subsequent step *B*, the photogenerated protons are used to catalytically cleave the acid-labile tetrahydropyranyloxy blocking moiety linked to the polymer backbone. The net result is a big change in polarity between exposed and non-exposed zones of the resist film. This allows for the development of the deblocked, polar zones in aqueous alkaline solution. Since one proton can initiate a large number of chemical changes, chemical amplification [3–5] is achieved, leading to highly sensitive resist materials.

We have found that the desired properties are combined in new polymers consisting of maleimides and reversibly blocked *p*-hydroxystyrene [6]. Each of the three monomers is adding specific properties to the final resist (*Fig. 1*). Synthetic routes yielding the desired monomers were established, along with a polymerization method leading to polymers having the desired monomer built-in ratio and molecular weight distribution. Resist formulations were obtained by dissolving the polymers, along with triphenylsulfonium triflate (photoacid generator), in cyclohexanone. If the corresponding resist films were imaged at 250 nm, resolution below 1/4 micron was achieved (*Fig. 2*).

3. Perspectives

Microlithography is a valuable technique for the generation of small-size patterns. New resist materials, which can be imaged at shorter wavelength to allow
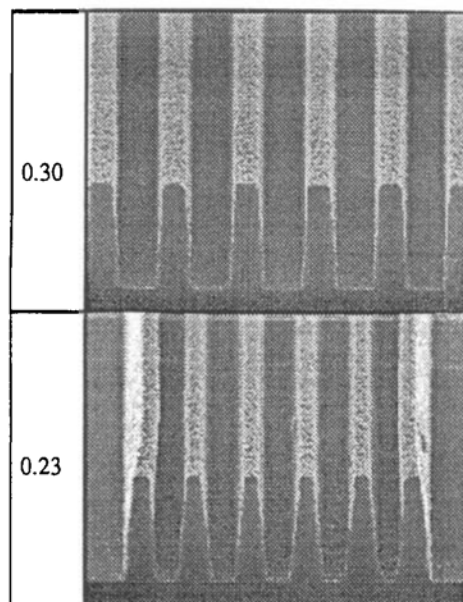

Fig. 2. *SEM Pictures of 0.23 µm and 0.30 µm line/ space patterns in a resist based on maleimide polymers*

ever better resolution, will be needed for the manufacturing of future generation ICs. Our goal is to provide our customers, manufacturers of microelectronic devices, with these materials. Therefore, a resist chemist's work has to start today, looking at new type materials, tailor-made for the shorter illumination wavelengths of the future. Furthermore, we are also looking at other applications, involving the need for highly specified photosensitive materials.

[1] L.F. Thompson, C.G. Willson, M.J. Bowden, ACS Symposium Series, Vol. 219: Introduction to Microlithography: Theory, Materials, and Processing, 1983.
[2] A. Reiser, in 'Photoreactive Polymers, The Science and Technology of Resists', Wiley Interscience, New York, 1991.
[3] H. Ito, C.G. Willson, *Polym. Eng. Sci.* **1983**, *23*, 1012.
[4] J.M.J. Fréchet, E. Eichler, H. Ito, C.G. Willson, *Polymer* **1983**, *24*, 995.
[5] J.M.J. Fréchet, H. Ito, C.G. Willson, Proc. Microcircuit Eng. 260, Grenoble, France, 1982.
[6] U. Schaedeli, N. Münzel, H. Holzwarth, S.G. Slater, O. Nalamasu, *Proc. SPIE* **1994**, *2195*, 98.

Colored Systems with Improved Weatherfastness

Laurent Chassot*

Abstract. Weatherfastness of pigmented organic coatings is a classical problem in the industrial world. We describe the photoreactivity of some heterocyclic pigments from the 1,4-dioxopyrrolo[3,4-*c*]pyrrole (DPP) family in suspension and in a polymer matrix, and the discovery of the photostabilization of organic crystals by nitroxy radicals.

