

## Synthesis and Application of Phenol Derivatives as Ultra Violent 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 these compounds make them to be considered as UV absorber important and effective class of UV-absorbers. In this study some derivatives of phenols were synthesized as UV absorbers. 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 reduced. In the presence of TINUVIN 315 3206 as witness and phenol derivatives, 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.

**Key words:** Phenols • Alkyd paint • Pollutants • UV-absorbers • VOC

### INTRODUCTION

Absorbers of UV radiation (UVAs) are having high absorption coefficients ( $\epsilon$ ) 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 all waves in District between 290 and 350 nm. UVAs commute the absorbed radiation energy into less harmful thermal energy via a photo physical process involving ground state and excited state molecules [3]. A simple mechanism is commonly used, the reaction of an alkyl radical with a nitroxyl radical [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  $\lambda_{max}$  in the short-wavelength region are unable to cover sufficiently the harmful long-wavelength region up to 380 nm. On the contrary, UVA having  $\lambda_{max}$  over 350 nm may account for inherent yellow tinge. This can adversely affect Scintillation paint in the coating [5]. UV absorbers must have at least three navigates to be effective.

First, they must strongly absorb UV radiation that would be harmful to the polymer or coating. Second, they must harmlessly disperse the energy that they absorb. Finally, they must persist in the matrix for the expected lifespan [6]. Mainly, there are two represented mechanisms for UVAs. The UVAs made from phenols 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 intra molecular H-tunneling or proton transfer process between carbonyl and OH or NH groups in combination with OH or NH that are located in the vicinity with carbonyl group (Figure 1) [9].

Tautomeric forms as well as proton transfer processes of phenols make them potentially UVAs. Phenols such as UV absorbents are capable therefore 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 they dry slower and are employed as high gloss coatings and wood finishes,

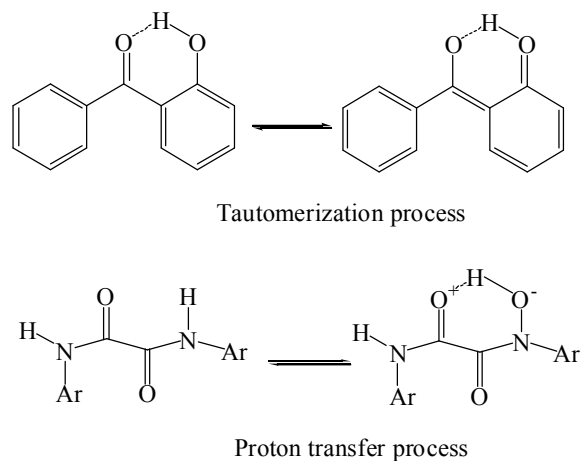


Fig. 1: Tautomerization and proton transfer for UVAs

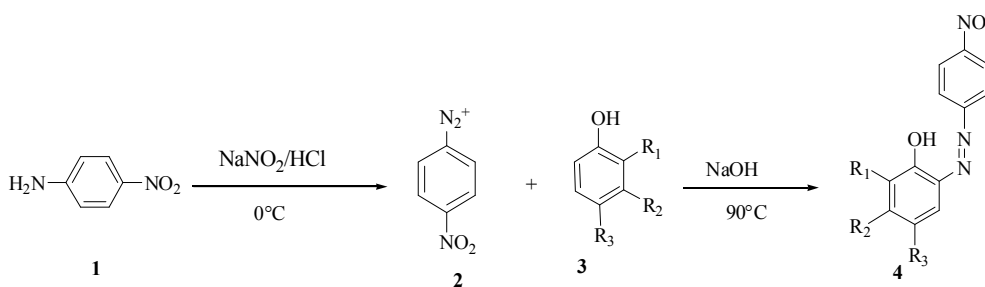
They are economic benefit Because the major components of an alkyd coating, i.e. fatty acids and triglyceride oils, are derived from low cost renewable resources, this has kept the cost of alkyd coatings very low despite ever increasing cost of petroleum, which is the predominant raw material source of most other coatings such as vinyls, acrylics, epoxies and polyurethanes, 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].

### Experimental

**Materials:** All chemicals were purchased from Merck Chemical Co. (Germany).

**Techniques:** Structures of synthesized compounds were elucidated by IR and UV. Melting points were measured with an electro thermal 9100 apparatus. IR spectra were measured by a Nexus 870 FT-IR spectrometer (Thermo Nicolet, Madison, WI). UV spectra of compounds were recorded as  $2 \times 10^{-5}$  molar solutions in chloroform and  $\epsilon$  of compounds were calculated by Beer-Lambert Law ( $A = \epsilon bc$ ).  $\lambda_{max}$  and  $\epsilon$  summarized.  $^1\text{H}$ NMR spectra were measured with BRUKER DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz, respectively The glosses of samples recorded using Sheen gloss meter 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,  $100\mu$  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 Ultra Violent Absorber:** Diazonium salt 2 was prepared by adding HCl /  $\text{NaNO}_2$  to 4-amino-3-nitrobenzenesulfonic acid 1 at  $0^\circ\text{C}$ . This salt was coupled to phenol 3 and produced azo compound 4, using a buffer of pH 8 (Figure 2) [12].



