

Synthesis and Application of Heterocyclic as ultraviolet Absorbers

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Abstract:

The lifespan of organic coatings is reduced in outdoor applications by attacks of solar radiation, oxygen and atmospheric pollutants. Degradation of coating and recoating introduce pollutants into the environment. For solvent base coatings like alkyd paints volatile organic compounds (VOC) are main source of pollution. Undesirable mechanical, physical and chemical consequences of the resulting degradation can be substantially restricted by properly selected photo stabilizers. Tautomerization in this compounds make them to be consider as UV absorber important and effective class of UV-absorbers. In this study some new derivatives of absorbers were synthesized. Structures of compounds were elucidated by spectroscopic data and these compounds were added to red alkyd paint as UV absorber. After a week exposure to 80 watt UV-lamp, gloss of high gloss alkyd paint (92 %) reduced to 3 %, although that was 7.1 % for polyester paint. In the presence of TINUVIN 315 3206 and synthesized compounds, stability of paints against UV radiation improved significantly.

Results indicated that fastness of high gloss red alkyd paint was improved sufficiently. This makes coating more stable and reduces the environmental contamination. Consequently, less recoating will lead to decreasing VOC, costs and other environmental pollutants.

Keywords: phenols, Alkyd paint, Pollutants, UV-absorbers, VOC.

Introduction

Absorbers of UV radiation (UVAs) are colorless or nearly colorless compounds having high absorption coefficients (ϵ) in the UV part of the solar spectrum[1]. They protect coatings against photo induced damages by absorbing the harmful solar radiation preferentially to binder [2]. UVA must absorb, above all, radiation in the region between 290 and 350 nm. UVAs transform the absorbed radiation energy into less harmful thermal energy via a photo physical process involving ground state and excited state molecules [3]. Light screening, quenching of excited states and scavenging of alkyl peroxy is considered to be involved to some extent in the UVA mechanism [4]. An absorption maximum between 330 and 350 nm in the UV absorption spectrum of UVA is considered a necessary condition for an adequate efficiency in coatings. UVAs having too far λ_{max}

in the short-wavelength region are unable to cover sufficiently the harmful long-wavelength region up to 380 nm. On the contrary, UVA having λ_{max} over 350 nm may account for inherent yellow tinge. This can adversely affect color in the coating [5]. UV absorbers must have at least three properties to be effective. First, they must strongly absorb UV radiation that would be harmful to the polymer or coating. Second, they must harmlessly dissipate the energy that they absorb. Finally, they must persist in the matrix for the expected lifespan of the article [6]. Mainly, there are two represented mechanisms for UVAs. The phenolic UVAs act by establishing rapid enol – keto equilibrium in the presence of UV radiation [7,8]. IR and Raman spectra indicated the trans-planar geometry and presence of intramolecular H-tunneling or proton transfer process between carbonyl and imines groups (Fig 1) [9].

