Synergistic effect combining amines and aminoacrylates with Type I photoinitiators

Authors: Dr. C. Palumbo, E. Cremona

R&D Application and testing Laboratory of IGM Resins Italia, Via Roberto Lepetit 34, 21040 Gerenzano, Italy

ABSTRACT

A new perspective on the synergistic effect of amines in combination with Type I photoinitiators is proposed in this comparative study. The aim of the study is to understand whether the combination with amines could lead to an increase of the rate of surface cure, due to reduction in Oxygen inhibition effects. The correlation study between amines and Type I photoinitiators both on reactivity and yellowing was carried out. The presence of the amines leads to an increase in reactivity and brings to a yellowing effect. All photoinitiators see their reactivity almost doubled in the presence of amines. The presence of the amine leads to a yellowness increase. Aromatic amines show the highest level of yellowing, instead the acrylated amines are less yellowing and comparable each other. For each photoinitiator the yellowing data in the presence of amines can be correlated to the reactivity. Furthermore, a theoretical study has been done on the influence of the nitrogen content of amines to their reactivity and yellowing: the content of photoinitiator can be customized to reduce the yellowing and increase reactivity. In the graphic arts different characteristics in conflict with each other are often required. Using the combination of Type I Photoinitiators and amines a good compromise can be reached between high quality and environmentally friendly technology.

INTRODUCTION

In the landscape of coating technologies and of sustainability compliance, UV radiation curing is gaining ground because of its intrinsic characteristics. UV coatings are indeed sustainable from different perspectives:

- solvent-free
- 100% dry weight - high yields
- low VOC release
- high printing speed

These peculiarities are due to the composition of the UV coating or ink formulation, of which the photoinitiating system surely plays a key role. In fact, photoinitiators are the molecules that absorb UV light and form the reactive initiating species which trigger the polymer crosslinking reactions.

IGM product portfolio includes photoinitiators that can be used alone or in combinations, with other photoinitiators of with the so-called co-initiators. Many photoinitiators can be used in both clear OPV and pigmented systems, such as inks. Furthermore, some of the photoinitiator – co-initiator systems can be used for food-packaging applications because of their low migration and extraction values in combination with high performance. Surely the performances of photoinitiators are very often tuned by and linked to the presence of amines in the formulation. In fact, it is well known that amine can act as co-initiators in the presence of Norrish type II photoinitiators, producing the initiating radicals [***Reference 1***]. For this reason, plenty of combinations of type II photoinitiators with amines have been described.

Norrish type I photoinitiators instead, when exposed to UV light, react, and form the active radical species, thus they wouldn't require an amine as co-initiator for the photocuring itself. For this reason, only few examples of the use of amines with type I photoinitiators are reported in the literature.

Nevertheless, both type I and type II photoinitiated UV curable systems are affected by oxygen inhibition of the curing, exactly as many other free radical polymerizing systems. In fact, atmospheric oxygen can penetrate the coating film and react with the photoinitiator, preventing it from reacting in the correct photocuring reaction. This mechanism leads to a lower cross-linking grade of the cured film and to a slower cross-linking reaction. To overcome this effect and to increase the cross-linking rate, oxygen scavengers can be used, which react with oxygen molecules before the quenching of the photoinitiator occurs [**Reference 2, Reference 3**].

At the light of these data, reducing the oxygen inhibition of the curing with a radical scavenger appears of great interest.

The amines, as outlined in the previous paragraph, are often used in the UV formulations as co-initiators, nevertheless are also active oxygen scavengers since they react with oxygen in the reactions showed in **Figure 1**. They form a peroxy radical, which readily reacts with another amine molecule, extracting hydrogen and producing another amine radical. The latter could either start a new scavenging cycle or act as co-initiator in presence of type II photoinitiator.

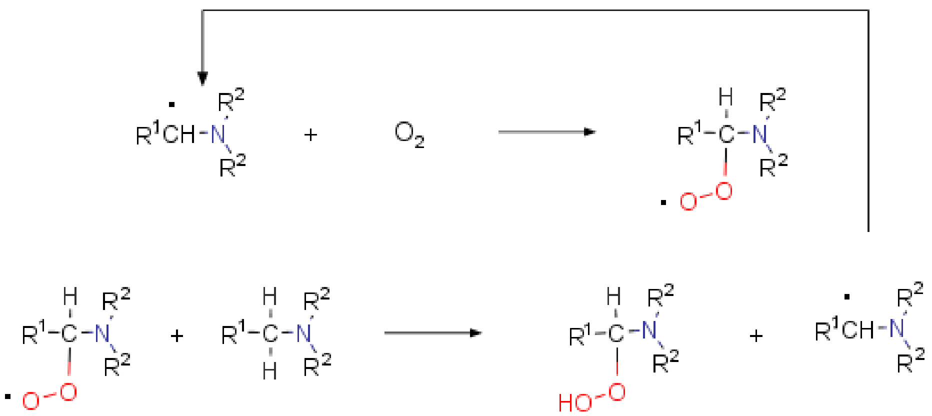

Figure 1: Oxygen scavenging operated by amines. The active species is regenerated, ready for a new cycle of quenching.

The activity of amines as synergistic oxygen scavengers in combination with Type I photoinitiators appeared of great interest and has been investigated within this study.

For the purpose, to have a complete overview onto different classes of compounds, the full range of amines in IGM's portfolio was considered. Thus, every aromatic benzoate derivative, a polymeric benzoate and acrylated amines were tested, as reported in **Table 1**. The amine acrylates and polymeric amines have higher molecular weight and equivalent weight respect to benzoates; thus, they are usually less reactive respect to monomeric or low molecular weight amines.

Commercial name	Description and class
Omnirad EDB	monofunctional aromatic amine, benzoate derivative
Omnirad EHA	monofunctional aromatic amine, benzoate derivative
Omnipol ASA	polymeric aromatic amine, benzoate derivative
Photomer 4250	acrylated amine and amine modified diacrylates
Photomer 4775	
Photomer 4771	
Photomer 4068	
Photomer 4967	
Photomer 5006	

Table 1: amines range

EXPERIMENTAL PART AND RESULTS

All trials were carried out in a clear coating and in a pigmented system.

OPV experiments

OPV (Over Print Varnishes-clear) experiments were carried out preparing the formulations and curing the film under UV light with a Hg lamp and a LED 395nm lamp.

The overprint varnish based on a 10-functional aromatic urethane acrylate was prepared, containing a 5%w of photoinitiator and a 9%w of amine, and applied on a paperboard substrate using a bar-coater to obtain a layer thickness of 6 µm.

Tests

- Curing with UV Hg lamp in air
- Curing with UV LED 395 nm in air
- Tack-free (TF) was recorded as the highest belt speed at which the surface is no more tacky.
- Yellow and white index were measured using a BYK Color-guide 45/0 (belt speed = TF speed minus 30%. All samples were conditioned for 12 hours at room temperature in the dark before testing.

FLEXO INKS experiments

Flexo inks experiments were carried out preparing the formulations and curing the film under UV light with a Hg lamp and a LED 395nm lamp.

