperoxide:

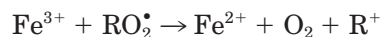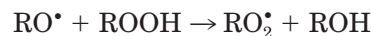$$2RO_2^\bullet \to 2RO^\bullet + O_2$$

$$RO^\bullet + RO_2H \to RO_2^\bullet + ROH$$
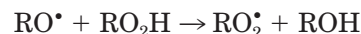
In the present case, two mechanisms with and without ROOH can be suggested: (a) one-step mechanism:

2 CpFe$^+$Aren

$$+ ROOH \xrightarrow{h\nu} [2\,CpFe^+Aren \cdots ROOH]^*$$
$$\downarrow$$
$$Fe^{3+} + RO^\bullet + OH^- + Fe(Cp)_2 + 2\,Aren$$

(b) two-step mechanism:

$$2\,CpFe^+Aren \xrightarrow{h\nu} Fe^{2+} + Cp_2Fe + 2\,Aren$$

$$Fe^{2+} + ROOH \to Fe^{3+} + RO^\bullet + OH^-$$
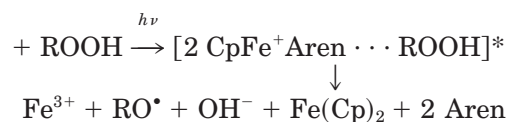
Subsidiary reactions take place onward:[19d]

$$2RO_2^\bullet \to 2RO^\bullet + O_2$$

$$RO^\bullet + ROOH \to RO_2^\bullet + ROH$$

$$Fe^{3+} + RO_2^\bullet \to Fe^{2+} + O_2 + R^+$$

The same holds true with $O_2$, where a radical anion $O_2^{\bullet-}$ can be formally generated and plays the role of a strong oxidant in further reactions.

The possible reduction of Fe(III) to Fe(II) could *a posteriori* be an item of explanation regarding the decrease in photolysis rate of the ferrocenium salt under $O_2$ when the last-mentioned is in presence of hydroperoxide [Figs. 4(a) and 5(a)].
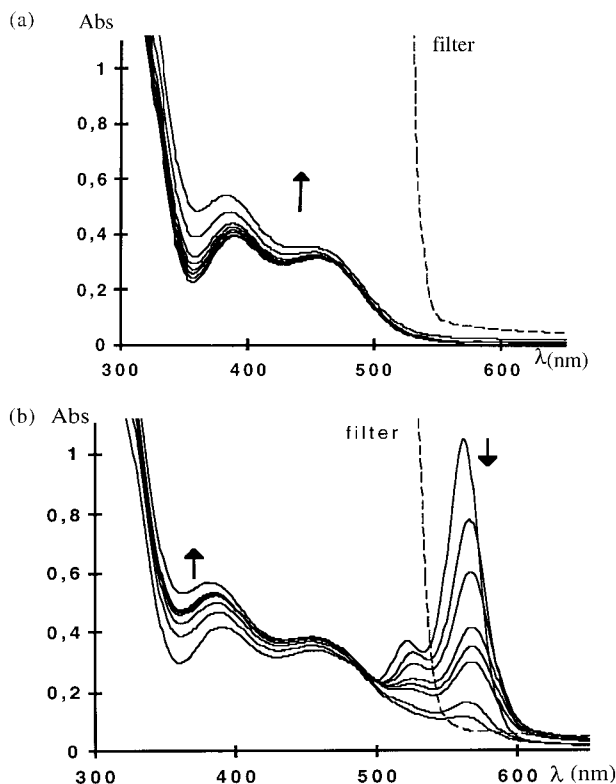
**Figure 6** (a) Photolysis of ferrocenium salt ($5 \times 10^{-3}M$) in CH$_3$CN, in the presence of O$_2$, at $t$: 0, 1, 2, 3, 4, 5, 10, and 20 min (535 nm high-pass filter). (b) Photolysis of system ferrocenium salt ($5 \times 10^{-3}M$) and Rose Bengal ($8 \times 10^{-6}M$) in CH$_3$CN, in the presence of O$_2$, at $t$: 0, 1, 2, 3, 4, 5, 10, and 20 min (535 nm high-pass filter).