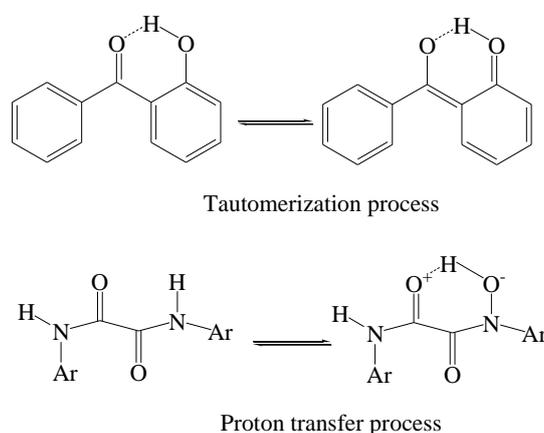


Figure 1. Tautomerization and proton transfer for UVAs

Tautomeric forms as well as proton transfer processes of phenols make them potentially UVAs. Pursue the ability of phenols as UVAs, some derivatives of phenols were synthesized according to the following schemes. Generally red pigments and dyes have less fastness on exposure to UV radiation [10]. Alkyd coatings are a main class of organic coatings. Although they have some advantages in comparison with other coatings, such as high gloss, they contain approximately 35-40% volatile organic compound (VOC), which are released to the environment during film formation. VOCs are environmental pollutants, Red pigments and dyes have less fastness when exposed to UV or sunlight [11]. The standard diazotization methods often have to be adjusted to match the solubility and reactivity of the amine or to minimize the decomposition of the diazonium salt. There appears to be no general method to prepare the desired diazonium salt in good yield.' A literature review, whilst showing numerous studies on the diazotization of substituted 2aminobenzothiazoles, afforded only two references pertaining to the diazotization of 2,6-dia&nobenzothiazole [12, 13]. Benzodiazepines are bicyclic heterocyclic compounds possessing

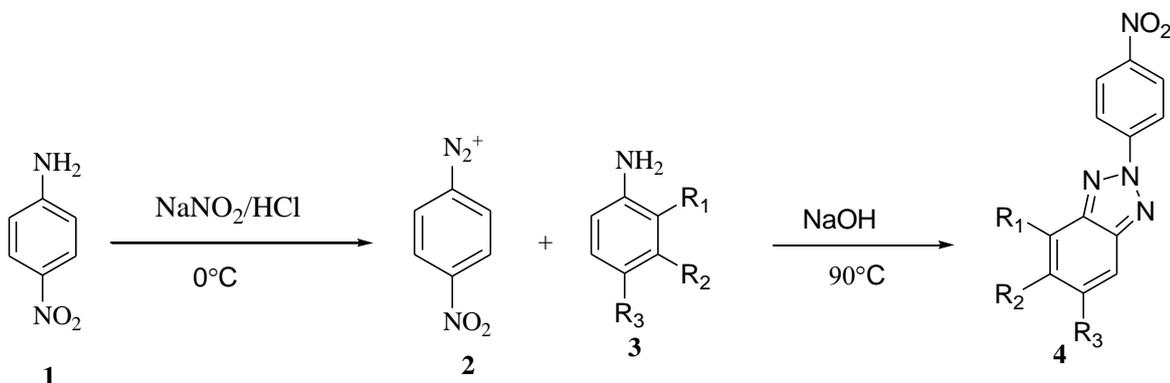
various types of general class of stabilizing additives activities [14, 15].

Experimental

Structures of synthesized compounds were elucidated by IR and UV. All reagents and solvents were obtained from Merck Chemical Inc. Melting points were measured with an Electrothermal 9100 apparatus. These data were in good agreement with the calculated ones. IR spectra were measured by a Nexus 870 FT-IR spectrometer (Thermo Nicolet, Madison, WI). UV spectra of compounds were recorded as 2×10^{-5} molar solutions in chloroform and ϵ of compounds were calculated by beer-lambert equation ($A = \epsilon bc$). λ_{\max} and ϵ summarized. The glosses of samples recorded using Sheen glossmeter at 60. 0.1 gram of each synthesized compounds added to 50 g high gloss red alkyd paint, except samples 1 and 2. For each prepared sample, 100 μ film of paint applied on paper. After 24 hrs the applied films dried completely. Half of each film covered to prevent UV/Vis diffusion, and the other half exposed to the 80-watt UV lamp for a week. Sample 1 exposed to daylight. The gloss of samples were measured.

Synthesis of triazoles

Diazonium salt **1** was prepared by adding HCl / NaNO₂ to 4-nitrobenzenamine **2** at 0 °C. This salt was coupled to Aromatic amins **3** and produced azo compound [16], Then To a mixture of azo compound was added drop wise a 10 % w/w aqueous NaOH solution within 0.5 hr. The reaction mixture was stirred at 90 °C for 2 hr. (Fig 2).



