

# New Benzotriazole Phthalocyanine Nickel(II) Photostabilizer for Low Density Polyethylene

Ziade T. Almkali<sup>1</sup>, Einas A. Al-Nasir<sup>1</sup>, Ali H. Al-Mowali<sup>2\*</sup>, Ebrahim K. Ebrahim<sup>1</sup> and Fais J. Mohammed<sup>3</sup>

1. Chemistry Department, Polymer Research Centre, University of Basrah

2. Chemistry Department, College of Science, University of Basrah

3. Basrah Petrochemical complex, Basrah

\*E-Mail of the corresponding author: ali\_almoali@yahoo.com

## Abstract

Benzotriazole Phthalocyanine Nickel(II) has been prepared and characterized by elemental analysis and FT-IR techniques. This new compound imposes three pathways to stabilize low density polyethylene (LDPE) due to nature of its complex structure. The prepared complex contains four benzotriazoles which absorb U.V. light while Nickel(II) derivative destroys hydrogen peroxides and scavenges free radicals. The experimental investigation carried out on Benzotriazole phthalocyanine Nickel(II) shows that this complex has excellent photostabilizer for LDPE compared with commercial antioxidants.

**Keywords:** Photostabilizer, Phthalocyanine Nickel(II) derivatives, LDPE

## 1. Introduction

Pure LDPE is not affected by U.V. light since it composes from C-C and C-H bonds but practically LDPE during its preparation at high temperature and storage produces trace materials such as hydroperoxides, carbonyl groups and unsaturated Vinylidene group. The presence of one or more of these groups initiates photooxidation by U.V. light (280-400 nm). Scheme(1) shows the pathway of photooxidation of LDPE (Rabek 1987, Jelcic et al 2003, Al-Mowali et al 2007, Hsu et al 2012). Four classes of photostabilizer are known depend on their action such as U.V. Screeners, U.V. absorber, Excited state quenchers and Free radical Scavenger (Al-Mowali et al 2002, Kawamura et al 2003, Peterson et al 2004, Pham et al 2008, Karak 2009).

The aim of this work is to prepare new photostabilizer which hopefully include all four classes described before. Therefore a complex of the form 2, 2', 2'', 2'''-2H-Benzotriazole-3, 3', 3'', 3'''-tri-amino phthalocyanine (NiNH<sub>2</sub>B<sub>4</sub>) has been synthesized and characterized by CHN and FT-IR techniques and photostabilization to LDPE is fully examined and compared to standard photostabilizers.

## 2. Experimental

### 2.1 Materials

Phthalic anhydride, Nickel chloride, Urea, Nitrobenzene, o-Nitroaniline were obtained from Fluka, Ammonium molybdate tetrahydrate, Ammonium Chloride, Sodium Nitrite were obtained from Aldrich, zinc powder was obtained from Merck. Solvents were used after being purified according to standard method. LDPE obtained from Basrah petrochemical company with specification (Density=0.921-0.924 gm/cm<sup>3</sup>, Melt index = (0.28-0.38 gm/10 min)).



water . Fine crystals was obtained with 85% yield .

#### 2.4 Preparation of 3,3',3'',3'''-tetraaminophthalocyanine Nickel(II) compound (NiNH<sub>2</sub>)

NiNO<sub>2</sub> compound (10mmole) in 45ml of distilled water was added to (40mmole) of sodium polyphosphide dissolved in 25ml of distilled water at 20°C . The mixture was stirred vigorously at 20°C for 24 hours , and then added to 50ml of 1N HCl with stirring for about 30 minutes (Al-Lami et al , 2013) . The solid product was collected and added to 50ml of 1N NaOH , stirred for about 30 minutes and the fine crystals was obtained with 87% yield .