### The Photolysis of a Ferrocenium Salt in the Presence of a Xanthenic Dye: Rose Bengal

To demonstrate the sensitizing role of the dye, a high-pass filter ($\lambda = 535$ nm transmission = 40%) was inserted to avoid, on one hand, direct absorption of the ferrocenium salt and favor, on the other hand, the absorption of Rose Bengal ($\lambda_{max}$ = 564 nm in acetonitrile). Figure 6(a) depicts the photolysis of the ferrocenium salt with the 535-nm filter, and is used as a reference in the subsequent part of the report, because a slight degradation of CpFe$^+$Aren was observed despite the use of a filter. The results of the photolysis of the system Rose Bengal/ferrocenium salt do not warrant any conclusion on the sensitization phenomenon of CpFe$^+$Aren by the dye [Fig. 6(b)]. Indeed, the increase in optical density at 355 nm corresponding to the formation of products generated by the photolysis of ferrocenium salt (Fe(III) in the presence of oxygen) is very small. On the

other hand, the colored form of Rose Bengal ($\lambda_{max}$ = 564 nm) rapidly disappears. If one compares the results of Figure 6(a) and (b), however, there is a large difference in the beginning of the photodegradation of the solutions: on illuminating for 1 min, the optical density at 355 nm is six times higher with the dye than with no Rose Bengal. It may, therefore, be inferred from this abrupt increase in solution absorption that the sensitization mechanism is not very effective, because the products formed from compound CpFe$^+$Aren on illumination may lead to the displacement of the ionic form of the dye and modify the absorption of the dye.

Indeed, xanthenic dyes exhibit several groups that are likely to ionize. Therefore, they can exist in different forms: cationic, molecular, mono- or dianionic. The existence or the predominance of one or the other of these forms depends on the nature of the solvent and the pH of the medium.[20] These different forms absorb in different ranges of the luminous spectrum (Fig. 7). To confirm the effect of the pH on the photolysis reaction, a new experiment was carried out in strongly basic medium (Fig. 8): the presence of NaOH ($2 \times 10^{-2}M$) gave rise to larger amounts of photolysis products of ferrocenium salt than those observed previously [Fig. 6(b)]. Photolysis of ferrocenium salt in basic solution (Fig. 9) shows that the evolution of the absorption spectrum is almost similar to that reported in neutral solution [Fig. 6(a)]. The formation of an arenic compound and a Lewis acid, that are responsible for the cationic initiation of the polymerization of the epoxide according to the following mechanism has been suggested:[21]
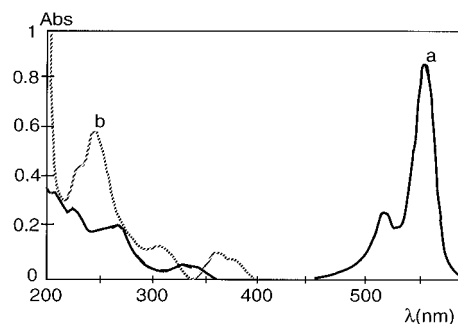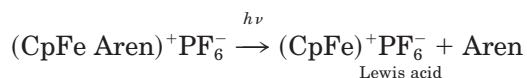
$$(\text{CpFe Aren})^+\text{PF}_6^- \xrightarrow{h\nu} (\text{CpFe})^+\text{PF}_6^- + \underset{\text{Lewis acid}}{\text{Aren}}$$



**Figure 7** Absorption spectrum of Rose Bengal: (a) in acetonitrile (anionic form); (b) in acetonitrile/water, pH = 2 (cationic form).
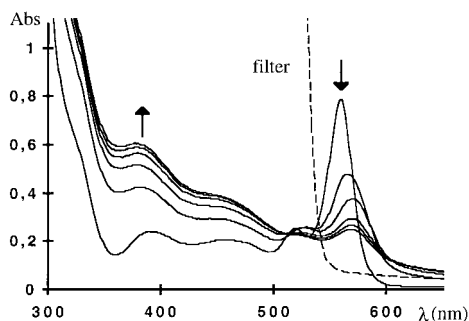
**Figure 8** Photolysis of system ferrocenium salt (3 $\times$ $10^{-3}M$), Rose Bengal (8 $\times$ $10^{-6}M$), NaOH (2 $\times$ $10^{-2}M$) in CH$_3$CN, in the presence of O$_2$, at $t$: 0, 5, 10, 15, and 20 min (535 nm high-pass filter).