4	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
a		phenyl	H
b	H	phenyl	
c	NO	phenyl	
d	H	H	NO <sub>2</sub>
e	H	NO <sub>2</sub>	H
f	H	OH	H

Fig. 2: Synthesis route of phenols as UV absorber

**2-(2-(4-nitrophenyl)diazenyl)naphthalen-1-ol (4-a):**

**Redish:** Violent, power:(82%), mp=226°C (decomp), IR(KBr,cm<sup>-1</sup>), 3347 (OH), 1562,1346(NO<sub>2</sub>), 1430 (N=N).

**3-(2-(4-nitrophenyl)diazenyl)naphthalen-2-ol (4-b):**

**Redish:** Red orange, power (75%), mp=272°C (decomp), IR(KBr, cm<sup>-1</sup>), 3220 (OH), 1571 (C=C), 1567 (N=N). <sup>1</sup>HNMR(500MHz,CDCl<sub>3</sub>) δ: 6.82-8.46 (m, Aromatic, H in SO<sub>3</sub>H), 12.08(1H, S, OH).

**3-(2-(4-nitrophenyl)diazenyl)-1-nitrosophthalen-2-ol (4-c):**

**Redish:** Black violet, power: (75%), mp=188°C (decomp), IR(KBr,cm<sup>-1</sup>), 3417.24 (OH), 1420 (N=N), 1590,1390(NO<sub>2</sub>).

**2-(2-(4-nitrophenyl)diazenyl)-4-nitrophenol (4-d):**

**Redish:** Red, power, (80%), mp=211°C (decomp), IR(KBr, cm<sup>-1</sup>), 3385 (OH), 16.01,1391 (NO<sub>2</sub>), 1494 (N=N).

**2-(2-(4-nitrophenyl)diazenyl)-5-nitrophenol (4-e):**

**Redish:** Orange. Power, (88%), mp=275°C (decomp), IR (KBr, cm<sup>-1</sup>), 3454 (Broad, 2OH), 1554,1358 (NO<sub>2</sub>). <sup>1</sup>HNMR(300MHz, CDCl<sub>3</sub>) δ: 8.73-8.07(H, m, Aromatic),8.07(1H, S, OH), 8.70 (OH).

**4-(2-(4-nitrophenyl)diazenyl)benzene-1,3-diol (4-f):**

**Redish:** Vermilion, power:(82%), mp=210°C(decomp), IR(KBr, cm<sup>-1</sup>), 3424 (Broad, 2OH), 1623 (C=C), 1510,1399 (NO<sub>2</sub>), 1448 (N=N). <sup>1</sup>HNMR (500MHz, CDCl<sub>3</sub>) δ: 7.13-8.07(H, m, Aromatic), 8.70,8.73(2H, 2S, OH).

## RESULTS AND DISCUSSION

$\lambda_{\max}$  of this phenols is between 241-302 nm and  $\epsilon > 10000$ . Therefore, synthesized phenols are reasonable to use as UV-absorbers in coating to maintain ablaze. In IR spectra, OH stretching appears above 3300 cm<sup>-1</sup>. In addition to resonance of aromatics proton peaks, phenol 4-b had the shortest (241 nm) and 4-f the longest (302 nm)  $\lambda_{\max}$  in UV, (Table 1). Therefore, increasing conjugation in this phenols extended their applications to UVAs. Regarding molar extinction coefficient ( $\epsilon$ ) is another important factor in effectiveness of UVAs, all this phenols 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 92 to 3 %. All additives were good gloss protecting against UV radiation.

Table 1: UV spectral data for phenols

Molecules	$\epsilon$	$\lambda_{\max}$
4-a	30000	272
4-b	25000	241
4-c	50000	275
4-d	45000	276
4-e	15000	243
4-f	17500	302

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

Name	Gloss		
	UV absence	UV exposure	$\Delta$ Gloss
Sample 1*,**	91	70	21
Sample 2*	91	3	88
TINUV315 (as witness)	92	86	6
4-a	91	66	25
4-b	91	64	27
4-c	91	79	12
4-d	91	76	15
4-e	91	59	32
4-f	92	67	25

In regard with the results of gloss of color testing of samples 1 and 2, UV radiation was more effective than daylight on gloss of color changing. In the presence of TINUVIN 315 and synthesized phenols, the stability of paints against UV radiation improved significantly.

## CONCLUSIONS

It is reasonable to use of this phenols as additive UV absorbent in such polymeric coating and dyes to increase the stability of coatings against radical destruction that contribute to the health of the community and the life of the coating increases which is used in industries as a economic aid and subsequently to decrease environmental contamination and Volatile organic compounds (VOC) and polymeric pollutants so are environmentally friendly.

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