

Maleimide Reactive Oligomer for Wood Coating

Wenfeng Kuang¹, Mahmood Sabahi¹ and Chau Nguyen¹

¹Albemarle Corporation
451 Florida St
Baton Rouge LA 70801

Abstract

A maleimide reactive oligomer has been evaluated using a typical formulation for wood floor coatings as a test vehicle. A maleimide functional oligomer is used in place of a traditional photoinitiator package. The results showed that the maleimide oligomer has good curing properties, low extractability, and excellent abrasion resistance and stain resistance when compared to a traditional formulation.

Introduction

The typical methods for applying coatings on wood substrates are either by roller coating, spraying, vacuum or curtain coating. The coatings are usually UV (ultraviolet) cured acrylates or styrene/unsaturated polyester. The styrene/unsaturated polyester systems are attractive to the end user due to their low viscosity, good reactivity, and excellent adhesion to most wood substrates. The popularity of these materials lies in the low cost when compared to UV curable acrylates. However, UV curable acrylates have come into favor because of factors associated with styrene/unsaturated polyester systems such as high styrene content, low flash point products, high film weights, odor and low cure speed. The advantage of using UV cured acrylates in wood coatings are higher productivity, lower energy cost, lower odor and better film properties. Another advantage to using an acrylate based formulation rather than unsaturated polyesters for wood coatings is that the choice of photoinitiator is not limited to type I cleavage systems (often more expensive than the type II abstraction counterparts), since type II long lived excited state triplet are readily quenched by styrene. Though type II photoinitiators require a source of labile hydrogens, in most cases the use of a tertiary amine acts as a synergist for the photoinitiator and also mitigate the effects of oxygen inhibition. In either case, the use of photoinitiators in wood coatings can lead to premature yellowing, odor or degradation of the coating due to residual unreacted photoinitiator.

Herein, we present an alternative photoreactive species that uniquely produces free radicals to initiate polymerization by UV irradiation and can also react via free radical addition. The approach has been to use a photobleaching photoinitiator bound covalently to an oligomer. These photoinitiating oligomers are based on various structural groups common to the UV curing industry (urethane, polyester and epoxy) with the addition of a photobleaching Type II photoinitiator functional group, which leads to a polymerizable photoinitiator. This approach utilizes the chemistry of maleimide, in which the photoactive chromophore can be consumed in a free-radical mechanism via UV irradiation and/or subsequent polymerization. The use of maleimides as a potential alternative to traditional photoinitiators has been investigated extensively by Hoyle et al.¹⁻⁴ This approach is unique in that the maleimide acts both as a photoinitiator and can be consumed as comonomer. The mechanism of initiation by UV irradiation involves a hydrogen abstraction or electron/proton transfer dependant on the hydrogen donor source. The mechanism for free-radical polymerization involves radical

addition across the double bond of the maleimide. A depiction of both these processes is shown in Figure 1. The consumption of the maleimide chromophore makes it a potentially viable solution to the problem of achieving non/low extractables for UV cured products without comprising performance.

A prefinished wood flooring formulation was chosen as the application for evaluating the maleimide reactive oligomer (MIRO) system. The MIRO system was evaluated as a replacement for the photoinitiator package and screened with various amine synergists as coinitiators. A battery of evaluations, which included: solvent resistance, stain resistance, abrasion and hardness were used to screen the performance of these formulations.