**Figure 10** Photolysis of system ferrocenium salt (3 $\times$ $10^{-3}M$) and thionine $^-$(OD = 1), in CH$_3$CN, in the presence of O$_2$, at $t$: 0, 1, 5, 10, 20, 30, and 40 min (535 nm high-pass filter).

Accordingly, the Lewis acid liberation could account for the modification of the ionic form of the dye, thus preventing the continuation of the photosensitization process, because the dye form existing in acid medium does not absorb beyond 400 nm (Fig. 7).

### The Photolysis of a Ferrocenium Salt in the Presence of Thionine

The choice of the second dye fell on a compound of the thiazine family, that may also exist in two forms, according to the pH of the medium: an acid form absorbing at 605 nm and a basic form absorbing at 530 nm.

In acetonitrile medium, thionine exists in its acid form. Reference to research work carried out in ref. 21 shows that no basic form is liberated during the photolysis reaction. Therefore, in contrast with the case of xanthenic dyes, the absorption of the dye cannot be displaced. Dye absorp-
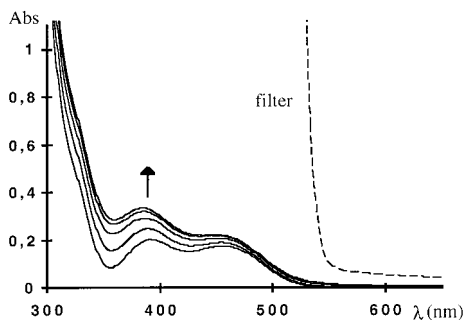
tion can only be intensified at 605 nm, if the solution liberates acid species.

The 535-nm high-pass filter was retained. The results are shown in Figure 10. During the first 10 min of illumination, the optical density at 605 nm slightly increased, which seems to confirm the presence of acid species in the solution. The photodegradation of the ferrocenium salt in the presence of thionine was more pronounced than in the case of ferrocenium salt alone (Fig. 9) or Rose Bengal/ferrocenium salt [Fig. 6(b)].

The experiment with thionine allows, therefore, the assertion that ferrocenium salt can be photosensitized by a dye of the thiazine type which is, then, photoreduced. The formation of Fe(III) lends support to a photooxidation reaction of the ferrocenium salt.

### The Photolysis of a Ferrocenium Salt in the Presence of Rose Bengal and an Amine

*Preliminary investigation: Rose Bengal/N-methyldiethanolamine:* The association xanthenic dye/ electron donor has been described extensively in visible light-induced photopolymerization reactions of acrylates. Indeed, the polymerization is initiated by formation of A$^{\bullet}$ radicals generated from the electron transfer that takes place between the dye and the amine, according to the following reaction scheme:[20c]



**Figure 9** Photolysis of ferrocenium salt (3 $\times$ $10^{-3}M$) in the presence of NaOH (2 $\times$ $10^{-2}M$) in CH$_3$CN, in the presence of O$_2$, at $t$: 0, 5, 10, 15, and 20 min (535 nm high-pass filter).
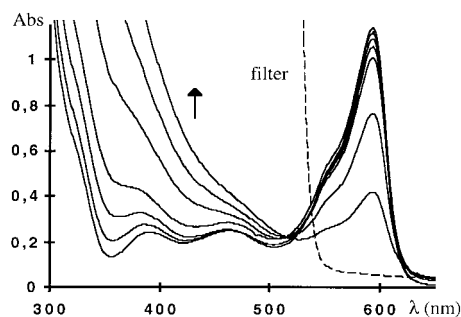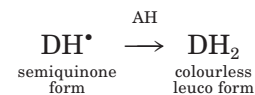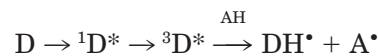
$$D \rightarrow {}^1D^* \rightarrow {}^3D^* \xrightarrow{\text{AH}} DH^{\bullet} + A^{\bullet}$$

$$\underset{\substack{\text{semiquinone}\\\text{form}}}{DH^{\bullet}} \xrightarrow{\text{AH}} \underset{\substack{\text{colourless}\\\text{leuco form}}}{DH_2}$$