1. Introduction

Pigments are finely divided, organic or inorganic, crystalline solids. They are used mainly for the coloration of polymeric materials like surface coatings (paints), plastics, synthetic fibers, and printing inks [1]. Contrary to dyeing, the coloration is obtained by dispersion of the microcrystals (0.01–1 µm) without dissolution of the chromophore molecules. Colored materials are made by purpose to absorb light, and it has been estimated that half of the annual production of polymers is employed outdoors [2]. Light stability is then a crucial property, because the consumer's interest is in having articles with long life expectancies. For example, the shade of an automotive coating has to be stable for more than four years. For the manufactur-

er, this means bringing systems onto the market which have better light and weather stability.

Photodegradation of systems containing inorganic pigments like TiO_2 is well documented [3]. However, the diversity of the photochemical processes underlying the degradation of organic pigments renders the field difficult and the literature covering the subject is scarce. Nevertheless the Pigment Division of *Ciba* started in its research center at Marly a project on colored systems with improved light- and weatherfastness [4].

2. Description of the Problem

A colored system has two major components, the pigment and the polymeric material (*Scheme*). Both of them will absorb part of the incoming light and partic-

---
**Correspondence*: Dr. L. Chassot
Ciba-Geigy Ltd.
Research Center Marly
Pigment Research
CH–1723 Marly

subsequent step B, the photogenerated protons are used to catalytically cleave the acid-labile tetrahydropyranyloxy blocking moiety linked to the polymer backbone. The net result is a big change in polarity between exposed and non-exposed zones of the resist film. This allows for the development of the deblocked, polar zones in aqueous alkaline solution. Since one proton can initiate a large number of chemical changes, chemical amplification [3–5] is achieved, leading to highly sensitive resist materials.

We have found that the desired properties are combined in new polymers consisting of maleimides and reversibly blocked p-hydroxystyrene [6]. Each of the three monomers is adding specific properties to the final resist (*Fig. 1*). Synthetic routes yielding the desired monomers were established, along with a polymerization method leading to polymers having the desired monomer built-in ratio and molecular weight distribution. Resist formulations were obtained by dissolving the polymers, along with triphenylsulfonium triflate (photoacid generator), in cyclohexanone. If the corresponding resist films were imaged at 250 nm, resolution below 1/4 micron was achieved (*Fig. 2*).

3. Perspectives

Microlithography is a valuable technique for the generation of small-size patterns. New resist materials, which can be imaged at shorter wavelength to allow
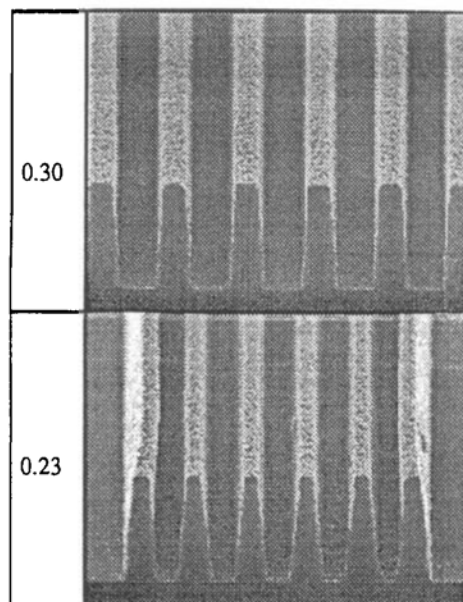
Fig. 2. *SEM Pictures of 0.23 μm and 0.30 μm line/ space patterns in a resist based on maleimide polymers*

ever better resolution, will be needed for the manufacturing of future generation ICs. Our goal is to provide our customers, manufacturers of microelectronic devices, with these materials. Therefore, a resist chemist's work has to start today, looking at new type materials, tailor-made for the shorter illumination wavelengths of the future. Furthermore, we are also looking at other applications, involving the need for highly specified photosensitive materials.