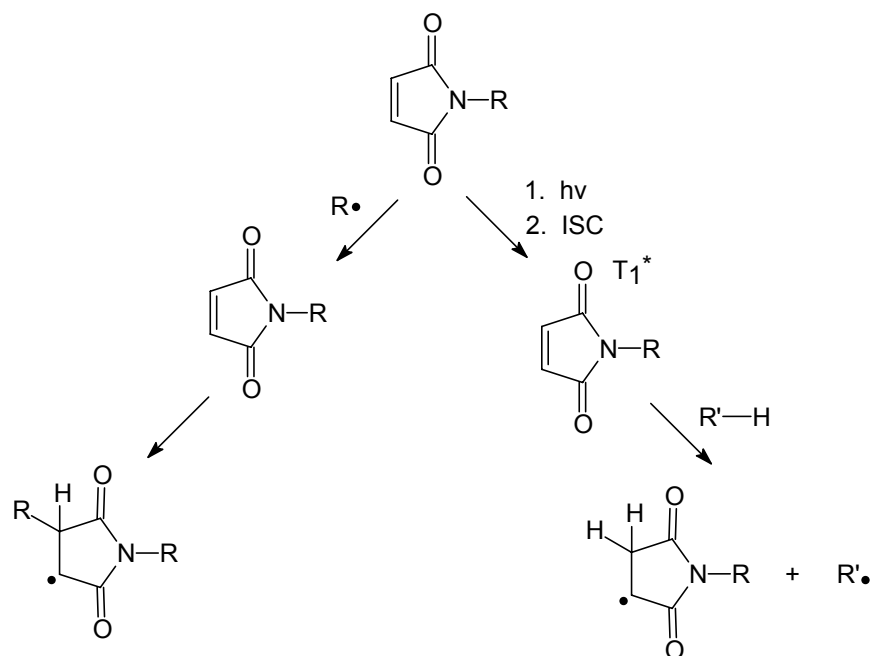


Figure 1. Mechanisms for the consumption of the maleimide photoactive chromophore by free-radical UV irradiation or addition.

Experimental

All materials purchased and obtained in these experiments were used without further purification. Ebecryl 350, Ebecryl 264, Ebecryl 3720, TMPEOTA, Ebecryl 7100 and P115 were obtained from UCB Chemicals Corporation. N-methyl-N,N-diethanolamine (MDEA), benzophenone (BP), hydroquinonemonomethylether (MEHQ) and methylethylketone (MEK) were obtained from Aldrich. FC-4430 was obtained from 3M. FirstCure HMPP (2-hydroxy-2-dimethyl-1-phenylpropane-1-one) and AS4 were obtained from the Albemarle Corporation. Viscosities were measured using a Brookfield LV viscometer with small sample adapter at 25°C, following mixing and allowing the formulations to set for 24 hours. Formulations were applied to Leneta charts (Form 5C) using a wire round rod and cured under a Fusion UV Systems Aetek lamp at designated speed. Final cured films were then evaluated for these performance parameters:

- (1) Methylethylketone (MEK) double rubs were performed on cured (No.3 wire round rod, 75 fpm, 38 mJ cm⁻² UVC) films three minutes after exposure using cheese cloth

wrapped on a 8 oz. ball peen hammer. Failure of the film was determined when there was a break in the continuous film. Coatings were applied onto Leneta charts (Form 5C).

- (2) Abrasion was determined by weighing the coating prior to and after 900 cycles on a Taber Abraser. Tests were performed with CS-17 wheels and 1000g load. Coatings were applied with a No.12 wire round rod and cured at 75 fpm (38 mJ cm⁻² UVC).
- (3) Hardness was determined using a Gardner Pendulum Hardness Tester with Koenig/oscillation model. Coatings were applied with a No.12 wire round rod on glass plates and cured at 75 fpm.
- (4) Staining (red wine, ketchup, coffee and shoe polish) was obtained after 24 hours and the tincture of mustard stain was determined after 1 hour. All stain materials were covered for the duration of the test period. Stain color density was measured using an X-Rite SpectroDensitometer, the uncoated white Leneta chart had a density of 0.13 to 0.14. Coatings were cured at 75 fpm with 38 mJ cm⁻² of UVC.
- (5) Spot testing was determined using a solution of ethanol/water (95/5) for 24 hours.
- (6) Extraction was determined by weighing the film prior to and following refluxing in methylethylketone for 6 hours in a Soxhlet extractor. The coatings were applied with a #12 rod and cured at 75 fpm.

Results

A prefinished wood flooring formulation was chosen as the test vehicle for evaluating the developmental maleimide oligomer (MIRO) as a photoinitiating oligomer. The composition of the standard formulation and the MIRO formulation are shown in Table 1. The maleimide reactive oligomer (MIRO) system was evaluated as replacement for the photoinitiator package. The viscosity of the standard formulation was 2575 cps compared to 4015 cps when MIRO was optimized and used at 8.6%.