#### 2.5 Synthesis of 2, 2',2'',2'''-2H-Benzotriazole-3,3',3'',3'''-tetraamino phthalocyanine Nickel(II) complex NiNH<sub>2</sub>B<sub>4</sub>

6.9g (0.05mole) of o-nitroaniline was added to heated Conc. HCl at 70°C and then the mixture was cool to zero degree . To this mixture 50ml of distilled water was added and then 50g of ice to cool the mixture at -5° C . 12.5ml of 5N sodium nitrite NaNO<sub>2</sub> was added through 30 minutes and pale yellow of dizonium salt was formed . To the diazonium salt formed 0.5g (0.008 mole) of urea in distilled water was added followed by 5.5 g (0.05mole) of phthalocyanine complex , 4 g (0.1mole) of NaOH and 0.15 mole of sodium carbonate dissolved in 150 ml distilled water with stirring . The mixture was stirred further for about 4 hours at temperature between -15°C to 10°C , and then the azo dye was filtered and dried under normal atmosphere for 24 hours . The azo dye was dissolved in 25% NaOH solution and then 7.5g zinc dust was added gradually for about 20 minutes with stirring . The mixture was stirred further for 6 hours and then neutralize by concentrated HCl (pH=7) in order to precipitate unreacted zinc followed by filtration of solid product and washed with CH<sub>2</sub>Cl<sub>2</sub> . The CH<sub>2</sub>Cl<sub>2</sub> solvent was removed by rotatory evaporator to form the final product , which recrystallized from the menthanol to give 30% fine crystals . Figure (1) shows the structure of the prepared complex .

#### 2.6 Preparation of samples for IR test

1 gm from each sample was inserted in the press at 175°C and 5 tons for 3 minutes . Then the pressure was increased to 15 tons for 9 minutes . The mixture was cooled to room temperature , then molded as a sheat of 0.05 mm thickness . FT-IR spectra for all samples were measured before and after mixing with NiNH<sub>2</sub>B<sub>4</sub> . Samples of LDPE with and without NiNH<sub>2</sub>B<sub>4</sub> , were exposed to UV light of 200 watt as a function of irradiated light times .Samples of LDPE containing NiNH<sub>2</sub>B<sub>4</sub> were prepared by mixing them using Hakee mixture at (140-150)°C for 15 minutes .

### 3 Results and Discussion

#### 3.1 Structural characterization

The prepared complex structures were established from FT-IR (Table 1) and elemental analysis (Table 2) . FT-IR spectra for all complexes (Figs 2-4) show two weak bands at (520-570)cm<sup>-1</sup> which attributed to stretching vibration of Ni-N, strong peaks at (1591-1600) cm<sup>-1</sup> which attributed to stretching vibration of C=C bond and strong bands at (1680-1692) cm<sup>-1</sup> for stretching vibration of C=N group. Complexes NiNO<sub>2</sub> , NiNH<sub>2</sub> and NiNH<sub>2</sub>B<sub>4</sub> show also stretching vibration and bending vibration bands for NO<sub>2</sub> , NH<sub>2</sub> for complexes NiNO<sub>2</sub> , NiNH<sub>2</sub> and stretching vibration for -C=N-, C=C and -N=C- groups for benzotriazole part of complex NiNH<sub>2</sub>B<sub>4</sub>. The elemental analysis for the prepared compounds are in good agreement with the calculated values as shown in table (2) .

#### 3.2 Efficiency of the prepared complex NiNH<sub>2</sub>B<sub>4</sub> as photostabilizer .

The efficiency of the prepared complex NiNH<sub>2</sub>B<sub>4</sub> U.V photostabilizer for low density polyethylene was compare with blank LDPE which containing no additive , LDPE containing BHT and irdanox 1076(1) and with LDPE cotaining comercial Viosorb 510 [2,(2'-hydroxy 5'-t-octyl phenyl)benzotriazol] photostabilizer (B). All films containing the above materials were placed at the same distance away from mercury lamp and exposed at the same periode of times to the U.V. source (Fig.5) . The photodegradation of the samples were followed by FT-IR from measurment of the change of transmittance intensity of carbonyl band against the time of U.V. irradiation according to the following equation (Al-Assadi 2012):

$$\% \Delta CO = [T_r - T_o] / T_i \times 100$$

Where T<sub>o</sub> : Transimittance befor U.V. irradiation

T<sub>i</sub> : Transimittance of carbonyl bond after time (t) of U.V. irradiation