[1] L.F. Thompson, C.G. Willson, M.J. Bowden, ACS Symposium Series, Vol. 219: Introduction to Microlithography: Theory, Materials, and Processing, 1983.
[2] A. Reiser, in 'Photoreactive Polymers, The Science and Technology of Resists', Wiley Interscience, New York, 1991.
[3] H. Ito, C.G. Willson, *Polym. Eng. Sci.* **1983**, *23*, 1012.
[4] J.M.J. Fréchet, E. Eichler, H. Ito, C.G. Willson, *Polymer* **1983**, *24*, 995.
[5] J.M.J. Fréchet, H. Ito, C.G. Willson, Proc. Microcircuit Eng. 260, Grenoble, France, 1982.
[6] U. Schaedeli, N. Münzel, H. Holzwarth, S.G. Slater, O. Nalamasu, *Proc. SPIE* **1994**, *2195*, 98.

Colored Systems with Improved Weatherfastness

Laurent Chassot*

Abstract. Weatherfastness of pigmented organic coatings is a classical problem in the industrial world. We describe the photoreactivity of some heterocyclic pigments from the 1,4-dioxopyrrolo[3,4-*c*]pyrrole (DPP) family in suspension and in a polymer matrix, and the discovery of the photostabilization of organic crystals by nitroxy radicals.

1. Introduction

Pigments are finely divided, organic or inorganic, crystalline solids. They are used mainly for the coloration of polymeric materials like surface coatings (paints), plastics, synthetic fibers, and printing inks [1]. Contrary to dyeing, the coloration is obtained by dispersion of the microcrystals (0.01–1 μm) without dissolution of the chromophore molecules. Colored materials are made by purpose to absorb light, and it has been estimated that half of the annual production of polymers is employed outdoors [2]. Light stability is then a crucial property, because the consumer's interest is in having articles with long life expectancies. For example, the shade of an automotive coating has to be stable for more than four years. For the manufactur-

er, this means bringing systems onto the market which have better light and weather stability.

Photodegradation of systems containing inorganic pigments like TiO_2 is well documented [3]. However, the diversity of the photochemical processes underlying the degradation of organic pigments renders the field difficult and the literature covering the subject is scarce. Nevertheless the Pigment Division of *Ciba* started in its research center at Marly a project on colored systems with improved light- and weatherfastness [4].

2. Description of the Problem

A colored system has two major components, the pigment and the polymeric material (*Scheme*). Both of them will absorb part of the incoming light and partic-

---
Correspondence: Dr. L. Chassot
Ciba-Geigy Ltd.
Research Center Marly
Pigment Research
CH–1723 Marly

ipate in photochemical events. Photodegradation of polymers is actively studied, and their stabilization has been improved dramatically by the introduction of UV absorbers and radical quenchers. The weather stability of the pigments becomes then a limiting factor, and we want to concentrate on their stabilization. The relevance of this choice is strengthened by *Fig. 1* where rapid degradation of the pigment relative to the vehicle is shown.

The chromophores studied here are members of a novel family of heterocyclic pigments 1, 1,4-dioxopyrrolo[3,4-c]pyrrole called DPP [5]. This new class of pigments can be considered as one of the most important breakthroughs in the red-pigment area. The amide group of 1 builds a one dimensional network whereas the π-π stacking directs the growth of the crystallite in the second direction. These two structural elements transform yellow fluorescent dyes into red microcrystalline materials.

Scheme

1
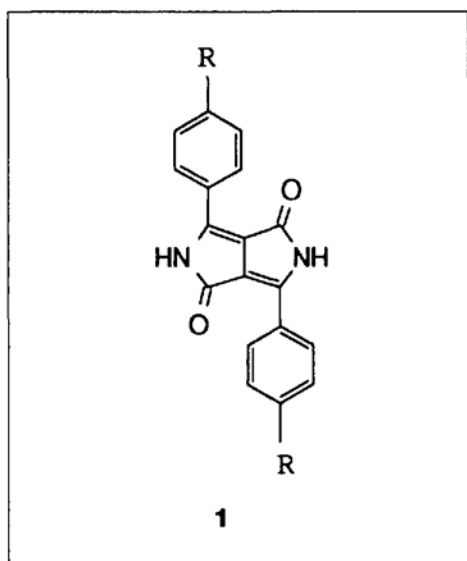
By definition, photochemical reactions start from an excited state. The quantum yield of a bimolecular reaction, which is often the case in degradation, is proportional to the lifetime of the activated state [6]. The fluorescence quantum yield of the chloro derivative of DPP in solution is close to unity. Nevertheless, the triplet state displays a long lifetime of 63 µs, and the dye bleaches rapidly under visible radiation [7]. Aggregation of DPP molecules totally quenches the emission and dramatically enhances the light stability. Due to the extraordinary fastness, this chromophore falls in the range of high-performance pigments and can be used in the automotive industry.