The formulation (industrial) was prepared with a 5%w of photoinitiator and a 9%w of amine and were applied onto a paperboard substrate using an IGT Reprotest model C1 Printability Tester to obtain a film weight of 1.5 g/m^2. The industrial formulas must remain undisclosed.

Tests

- Curing with UV Hg lamp in air
- Curing with UV LED 395 nm in air
- Through-Cure is recorded as the fastest belt speed in which the film passes the thumb twist test.

RESULTS OPV

To investigate the effect of the amines in the formulation containing Norrish type I photoinitiator, the initial tests were conducted on three type I photoinitiators belonging to different classes: an alpha hydroxy ketone (Omnirad 1173), a phosphine derivative (BAPO - Omnirad 819), and an aminoketone (Omnirad 379). Omnirad EDB, a well-known aromatic amine, was selected as reference as a very reactive co-initiator. The tests were conducted with mercury lamp at 120 W/cm in a clear OPV system aromatic polyurethane. The results in terms of tack-free were good, confirming a synergic effect of the amine due to the oxygen inhibition. In fact, the results in **Figure 2** show the increase in tack free for the formulations containing the amine, being the corresponding formulas free from amines less reactive. In the case of the alpha-hydroxy ketone, the tack free results are more than doubled.

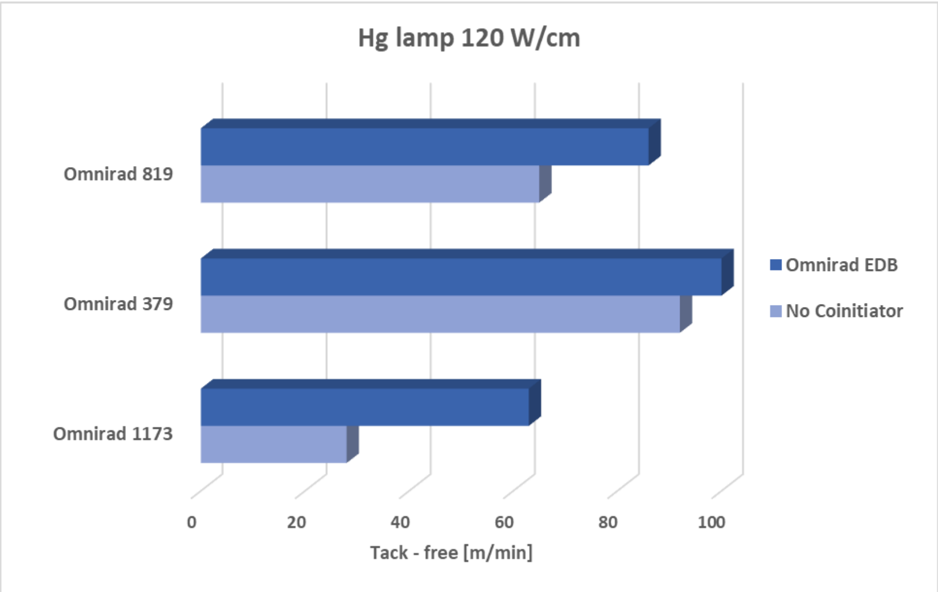

Figure 2: Preliminary tack free results. Hg lamp, OPV

Omnirad 1173 was therefore used in a complete screening of the reactivity boosting by the amines, checking the effect of amines of different nature. One of the characteristics of formulations containing amines is a slight to strong yellowing effect in the cured film, which is surely more evident in OPV clear systems. Because of this consideration, the yellowness of the cured film was checked as well.

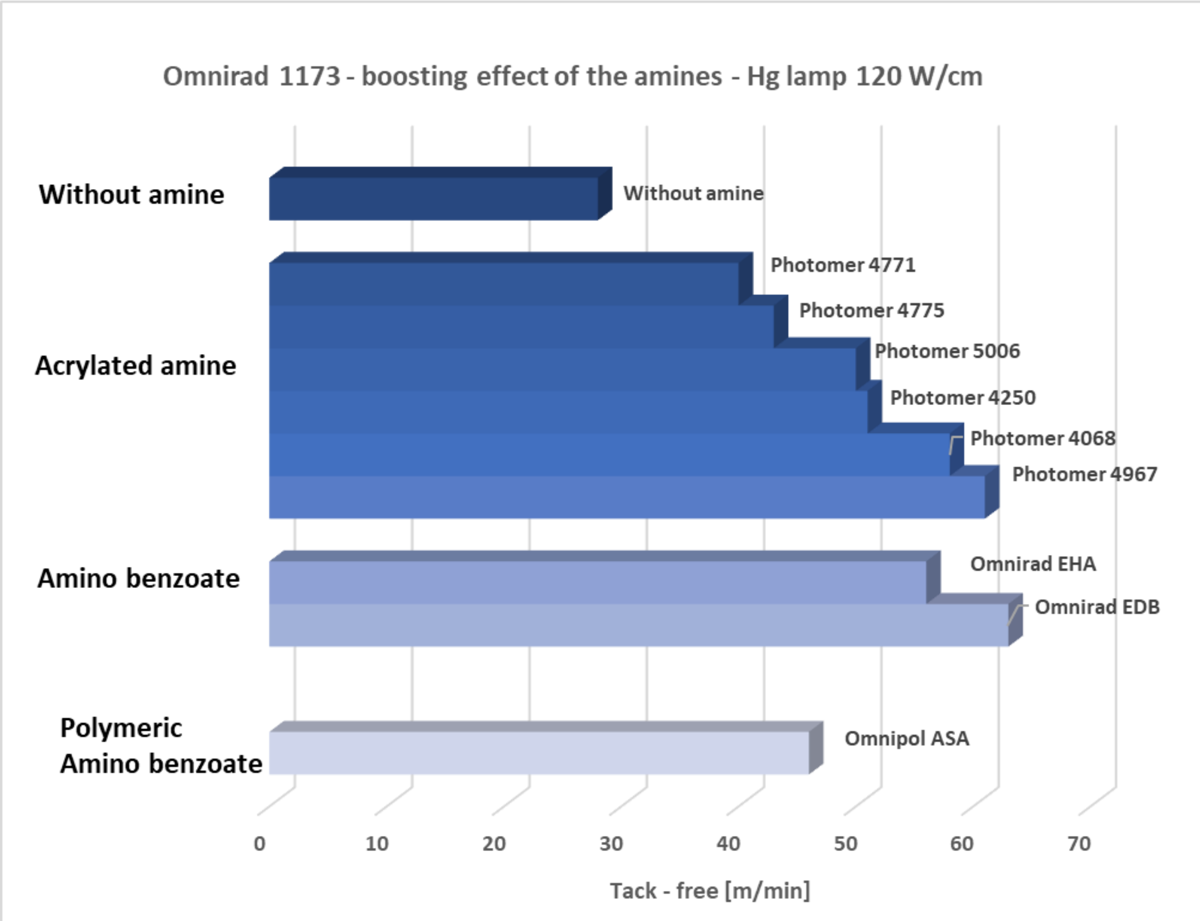

Figure 3: Tack free results. Test of the amine effect on Omnirad 1173 activity. Hg lamp, OPV