Figure (5) indicates that the prepared complex NiNH<sub>2</sub>B<sub>4</sub> is most effective as photostabilizer for LDPE. Percent of transmittance of %ΔCO as a function of irradiatad U.V. light is more less than that of other compounds . This most probably because the compound behave as screener , absorber , quencher and free radical scavenger when exposed to U.V. light .

#### 3.3 Conclusion

The design of NiNH<sub>2</sub>B<sub>4</sub> as photostabilizer for LDPE is very successful since its structure may acts as U.V. screeners , U.V. absorbers , excited state quenchers and free radical scavengers which all together drop the precent of transmittance of carbonyl group compared with other additives.

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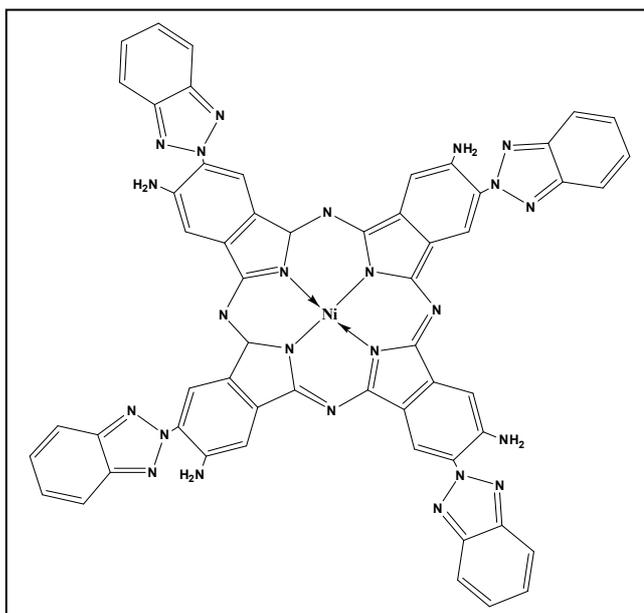