$$A^{\bullet} \rightarrow \text{polymerization}$$

When the photolysis of such a system is investigated in the presence of oxygen, in solvent medium at such concentrations, the photoreduction of the dye is not effective, due to reoxidation of the leuco form of the dye (deactivation of the triplet state by oxygen is competitive with amine quenching):

$$^{3}D^{*} \xrightarrow[O_2]{AH} D$$

$$DH_2 \xrightarrow{O_2} DH^{\bullet} + HOO^{\bullet}$$

$$DH^{\bullet} \xrightarrow{O_2} D + HOO^{\bullet}$$
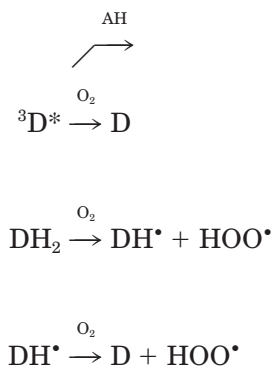
On the other hand, in the absence of $O_2$, photoreduction of the dye in its leuco form was observed (Fig. 11).

### Effect of $O_2$ on the Photolysis of the Three-Component System

In the presence of $O_2$ [Fig. 12(a)] the appearance of the photolysis products of the ferrocenium salt, in particular the presence of Fe(III) is substantial compared to that observed in the mixture ferrocenium salt/Rose Bengal [Fig. 6(b)]. The increase in optical density at 355 nm is in the same order of magnitude as that obtained on direct photolysis of the ferrocenium salt with a 350-nm high-pass filter [Fig. 4(a)]. The photoreduction of the dye is very low compared to that shown in Figure 6(b).
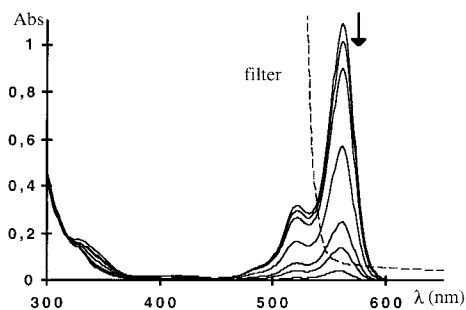


**Figure 11** Photolysis of system Rose Bengal (8 $\times 10^{-6}M$) and MDEA (1.7 $\times 10^{-1}M$) in CH$_3$CN, in the absence of $O_2$, at $t$: 0, 1, 2, 3, 4, 5, and 10 min of illumination (535 nm high-pass filter).
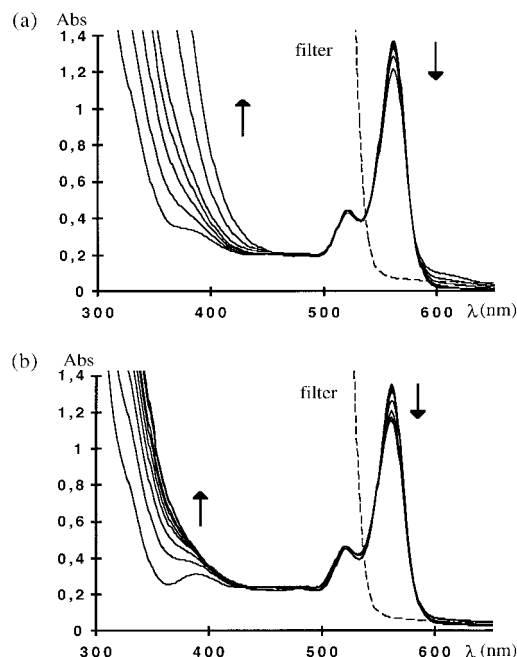


**Figure 12** (a) Photolysis of system ferrocenium salt (3 $\times 10^{-3}M$), Rose Bengal (8 $\times 10^{-6}M$) and MDEA (7 $\times 10^{-2}M$) in CH$_3$CN, in the presence of $O_2$, at $t$: 0, 1, 2, 3, 4, 5, 10, and 20 min of illumination (535 nm high-pass filter). (b) Photolysis of system ferrocenium salt (3 $\times 10^{-3}M$), Rose Bengal (8 $\times 10^{-6}M$), and MDEA (7 $\times 10^{-2}M$) in CH$_3$CN, in the absence of $O_2$, at $t$: 0, 1, 2, 3, 4, 5, 10, 20, and 30 min of illumination (535 nm high-pass filter).