However, both theoretical and practical difficulties come into play in the solid state. It is difficult to differentiate between
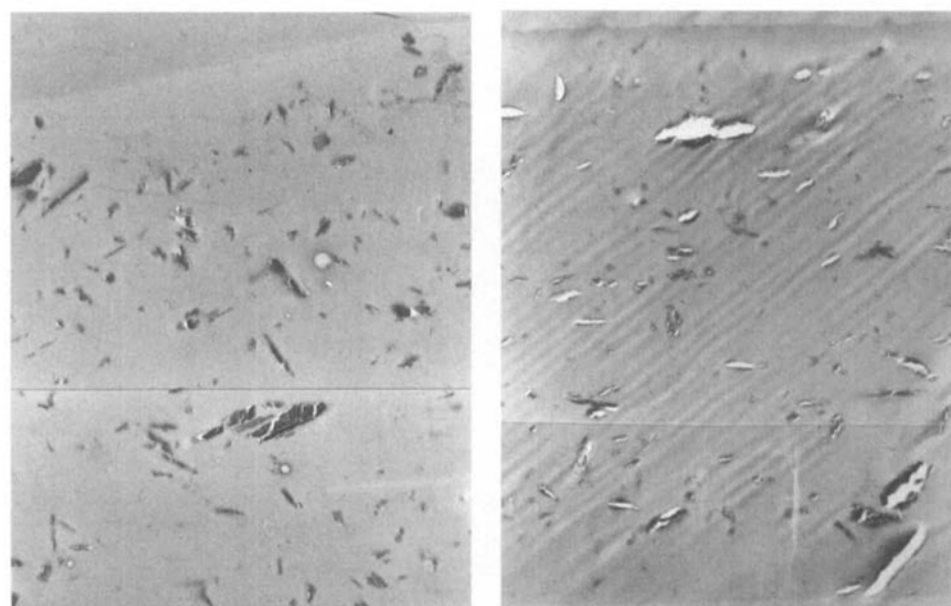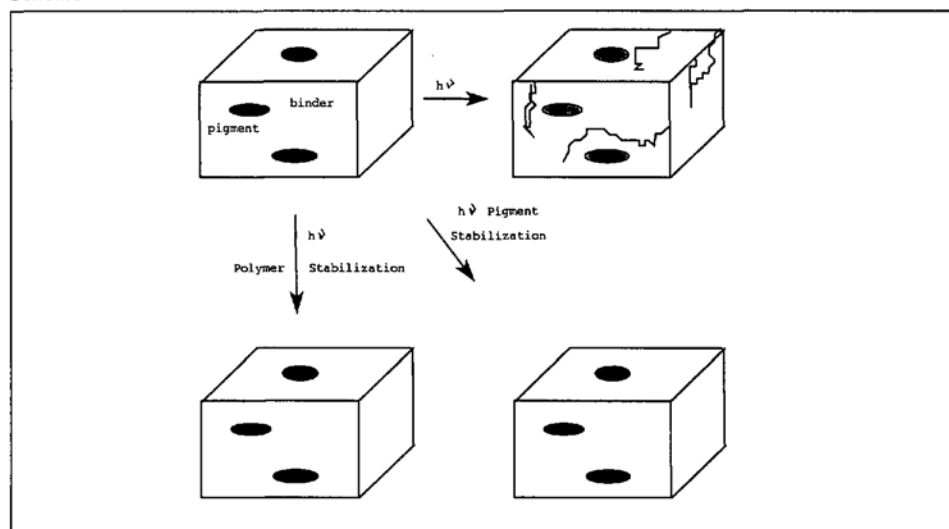