Table 1. Standard test vehicle and MIRO formulation.

Components	Standard	MIRO
Monomers/Oligomers		
Ebecryl 350	1.0	1.0
Oligomer blend*	75.18	71.08
TMPEOTA	16.0	16.0
MIRO	---	8.6
Photoinitiators		
Benzophenone	4.00	---
FirstCure HMPP	1.50	---
Amine Synergist		
FirstCure AS4	2.00	3.00
Additives		
FC4430	0.30	0.30
MEHQ	0.02	0.02
Viscosity (cps) 25 °C	2575	4015

*Oligomer blend consisted of: Ebecryl 3720/Ebecryl 264/TMPEOTA (35/40/25)

An evaluation of tertiary amine synergists was performed at optimal concentrations with the formulations shown in Table 2. The tertiary amines used in the comparison were free

amines, such as AS4 and MDEA; an aminoacrylate Ebecryl 7100 and an amine adduct, P115. The results for the performance parameters are shown in Table 3. The resistance to MEK double rubs was approximately the same with results greater than 150. Abrasion data shows that all the formulations were comparable in weight loss. Hardness data shows that all the formulations were similar except in the case of MDEA, where the Koenig hardness was observed at 20 oscillations. Stain resistance for all formulations were comparable with the AS4, MDEA, Ebecryl 7100 and P115 (in MIRO formulation) showing slightly higher numbers for mustard staining then the standard formulation. Spot testing showed no effect on any of the formulations tested. Extraction test data shows that the MIRO containing formulations with AS4, MDEA, Ebecryl 7100 and P115 were consistently lower than the standard formulation.

Table 2. Evaluation of tertiary amine synergists when used with MIRO.

Components	AS4	MDEA	Ebecryl 7100	P115
Monomers/Oligomers				
Ebecryl 350	1.0	1.0	1.0	1.0
TMPEOTA	16.0	16.0	7.0	13.0
Oligomer blend*	71.08	71.08	71.08	71.08
Photoinitiators				
Benzophenone	---	---	---	---
FirstCure HMPP	---	---	---	---
MIRO	8.60	8.60	8.60	8.60
Amine Synergist				
FirstCure AS4	3.00	---	---	---
MDEA	---	3.00	---	---
Ebecryl 7100	---	---	12.0	---
P115	---	---	---	6.0
Additives				
FC4430	0.30	0.30	0.30	0.30
MEHQ	0.02	0.02	0.02	0.02

Table 3. Performance results.

Performance Parameter	Standard Formulation	AS4	MDEA	Ebecryl 7100	P115
Solvent Resistance MEK double rubs	> 150	> 150	> 150	> 150	> 150
Abrasion (weight loss @900 cycles, mg)	15.8	14.5	14.3	14.9	15.5
Hardness (Koenig, oscillation)	50	50	20	54	52
Stain Resistance*					
Ketchup	0.13	0.13	0.13	0.15	0.14
Shoe Polish (red)	0.14	0.46	0.35	0.39	0.46
Mustard	0.14	0.21	0.20	0.21	0.20
Coffee	0.13	0.16	0.13	0.16	0.17
Spot Test Ethanol/H ₂ O (95/5)	No effect	No effect	No effect	No effect	No effect
Extraction (% weight loss)	9.77	4.60	6.04	6.31	5.97

*Background = 0.13 - 0.14

Conclusions

A maleimide reactive oligomer (MIRO) system has been shown to be comparable to a standard formulation for prefinished wood flooring. The MIRO can replace the photoinitiator package and give similar results for performance evaluations such as solvent resistance, abrasion and hardness; differences in stain resistance are within formulation variation and would not be great over a wood substrate. In particular, MIRO formulations were consistently lower than the standard formulation in test for extractables using MEK demonstrating a higher degree of cure. A maleimide reactive oligomer system can potentially substitute for the photoinitiator package using a variety of tertiary amine synergists without sacrificing performance.

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