### Effect on $N_2$ Bubbling

The presence or the absence of oxygen does not seem to modify the photoreduction process of the dye [Fig. 12(b)]. On the other hand, the quantity of Fe(III) produced when photodegradation of CpFe$^+$Aren takes place is lower in the absence of $O_2$. Yet, it remains higher than that observed on photolysis of ferrocenium salt alone, with no oxygen [Fig. 4(b)].

### The Photolysis of a Ferrocenium Salt in the Presence of Rose Bengal, N-Methyldiethanolamine and Cumene Hydroperoxide

The association of these four compounds permits the polymerization of thick pigmented films. The relative concentrations of each component are, therefore, fixed, so as to retain the same concentration ratio as for the experiments that were carried out with a filmformer. Figure 13(a) and 13(b) represents the photolyses of the system in the presence or the absence of oxygen. Addition of
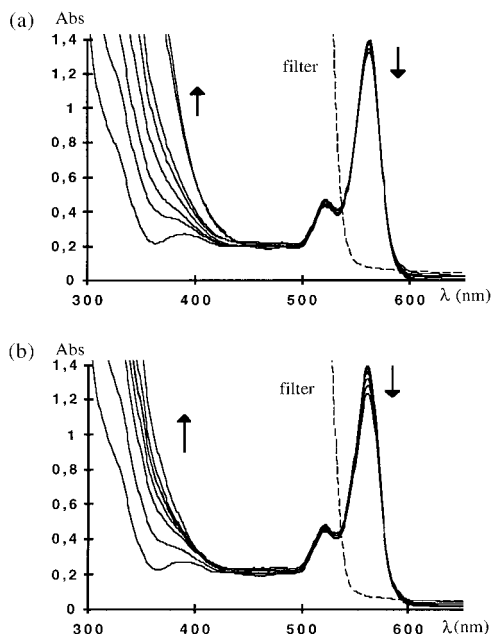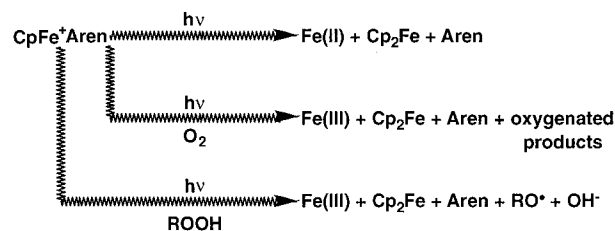
(a) Abs



(b) Abs



**Figure 13** (a) Photolysis of system ferrocenium salt $(3 \times 10^{-3}M)$, MDEA $(7 \times 10^{-2}M)$, Rose Bengal $(8 \times 10^{-6}M)$, and cumene hydroperoxide $(10^{-2}M)$, in CH$_3$CN, in the presence of O$_2$, at $t$: 0, 1, 2, 3, 4, 5, 10, and 20 min of illumination (535 nm high-pass filter). (b) Photolysis of system ferrocenium salt $(3 \times 10^{-3}M)$, MDEA $(7 \times 10^{-2}M)$, Rose Bengal $(8 \times 10^{-6}M)$, and cumene hydroperoxide $(10^{-2}M)$, in CH$_3$CN, in the absence of O$_2$, at $t$: 0, 1, 2, 3, 4, 5, 10, and 20 min of illumination (535 nm high-pass filter).

cumene hydroperoxide to the mixture does not significantly modify the kinetics of the photodegradation reaction of the dye-sensitized ferrocenium salt amine system [Figs. 13(a), 13(b), 12(a) and 12(b)]. The photoreduction of the dye is low compared to the photolysis of dye/ferrocenium salt [Fig. 6(b)]. Qualitatively, Figures 12(a) and 13(a) show that the sensitized photolysis results in a similar way to that obtained during the corresponding direct photolysis [Fig. 5(a)].