Fig. 1. *Electron micrograph* (magnification 11,150x) *of coatings pigmented with* p-*methyl-DPP*, (left: nonirradiated sample, right: irradiated sample) *degradation accelerated by dipping in MeCN*
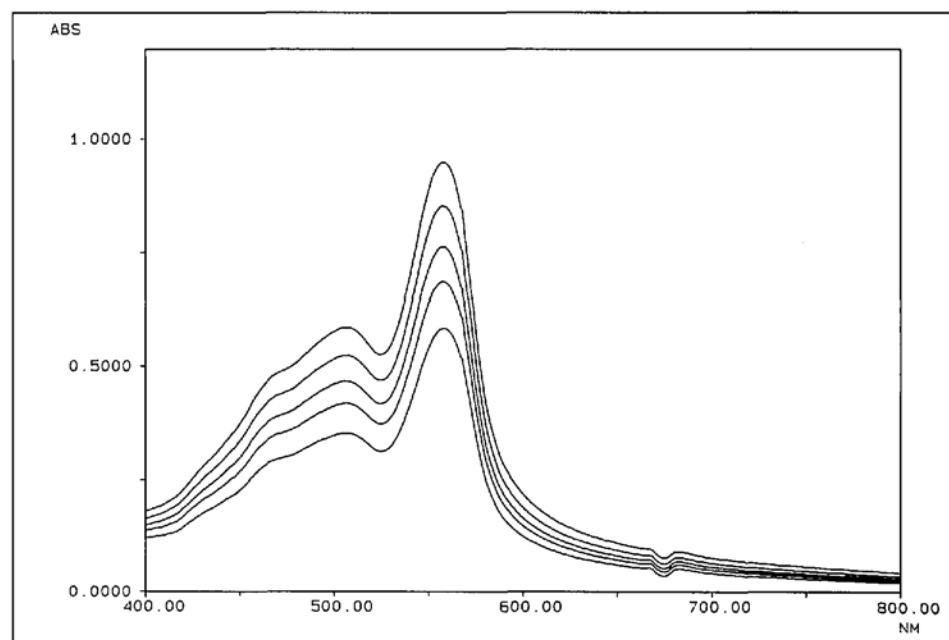

Fig. 2. *Photodegradation of a suspension of* p-*Cl-DPP, 0.01–0.03 µm particle size, MeCN*. Irradiation time 2, 4, 6, and 9 h.

a degradation caused by photochemistry of molecules weakly bound to the surface and a mechanism occurring by formation of a *Frenkel* exciton which, after migration to the surface, will dissociate and participate in redox reactions.

Also practical photochemistry is different from organic photochemistry normally dealt with. Color changes in automotive coatings are barely seen even after 2000 h of intense irradiation. Quantum yields of degradation of an organic pigment in a polymer matrix can be estimated to be less than 10^{-7}. The probability to have complex mechanisms is dramatically enhanced. Also it is almost impossible

to collect analytical data in a reasonable time, and mechanisms normally neglected in laboratory experiments cannot be ruled out. Therefore, a pragmatic approach is required and scientific arguments are used as a guideline, but rigorous proofs outside model systems cannot be given.

3. Results

A full chemical characterization of the degradation products has not been made, but in all cases degradation products absorb only in the UV region (*Fig. 2*). For *p*-methyl-DPP, the *p*-methylbenzoic acid,

p-methylbenzamide, and *p*-methylbenzonitrile derivatives form around 25% in weight of the degradation products. *Fig. 3* shows that irradiation of a sublimed layer of this pigment gives rise to an amorphous material. Thus, the photochemical reaction of the crystalline material follows complex steps giving destruction of the chromophoric nucleus.

3.1. *Testing in Acetonitrile*

We first developed an accelerated screening procedure. Our pigments are insoluble in MeCN, and we can follow by UV/VIS spectroscopy the photodegradation (irradiation with Xe-lamp 0.9 W/m^2) of a suspension in a time scale of 10–20 h. This technique was extended to paint films. Irradiation of a paint dipped in a closed vessel containing MeCN reduced the time needed to evaluate a color change by a factor of at least two orders of magnitude compared to the industrial weather-o-meter irradiation. Even though the correlation with the industrial test is not perfect, the method provides valuable but not infallible guidance.