Name	R ₁	R ₂	R ₃
4a	H	H	H
4b			H
4c	H	H	

Figure 2. Synthesis route of heterocyclic compounds

2-(4-nitrophenyl)-2H-benzo[d][1,2,3]triazole (4-a):

Redish: black violent ,power:(80%),mp=213⁰C, IR(KBr, cm⁻¹) 2917 (C-H), 1571 (C=C), 1322-1560 (NO₂), 1632.4 (N=N). ¹HNMR (CDCl₃) δ, 7.45-7.95 (8H,m, Aromatic), ¹³CNMR (125.8 MHz, CDCl₃) δ: 121.8-147.5 (11Aromatic).

2-(4-nitrophenyl)-2H-naphtho[1,2-d][1,2,3]triazole (4-b):

Redish: black brown ,power:(80%),mp=425⁰C , IR(KBr, cm⁻¹), 3477 (C-H), 1623 (N=N), 1562 (C=C), 1346-1557 (NO₂). ¹HNMR (CDCl₃) δ, 7.34-8.22 (10H,m, Aromatic), ¹³CNMR (125.8 MHz, CDCl₃) δ: 111.8-133.5 (16Aromatic).

2-(4-nitrophenyl)-5-phenyl-2H-benzo[d][1,2,3]triazole (4-c):

Redish:black violent ,power:(80%), mp=473⁰C , IR(KBr, cm⁻¹) 3410 (C-H), 1590 7(C=C), 1362-1560 (NO₂), 1624 (N=N). ¹HNMR (CDCl₃) δ, 7.24-8.30 (12H,m, Aromatic), ¹³CNMR (125.8 MHz, CDCl₃) δ: 121.1-147.7 (18 Aromatic).

Results and discussion

λ_{\max} of this triazoles is between 266-310 nm, and $\epsilon > 10000$. Therefore, synthesized triazoles are reasonable to use as UV-absorbers. In IR spectra, OH stretching appears above 3300 cm⁻¹. In

addition to resonance of aromatics proton peaks at 7-8 ppm Triazoles 4-a had the shortest (266 nm) and 4-c the longest (310 nm) λ_{\max} in UV, triazole 4-c more conjugated, its λ_{\max} shifted to 310 nm (Table 1). Therefore, increasing conjugation in this triazoles extended their applications to UVAs. Regarding molar extinction coefficient (ϵ) as another important factor in effectiveness of UVAs, all this triazoles were qualified due to their $\epsilon > 10000$ in UV region. As indicated in Table 2, daylight had little effect on gloss of sample 1. But, after a week exposure to 80 watt UV-lamp in the absence of UV stabilizer the gloss of alkyd paint reduced from 91 to 3 %. All additives were good gloss protecting against UV radiation. In regard with the results of gloss testing of samples 1 and 2, UV radiation was more effective than daylight on gloss changing. In the presence of TINUVIN 315 and synthesized triazoles, the stability of paints against UV radiation improved significantly.

Table1. UV spectra data for triazoles

Name	ϵ	λ_{\max}
4-a	15100	266
4-b	17700	303
4-c	10500	310

Table 2. UV Stability of red high gloss alkyd paint exposed to UV in the presence of triazoles as UV absorbers (* Without additive, **Exposed to daylight not to UV)

Name	Gloss		
	UV absence	UV exposure	Δ Gloss
Sample 1**	91	70	21
Sample 2*	91	3	88
TINUV315	92	86	6
4-a	91	64	27
4-b	91	66	25
4-c	91	81	10

Conclusion

It is reasonable to use of water soluble UVAs in such coating to increase the stability of coatings and, subsequently to decrease VOC and polymeric pollutants. This triazoles make coating more

stable and reduce the environmental contamination. Consequently, in addition to economical benefits, stabilization of paint would decrease VOCs and other contaminations. However further studies should be done to verify the mechanism of this triazoles as UVAs.

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