*Proposed Mechanism*

As a summary, photolysis investigation of the system ferrocenium salt, hydroperoxide, dye, amine, provided evidence for the following interactions: (a) in ferrocenium salt/oxygen, in the presence of air, the photolysis of CpFe$^+$Aren leads to Fe(III). (b) in cumene hydroperoxide/ferrocenium salt, in the absence of oxygen, the hydroperoxide as an oxidizing agent participates in the photooxidation mechanism leading to Fe(III). (c) in dye/ferrocenium salt, xanthenic, or thiazine

type, dyes photosensitize the photodegradation reaction of CpFe$^+$Aren. Formation of ferric ions and reduction of the dye to its leuco form, in the presence or the absence of oxygen, both take place; (d) in xanthenic dye/ferrocenium salt/amine, the photosensitization reaction is effective only in basic or neutral medium. The presence of amine allows the neutralization of acid forms liberated during the photolysis.

From these first observations, one can qualitatively suggest two possible pathways in the formation of radicals capable of initiating the photopolymerization reaction of acrylates, under polychromatic light: (1) either through direct photolysis of the ferrocenium salt (Scheme 1). The higher efficiency in the presence of amine (independently of some direct interactions) is explained by the fact that the generated Lewis acid CpFe$^+$ does not modify the acidity of the medium, which prevents the dye to change its original anionic form; (2) or through photosensitization of the ferrocenium salt by the dye in the presence of amine and hydroperoxide. Direct interaction between the dye and the amine or the hydroperoxide cannot be excluded (Scheme 2). The primary step involved in the photosensitized reaction can be as follows:

(a) an interaction between the dye and the ferrocenium salt: energy transfer is not clearly feasible [$E_T$ of the ferrocenium salt $\sim 184$ KJM$^{-1}$; ref. 23; and $E_T$ of the dye $\sim 167$ KJM$^{-1}$ ref. 24;
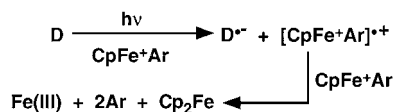
**DIRECT PHOTOLYSIS OF THE CpFe+(II)AREN COMPLEX**



**Scheme 1**

**DIRECT PHOTOLYSIS OF THE DYE**
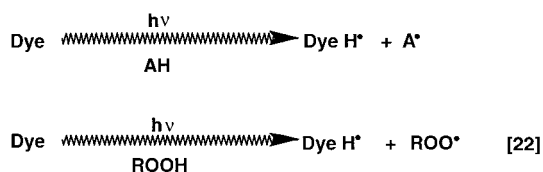


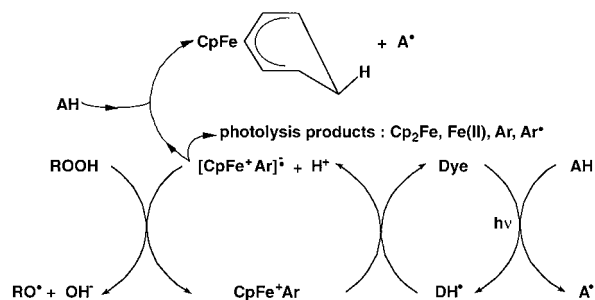**Scheme 2**
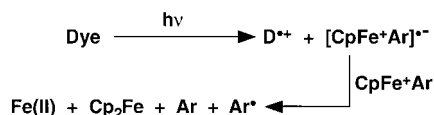
**Scheme 3a**



**Scheme 3b**



**Scheme 4**

singlet energy transfer is not favorable, and should not be able to account for the Fe(III) generation. If energy transfer occurred, the dye should not be consumed, and the ferrocenium salt would have to decompose as in the direct photolysis: this is not observed.

Calculated $\Delta G$ for electron transfer from the dye in its triplet state ($E_{ox} \sim 0.94$ ev[24]) to the ferrocenium salt ($E_{red} \sim -1.34$ ev[25]) is not favorable ($\Delta G \sim +58$ KJM$^{-1}$). Electron transfer from the dye to the salt in the singlet state cannot be excluded (Scheme 3a). Electron transfer from some appropriate sensitizer such as amines to the salt is also known.[26] In the case where an electron can be transferred (this case is depicted in scheme 3b) from the ferrocenium salt to the dye (may be according to a complex mechanism), Fe(III) should be directly generated as in the oxidation reaction by ROOH. However, (*i*) the nature of the initiating species is not clear, (*ii*) the role of the hydroperoxide is not explained, and (*iii*) the photoreduction of the dye is very low. Moreover, this process should not be operative with a dye such as Rose Bengal.