Fig (1) : Structure of NiNH<sub>2</sub>B<sub>4</sub> photostabilizer

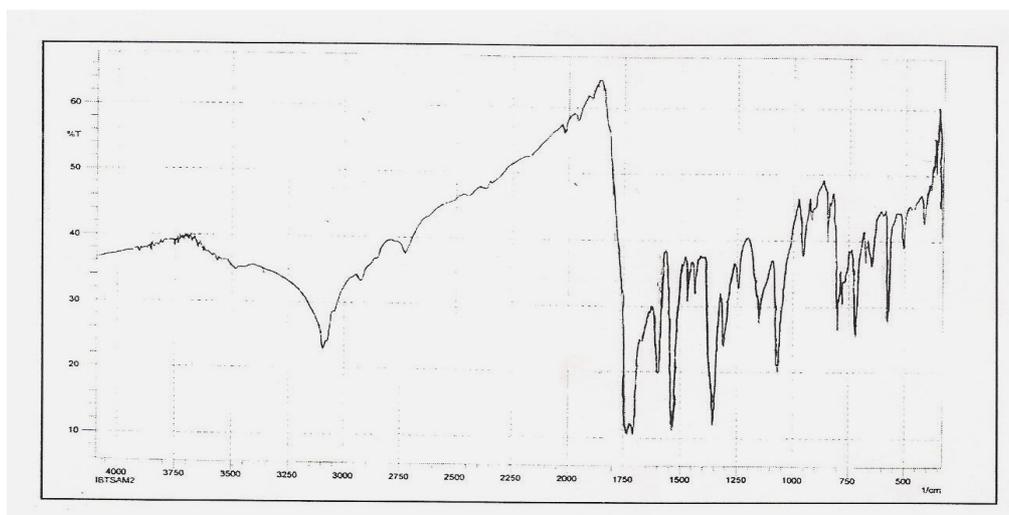
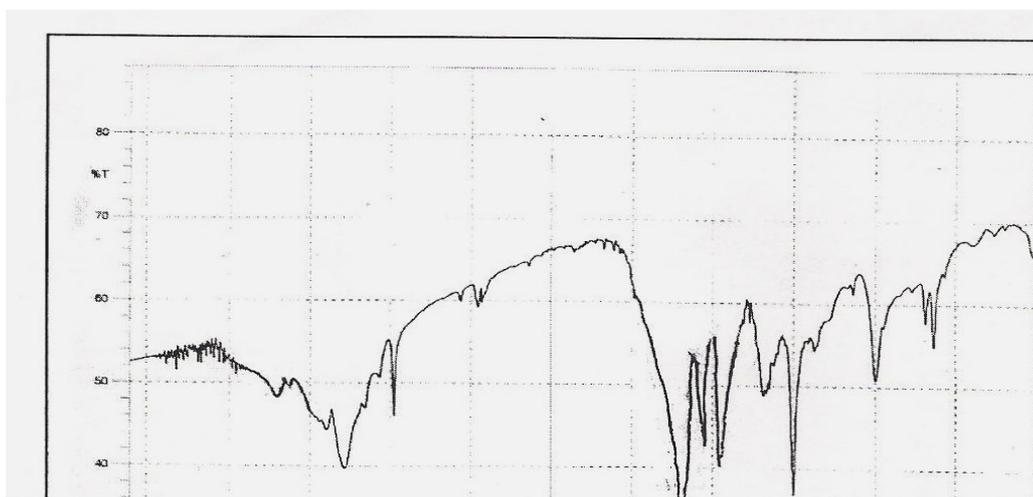
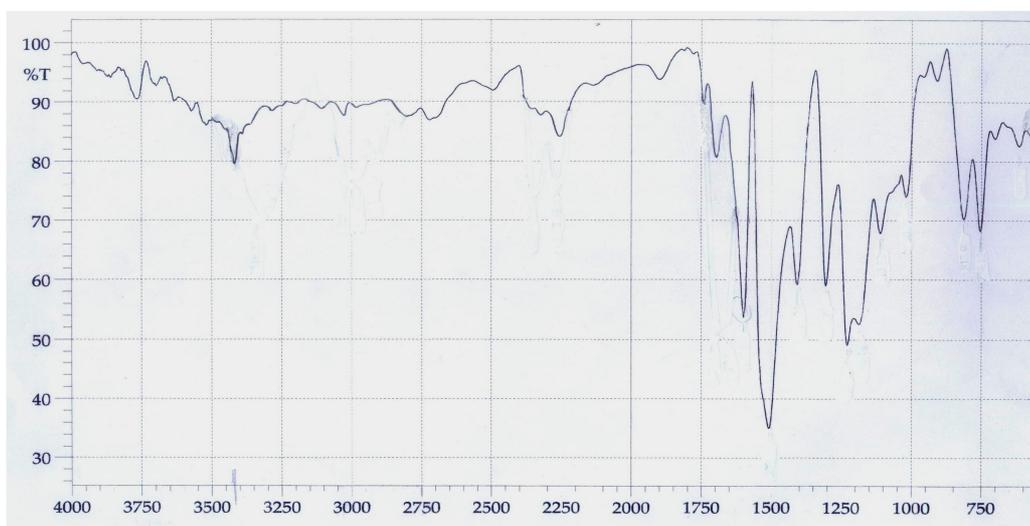