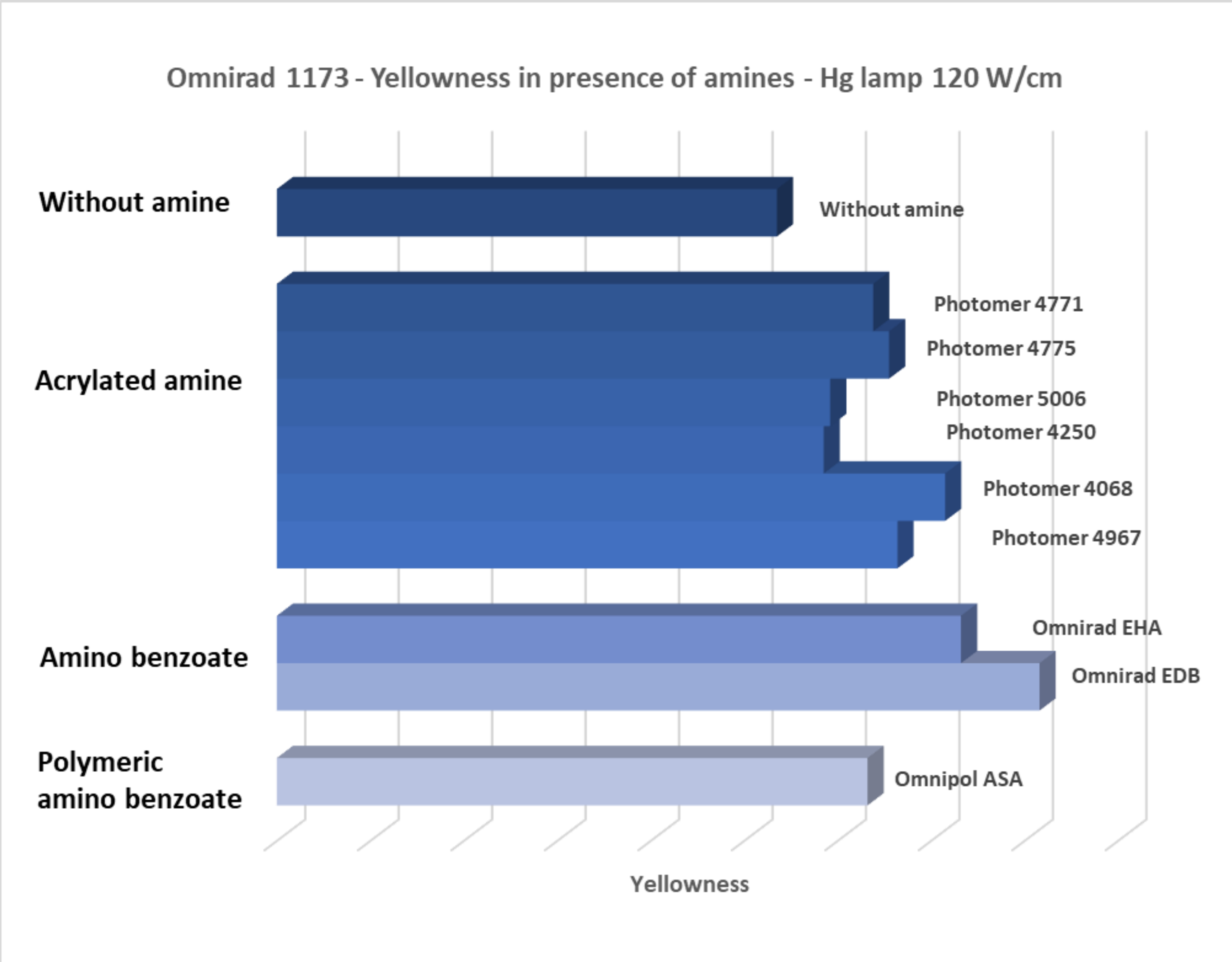

Figure 4: Yellowness results. Test of the amine effect on Omnirad 1173. Hg lamp, OPV

The results in terms of reactivity and yellowness are reported in **Figure 3** and **4**. Aromatic benzoate derivatives, a polymeric benzoate, and acrylated amines were tested. The tack-free numbers in the presence of the amines increased up to more than 2 times in the case of benzoates which are the most reactive amines, confirming the boosting effect observed during preliminary tests (**Figure 3**).

Remarkably, with polymeric acrylated amines good results were obtained, despite their having high molecular weight and less nitrogen chemical sites per weight unit and their being thus generically less reactive than benzoates.

A slight yellowing effect was observed, higher with benzoates, negligible with acrylated amines (**Figure 4**).

At the light of the results described so far, an in-depth study of the amines effect was conducted on other alpha-hydroxy ketones of IGM portfolio. The tack-free data obtained are shown in **figure 5**; for every photoinitiator the full scope of the amines was tested.