(b) A primary interaction between the dye and the amine: an alternative mechanism involves a known primary interaction between the dye and the amine and the generation of a DH$^\bullet$ radical, which should be quenched by the ferrocenium salt as reported in Scheme 4 (however, nothing is known about the feasability of this quenching process). This mechanism can explain quite well the absence of degradation of the dye and the enhancement of the polymerization efficiency through a scavenging of the DH$^\bullet$ radical, which has been recognized as a terminating agent of the growing macromolecular chains and that is quenched by the amine to yield the leuco form of the dye), the generation of new RO$^\bullet$ radicals and the increase of the A$^\bullet$ radical concentration
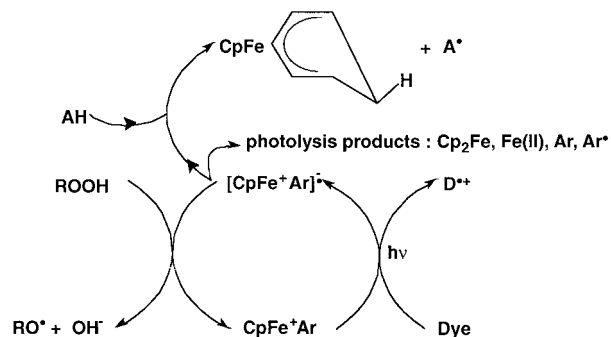
through a reaction of the ferrocenium salt radical anion with the amine.[25] Scheme 4, however does not seem to be able to account for the direct production of Fe(III), but can explain the initiation of the polymerization.

(c) An interaction between the dye and the complex followed by an interaction with the amine: the mechanism (Scheme 5) involves in the first place, an electron transfer from the dye to the complex, then secondary reactions similar to that proposed in Scheme 4. Regeneration of the dye can occur through electron transfer between D$^{\bullet+}$ and the amine. Fe(III) is presumably formed through an oxidative process. Decomposition of ROOH can occur.
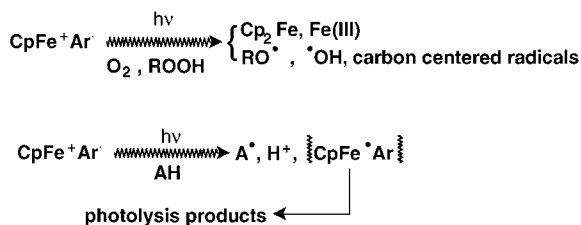
The efficiency of the different ways discussed above will be dependent on the relative kinetics of the competitive photoprocesses and the relative concentrations of the different partners: a time-resolved laser spectroscopy investigation will be presented in a forthcoming article.

At first sight, one can assume that both mechanisms can occur for the sensitized photolysis: dye/amine interaction and dye/ferrocenium salt interaction.

Under an irradiation carried out with a polychromatic light, a direct photolysis can likely oc-



**Scheme 5**

$$CpFe^+Ar^- \xrightarrow[O_2,\ ROOH]{h\nu} \begin{cases} Cp_2\ Fe,\ Fe(III) \\ RO^\bullet,\ ^\bullet OH,\ \text{carbon centered radicals} \end{cases}$$

$$CpFe^+Ar^- \xrightarrow[AH]{h\nu} A^\bullet,\ H^+,\ \{CpFe\ ^\bullet Ar\}$$

photolysis products ←

**Scheme 6**

cur (in addition to the sensitized photolysis) as shown in Scheme 6 according to tentative mechanisms proposed in the literature.[17b,26]

## CONCLUSION

The system developed during the present investigation[11] allowed the production of pigmented coatings with other colors than those already available on the market in 1993, which are white or black. Its performances hinted that it is possible to polymerize a hundred micron-thick films, which completely opacify the substrate in a one-step application. One of the great advantages of the present system is its one-step mode of operation (one layer-one step of irradiation). It is currently one of the highest performing potential systems for the curing of paints usable under industrial conditions (recently good results in the design of radiation curable paints have been elsewhere reported later on when using new acylphosphine oxides[27]). The photolysis investigation and the proposed mechanism should be considered as a first attempt to understand qualitatively what happens in such a multicomponent system in solution. As stated above, further works are now in progress on the investigation of the primary steps through fast spectroscopy, for example, the interactions of Rose Bengal with a ferrocenium salt.[28]

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