As mentioned earlier, the quantum yield of the pigment photodegradation is extremely low. This implies that, for stabilization by a quenching mechanism, extremly light-stable quenchers have to be found. Since 95% of the solar intensity is in the visible region [8], we directed our search to molecules which absorb only weakly in the visible.
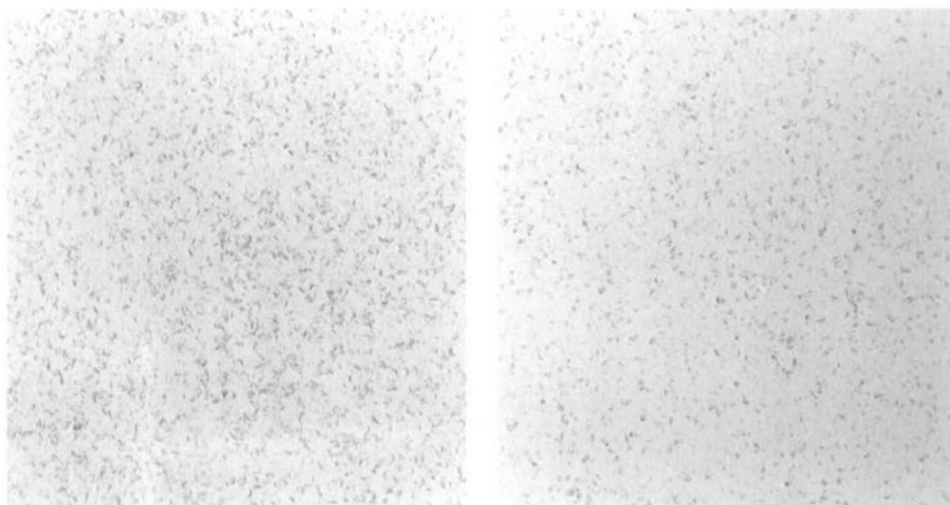

Fig. 3. *Electron micrograph of a sublimed layer of* p-methyl-DPP (*left*: nonirradiated sample, *right*: irradiated sample)
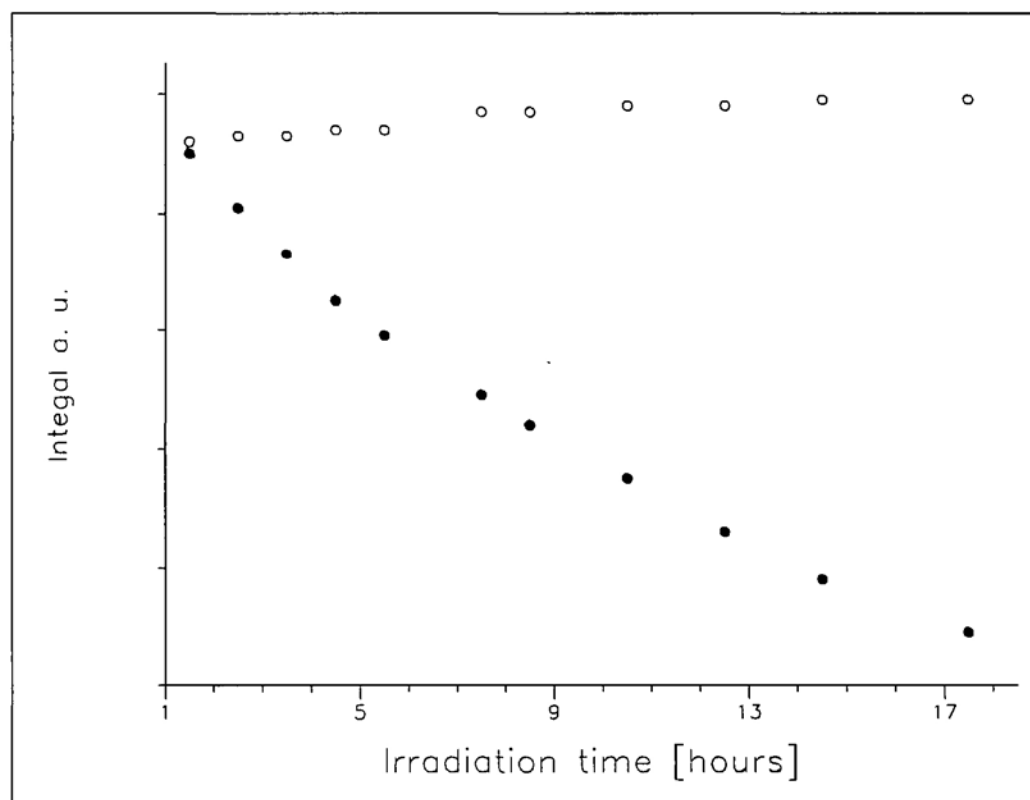