Fig (2) : IR spectrum of NiNH<sub>2</sub>



Fig(3) : IR spectrum of NiNO<sub>2</sub>



Fig(4) : IR spectrum of NiNH<sub>2</sub>B<sub>4</sub>

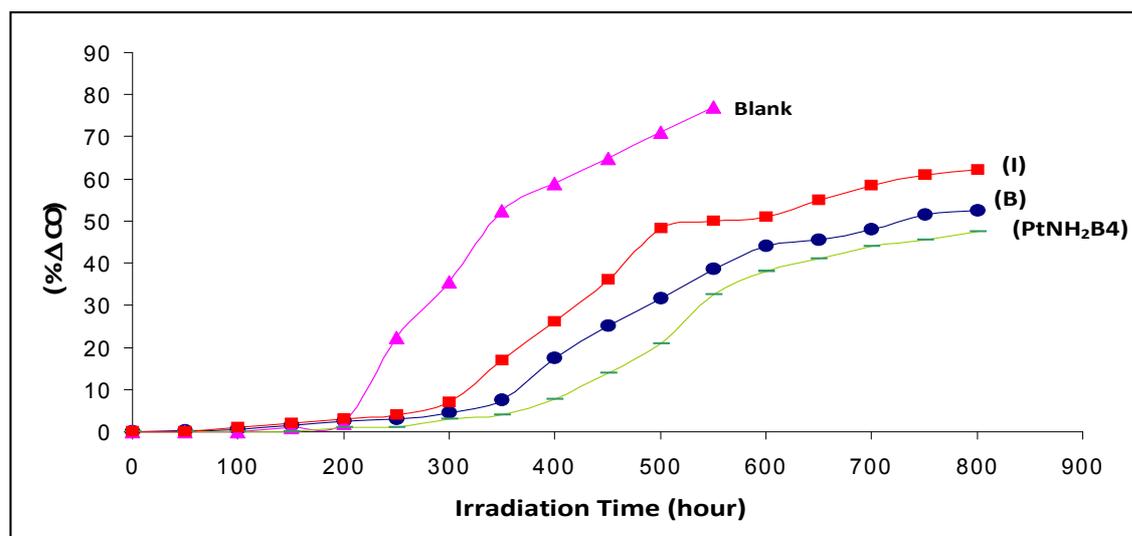


Fig (5) : change of transmittance intensity of carbonyl band against the time of U.V. irradiation

Table (1) : The IR absorption for the most important groups of prepared compounds

Comp.	$\nu$ (C=N)	$\nu$ (C=C)	$\nu$ (Ni-N)	$\nu_{asm}$ (C-H)	$\nu_{asy}$ (NO <sub>2</sub> )	$\nu_{sy}$ (NO <sub>2</sub> )	$\nu_{str.amin}$ (N-H)	$\nu_{bend}$ (N-H)
NiNO <sub>2</sub>	1692	1595	525 570	3085	1540	1356	-	-
NiNH <sub>2</sub>	1680	1591	533 560	3030	-	-	3410	1620
NiNH <sub>2</sub> B <sub>4</sub>	-	1600	505 540	3050	-	-	3420	-

Table (2) : Elemental analysis of the prepared compounds

compound	Chemical structure	experimental			theoretical		
		% C	% H	% N	% C	% H	% N
(NiNH <sub>2</sub> B <sub>4</sub> )	C <sub>56</sub> H <sub>36</sub> N <sub>24</sub> Pt	54.01	3.00	27.21	54.23	2.905	27.11
(NiNH <sub>2</sub> )	C <sub>32</sub> H <sub>24</sub> N <sub>12</sub> Pt	49.55	3.20	21.62	49.80	3.11	21.78
(NiNO <sub>2</sub> )	C <sub>32</sub> H <sub>16</sub> O <sub>8</sub> N <sub>12</sub> Pt	42.00	1.66	21.91	43.09	1.79	21.89

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