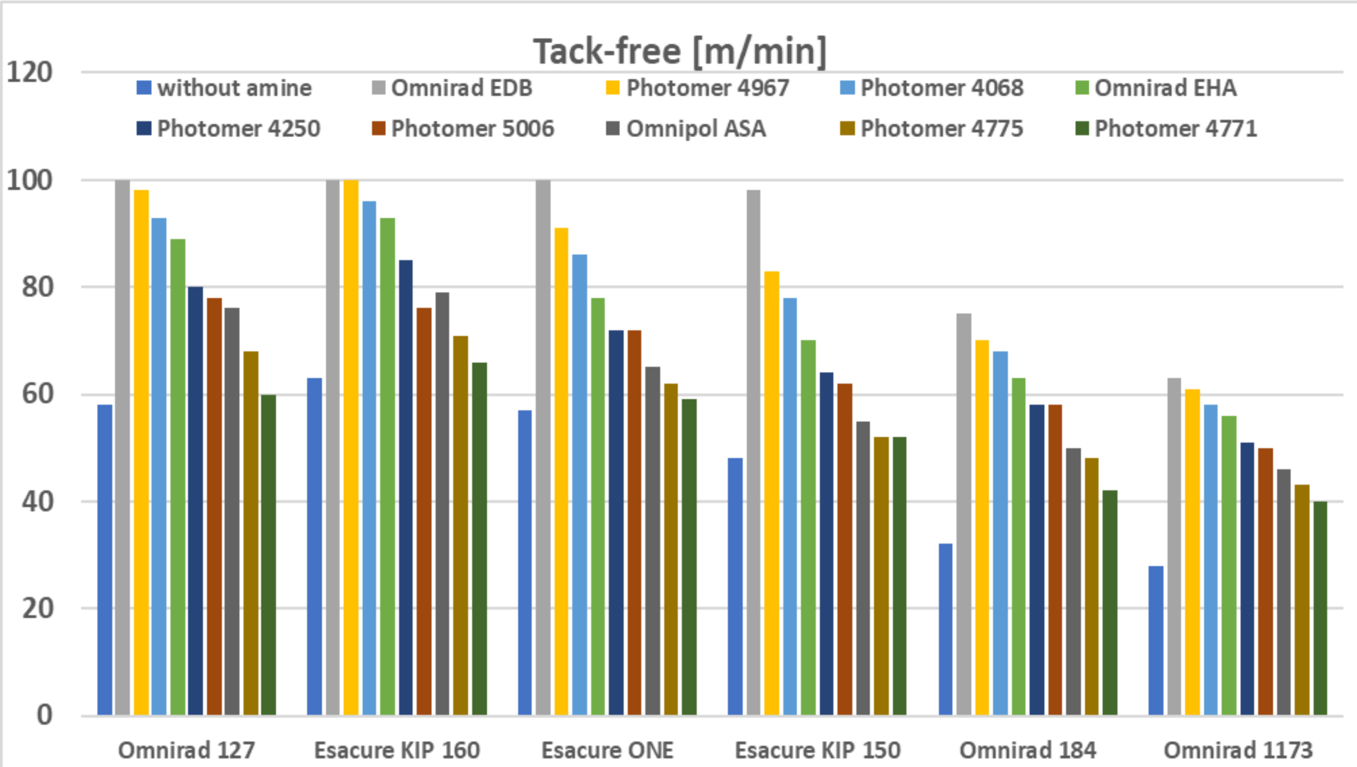

Figure 5: Tack-free results, alpha-hydroxy ketones, Hg lamp, OPV

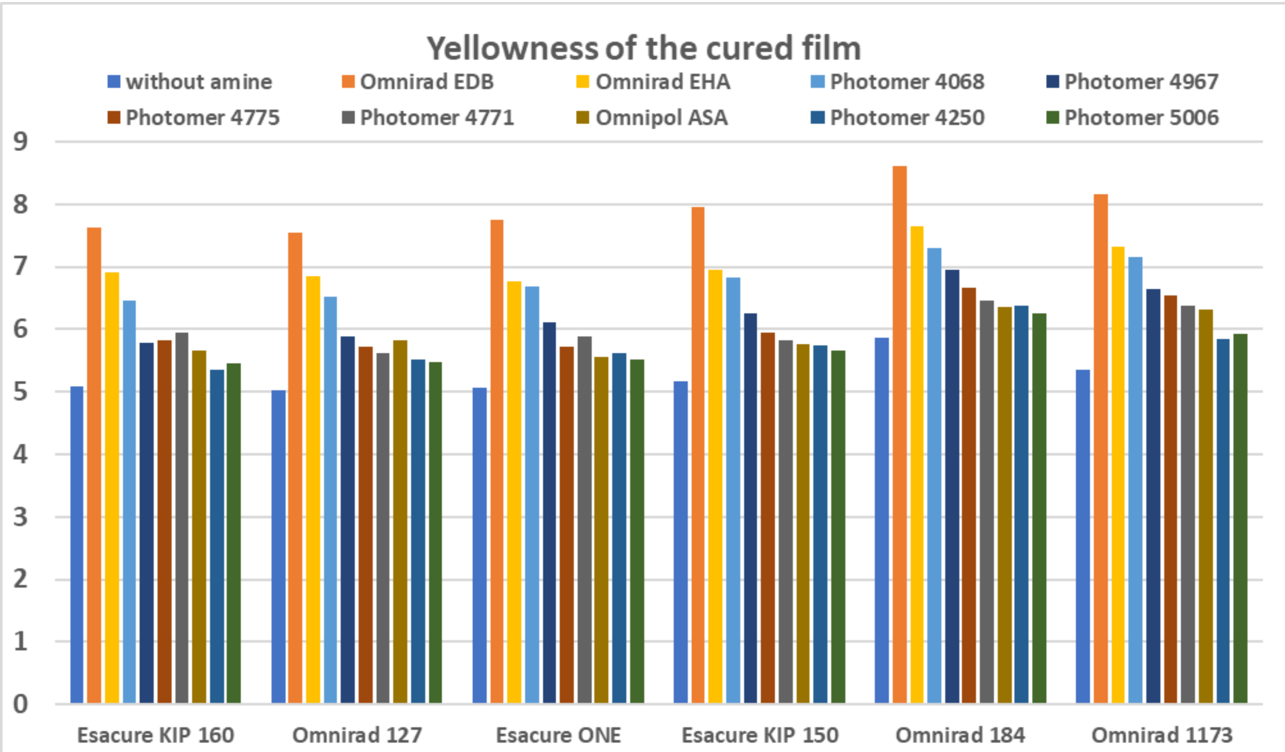

Figure 6: Yellowness results, alpha-hydroxy ketones, Hg lamp, OPV

The experimental results show a trend of reactivity increase with every photoinitiator, with the best tack-free in presence of our Omnirad EDB. Such kind of photoinitiator has low molecular weight and thus a high content of active nitrogen species. Remarkable results were obtained with every photoinitiator in combination with acrylated amines. In fact, acrylates have high molecular weight, being polymeric, and thus they have a lower content of nitrogen atoms per weight unit.

The yellowness effect has been evaluated as well showing very good compromise between reactivity and yellowing in presence of our acrylated amines such as Photomer 4250 (**Figure 6**).

The experiments were then carried out on phosphine derivatives and aminoketones.