Fig. 4. *Plot of the surface area under the absorption curve, 400–800 nm,* vs. *the irradiation time.* ●: *p*-Cl-DPP in MeCN, ○: the same suspension containing a piperidinoxy radical.

Irradiation time [hours]

Integal a. u.

Conventional UV stabilizers of the o-hydroxybenzotriazole family [9] did not reduce the degradation. Taking into account the overlap between the absorption spectrum of the chromophore and the spectrum of the solar light, we have shown that UV radiation is responsible for only 5–10% of the photochemistry of the DPP family [10]. Also, quenchers of the *H*indered *A*mine *Light Stabilizer* (HALS) type 2 show no activity. But the addition of the oxidized form of those additives 3 to the pigment completely stops the degradation as shown in *Fig. 4*. *N*itroxy *Light Stabilizers* (NILS) are extraordinary stable organic radicals which have an extinction coefficient below $100M$ cm^{-1} in the visible region.

4

2 R = H HALS

3 R = O˙ NILS
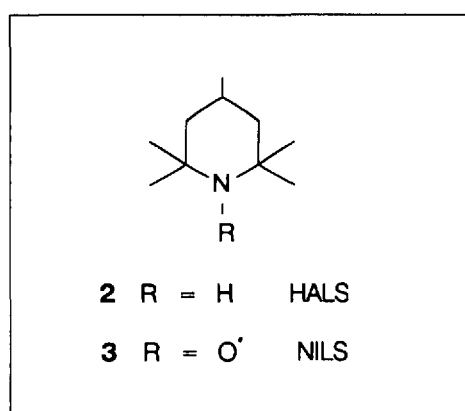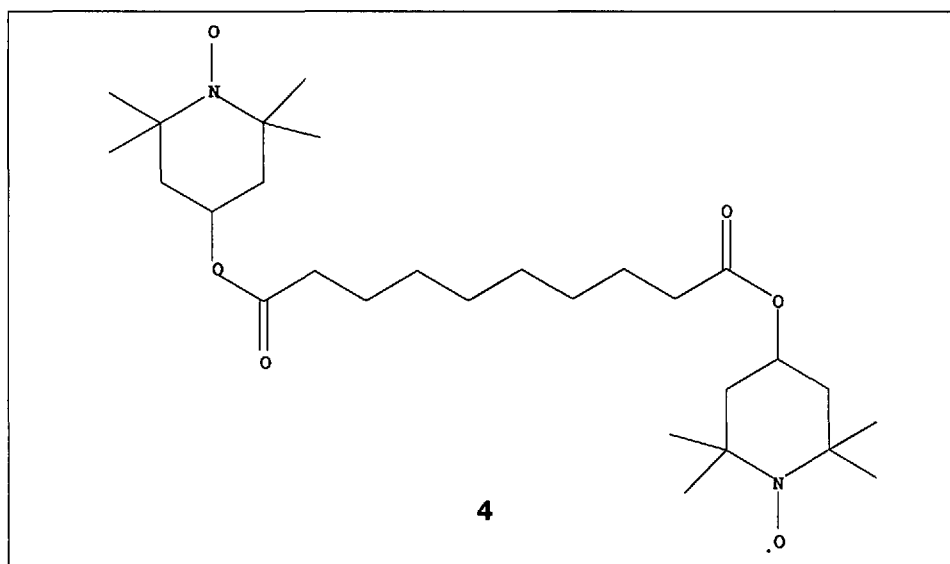
3.2. *Testing in Paint*

The paint used was a so-called white reduction containing organic pigment and TiO_2, 5:95 weight ratio, in a polyester resin. A melamine resin was used as a hardener. The nitroxy radical is added during the paint preparation, and the concentration is given in % weight with respect to the organic pigment. Exposure tests are done according to DIN 53387 which includes water spraying cycles. The degradation is given by the color difference ΔE (CEILAB units) [11] between irradiated and nonirradiated samples and the stabilization is given by the ratio k equal to ΔE(with additive)/ΔE(without additive).

A k value of 0.5 is obtained when the nitroxy radical 4 is added at a concentration of 10% to a paint containing p-chloro-DPP, and the value is constant between 250 and 2000 h of exposure. At the same concentration, the corresponding HALS did not show any stabilization effect ($k = 1.1$). The stabilization is a function of the NILS concentration. The same paint containing the additive in a concentration of 60% is stabilized by a factor of 5 ($k = 0.2$). Variation of the quencher 4-substituent shows that the working unit is the nitroxy

radical [12]. This new family of stabilizers has also been applied with success to other organic pigments like phthalocyanines, quinacridones, and azo pigments [13].

4. Discussion

NILS can react with radicals through bond formation. Also nitroxy compounds are efficient quenchers of molecular excited states of organic molecules and of oxygen.