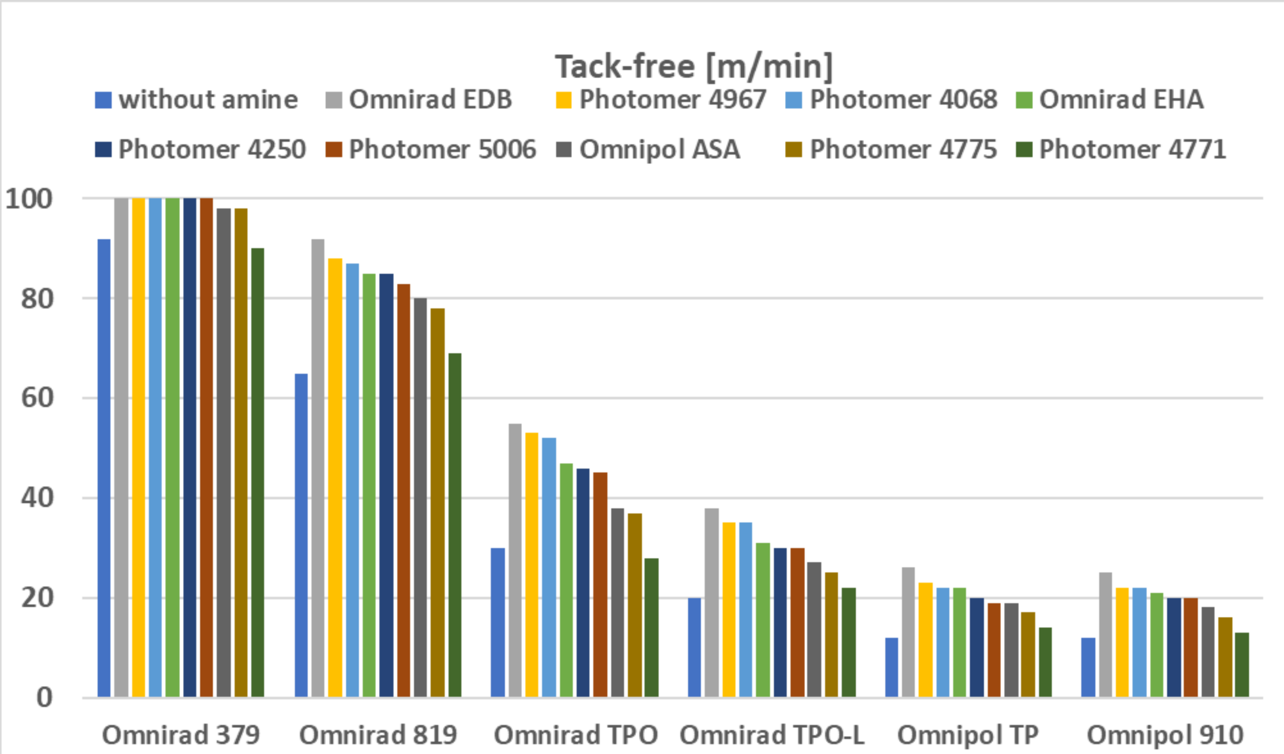

Figure 7: Tack-free results, amino ketones, phosphine derivatives, Hg lamp, OPV

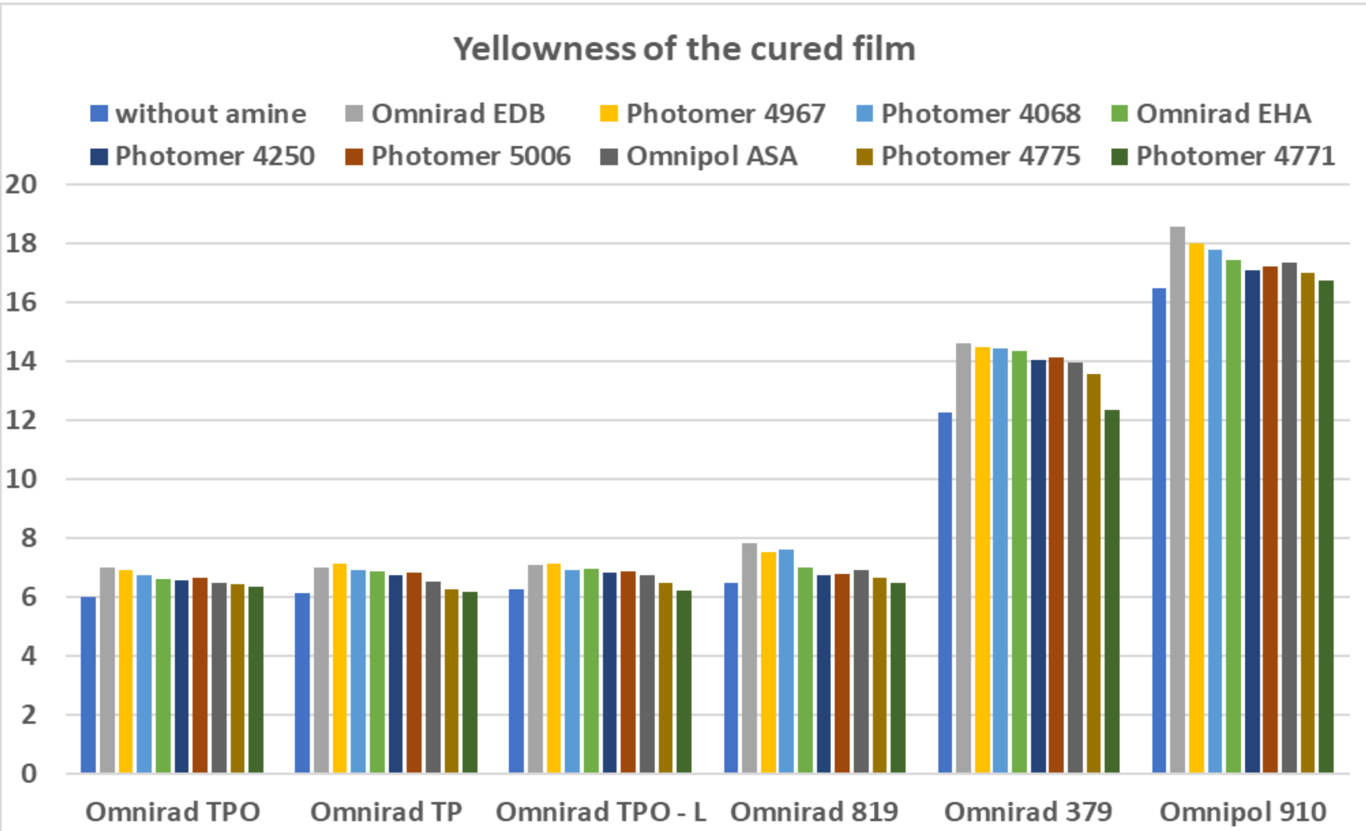

Figure 8: Yellowness results, amino ketones, phosphine derivatives, Hg lamp, OPV

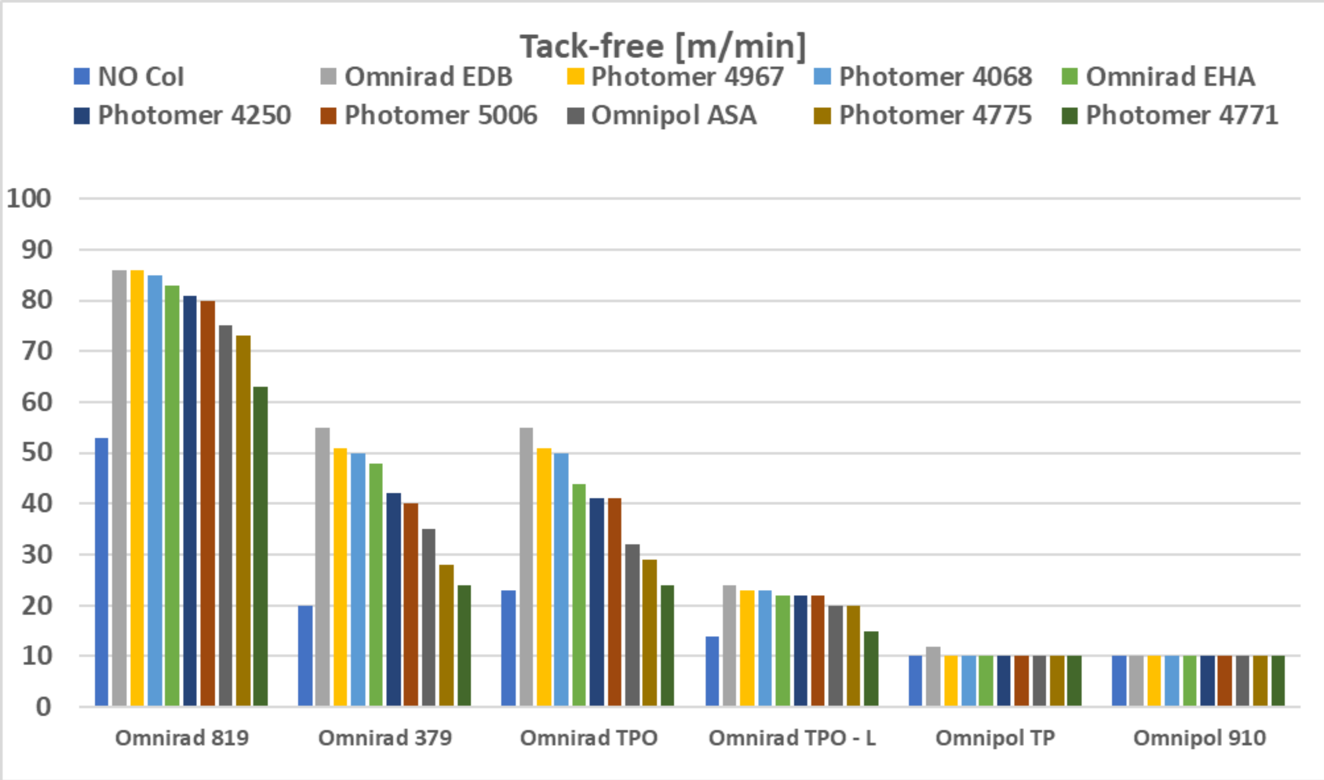

Figure 9: Tack-free results, amino ketones, phosphine derivatives, LED 395nm UV lamp, OPV

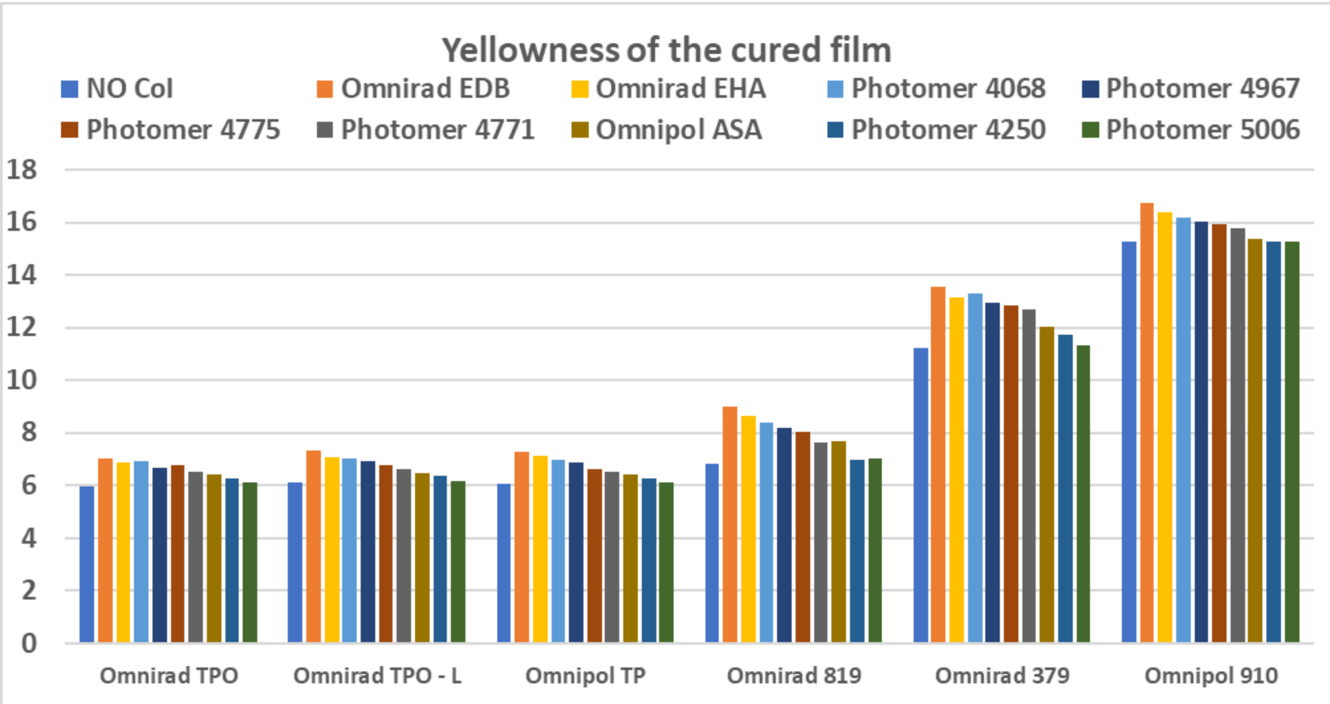

Figure 10: Yellowness results, amino ketones, phosphine derivatives, LED 395nm UV lamp, OPV

Good results in terms of reactivity were accomplished with amino ketone Omnirad 379 and phosphine derivatives such as BAPO and TPO, with both mercury (**Figures 7**, **8**) and LED 395 nm lamp (**Figures 9**, **10**). With the LED lamp the reactivity of Omnirad 379 and of TPO is more than doubled, with only slight increase of the yellow index in the cured film.

For each photoinitiator the yellowing data in the presence of amines can be correlated to the reactivity. The trend of the amines reactivity and yellowing can be summarized in the following chart, in which is also represented the balance between reactivity vs yellowing using Omnirad 379 as photoinitiator (**Figure 11**).

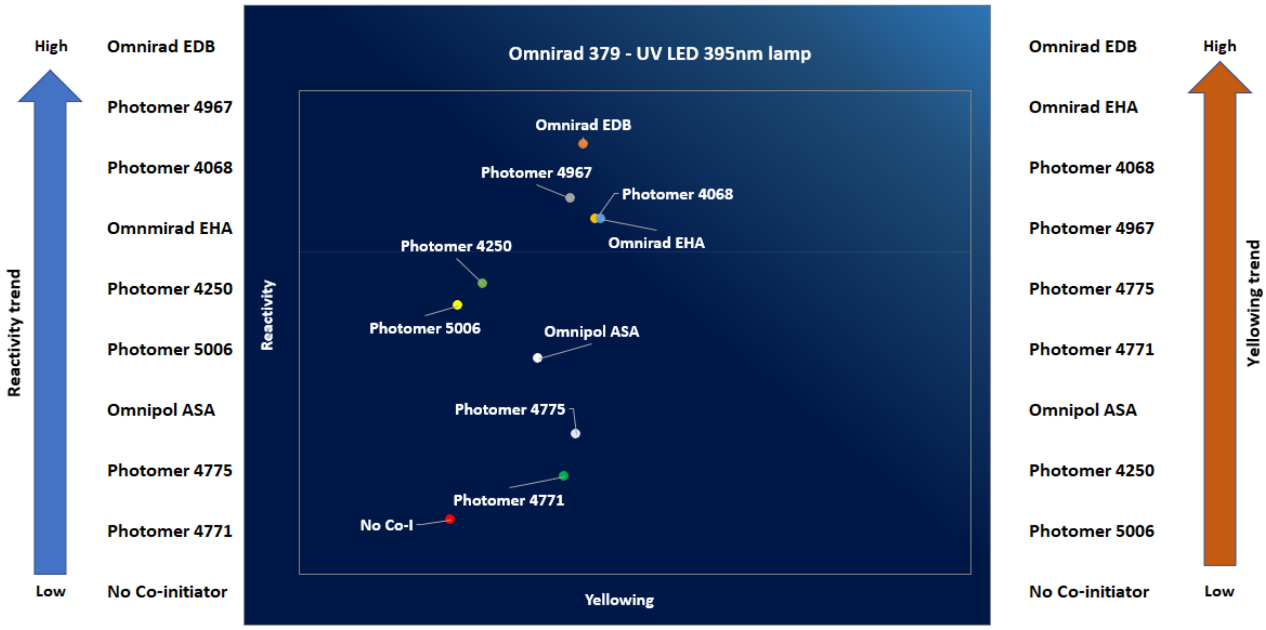

Figure 11: Reactivity *vs* yellowing diagram and amine trends

An in-depth study: benzoates *vs* acrylates

From the data commented so far it appears that some of the polymeric acrylated amines are good oxygen inhibitors and have a potential as synergists in presence of type I photoinitiators.