In MeCN, the degradation process stops when the light is turned off. This means that the pigment instability is not coming from any radical chain reaction. Therefore, stabilization takes place in this medium either from quenching of the pigment excited state or quenching of singlet oxygen. In solution, the singlet state of the DPP chromophore is quenched efficiently by nitroxy radicals, but its triplet state continues to produce singlet oxygen. Extrapolation to the solid state is not straightforward, and work is in progress to understand the different processes for the aggregates.

In a polymer matrix, the trapping of radicals has to be added to quenching of excited states as a possible mechanism. The difference of activity observed between HALS and NILS still speaks in favor of specific interaction between the piperidinoxy radicals and photochemical active species (from the pigment or the oxygen).

5. Conclusion

A brief description of the technical problem of the weatherfastness has been given. The complexity of the possible re-

actions and the time scale of the photochemical process make a rigorous scientific description of the problem difficult. Nevertheless, we found that piperidinoxy radicals quench the photodegradation, and that the lifetime of colored systems can be greatly improved with these additives. A quenching mechanism has been proposed but for definite proof of this type of quenching in the crystalline state, work is in progress.

[1] W. Herbst, K. Hunger, 'Industrielle Organische Pigmente', VCH Publishers, Weinheim, 1987, p. 1.
[2] J.F. Rabek, 'Photostabilization of Polymers', Elsevier Applied Science Publishers, London, 1990.
[3] G. Kaempf, H.G. Voelz, A. Klaeren, W. Papenroth, *Adv. Org. Coat. Sci. Techno. Ser.* 1982, 4, 239.
[4] A collaboration funded by the CERS/KWF commission has been started with Dr. *J. Moser* and his collaborators at the Ecole Polytechnique Fédérale de Lausanne.
[5] A. Iqbal, L. Cassar, A.C. Rochat, J. Pfenninger, O. Wallquist, *J. Coatings Technol.* 1988, 1.
[6] H.E.A. Kramer, *Chimia* 1986, 40, 160.
[7] V.J.P. Srivatsavoy, J.E. Moser, L. Chassot, in preparation.
[8] G. Kaempf, *Farbe und Lack* 1982, 4, 288.
[9] H.J. Heller, *Eur. Polym. J. Suppl.* 1969, 105.
[10] L. Chassot, in preparation.
[11] R. M. Johnston in 'Pigment Handbook', John Wiley & Sons Publishers, New York, 1973, Vol. III, p. 229.
[12] L. Chassot, *EP-A O 559 611.*
[13] L. Chassot, *EP-A O 559 613.*