The reactivity difference between polymeric or acrylated amines, such as Omnipol ASA or Photomer 4250, and monomeric amines such as the aminobenzoate Omnirad EDB, could be ascribed to the difference in molecular weight and nitrogen content. All the previously described experiments were conducted using amines at same percent weight, without considering the molecular weight and active content. Furthermore, the most reactive amines lead to an unwanted yellowness effect of the cured film. We have thus hypothesized that the yellowing effect and the activity could be modulated by adjusting the % content of amines. For instance, we have selected Omnirad TPO as photoinitiator and Photomer 4250 as acrylated amine and we have performed experiments with increased percent amount of the latter (**Figure 12**). Using 9%w amine in the formulation a tack free of 55 is obtained with Omnirad EDB, with the less reactive Photomer 4250 the tack free is 46 instead. In the figure are reported tack free results in presence of increasing amounts of Photomer 4250, ranging from 5 to 26% in the formula. Results show that increasing to 13 %w Photomer 4250 loading, higher reactivity is obtained, remarkably with a lower yellowing effect. The data confirm that the content of amine as oxygen inhibitor can be customized to reduce the yellowing and increase reactivity.

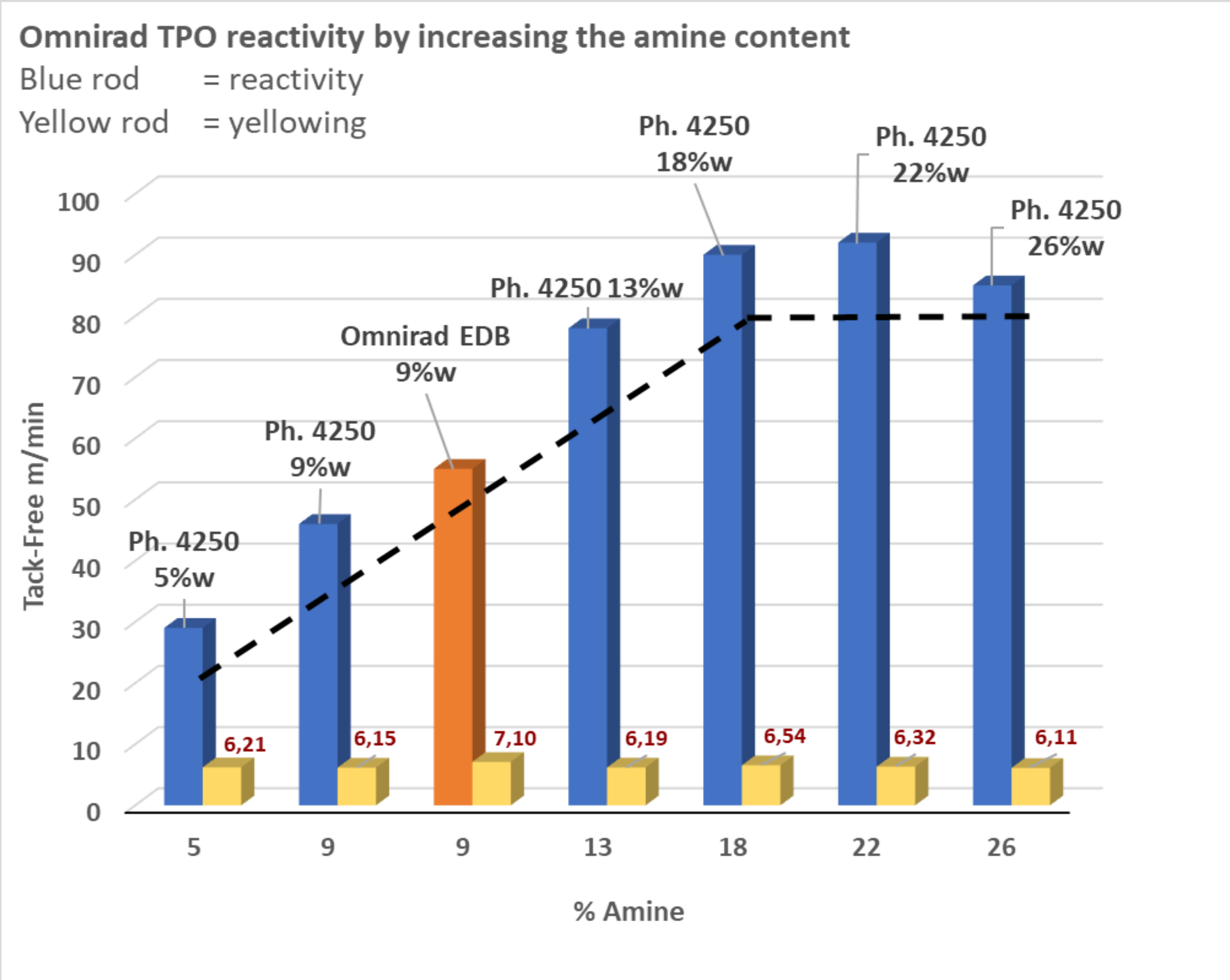

Figure 12: Omnirad TPO activity increasing the amine content

RESULTS CYAN FLEXO INK

The study continues with the tests on an industrial cyan flexo ink, of which was tested the through-cure with a selection of photoinitiators and using the full scope of amines. See in **figures 13** and **14** the data obtained under Hg lamp and LED 395nm light. Remarkably very promising results were registered with Omnipol 910, that doubles the reactivity in presence of benzoates. The experiments demonstrate that it is possible to boost type I photoinitiators in flexo inks with amines. Remarkably, photoinitiators as Omnirad 379, which are not very reactive themselves at 395 nm, can be potentiated using amines.

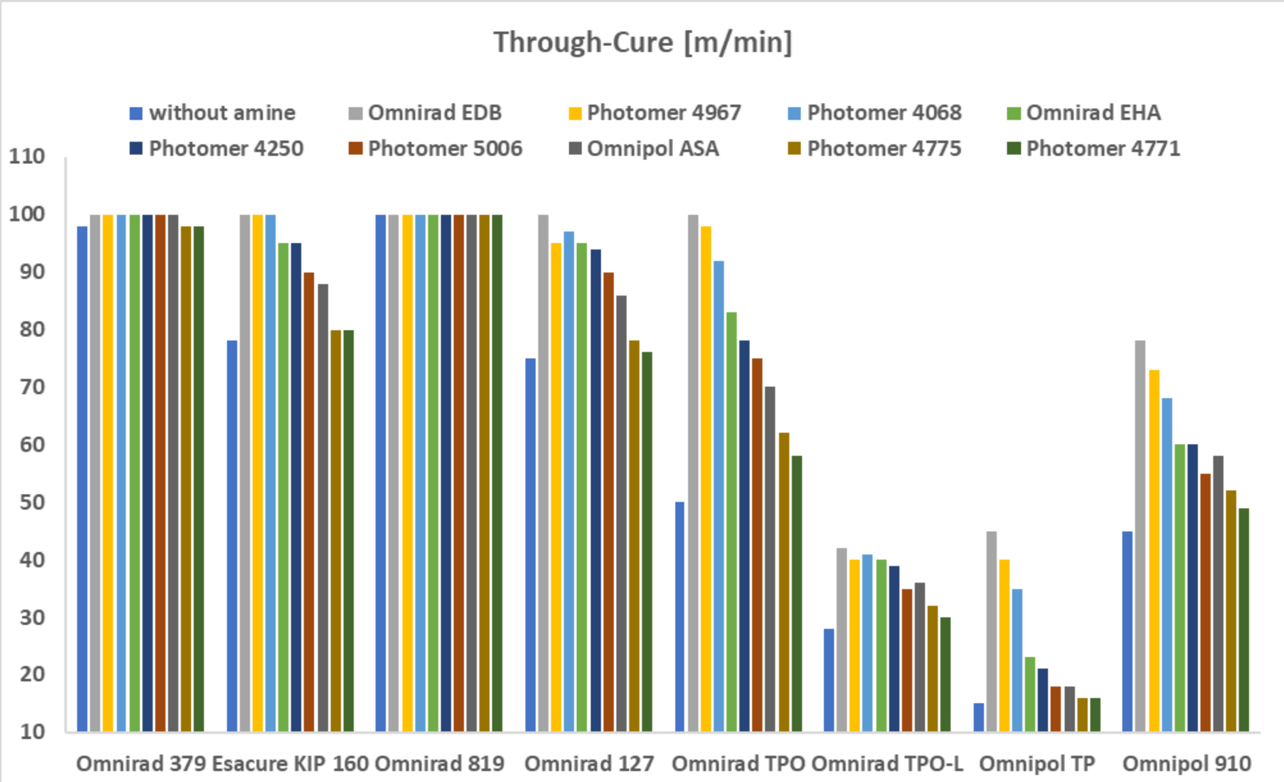

Figure 13: Through-cure in m/min with Hg lamp – flexo cyan ink
Through cure is recorded up to 100 m/min = upper limit speed of the UV oven

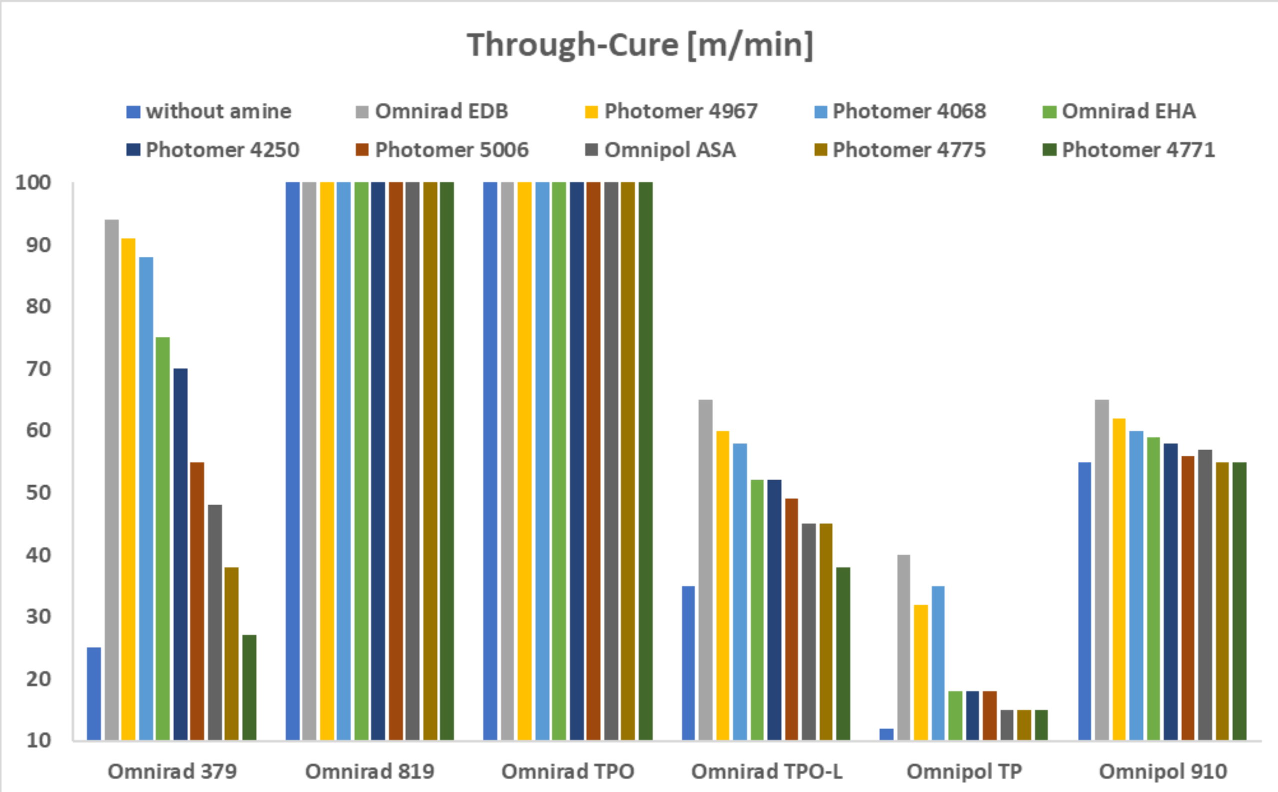

Figure 14: Through-cure in m/min with LED lamp @395nm – flexo cyan ink
Through cure is recorded up to 100 m/min = upper limit speed of the UV oven

CONCLUSIONS

The activity of IGM portfolio's amines as synergistic oxygen scavengers in combination with Type I photoinitiators has been investigated in this study. To the purpose and to have a complete overview onto different classes of compounds, the full range of amines in IGM's portfolio was considered.

In the OPVs, experimental results show that in presence of amines as oxygen inhibitors the reactivity of photoinitiator is boosted, with the best performances in presence of difunctional and monofunctional benzoates.

An in-depth study has been done with a benzoate in comparison to an amine acrylate, confirming that the content of acrylate amine can be customized to reduce the yellowing and increase reactivity.

Very promising results with flexo inks were registered as well. The experiments demonstrate that it is possible to boost type I photoinitiators in flexo inks with amines. Remarkably photoinitiators as Omnirad 379, which are not very reactive themselves at 395 nm, can be potentiated using amines.

BIBLIOGRAPHIC REFERENCES

1. "Chemistry & Technology of UV % EB Formulation for coatings, inks & paints", Vol.3 "Photoinitiators for free radical and cationic polymerisation", K.K. Dietliker, Edited by P.K.T. Oldring.
2. "Johnson, M.A., Oldring, K.T. (1990-1991), J. Oil Colour Chem. Assoc., 73 (10), 415-418, 420; 13.
3. Photoinitiation photopolymerization and photocuring – Fundamentals and applications, J-P. Fouassier