# Improvement of the Photostabilization of PVC Films in the Presence of 2N-Salicylidene-5-(Substituted)-1,3,4-Thiadiazole

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**ABSTRACT:** The photostabilization of poly(vinyl chloride) (PVC) films by 2N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds was investigated. The PVC films containing concentration of complexes 0.5% by weight were produced by the casting method from tetrahydrofuran (THF) solvent. The photostabilization activities of these compounds were determined by monitoring the carbonyl, polyene, and hydroxyl indices with irradiation time. The changes in viscosity average molecular weight of PVC with irradiation time were also tracked (using THF as a solvent). The quantum yield of the chain scission ($\Phi_{cs}$) of these complexes in PVC films was evaluated and found to range between $4.72 \times 10^{-8}$ and $8.99 \times 10^{-8}$. Results obtained showed that the rate of photostabilization of PVC in the presence of the additive followed the trend:

$$SN > SC > SB > SI > SP$$

According to the experimental results obtained, several mechanisms were suggested depending on the structure of the additive. Among them, UV absorption, peroxide decomposer, and radical scavenger for photostabilizer mechanisms were suggested. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2207–2214, 2011

**Key words:** photochemistry; poly(vinyl chloride) (PVC); UV–vis spectroscopy; photostabilizer; UV absorber

## INTRODUCTION

Poly(vinyl chloride) is second only to polyethylene among five kinds of general plastic materials, which was widely used in the industries including architecture, electronic, chemical engineering, packaging, transportation, etc.[1–4] However, low photostability of PVC leads to hydrogen chloride loss, discoloration, and finally serious corrosion phenomena, accompanied by changes of physical and chemical properties of PVC.

The low cost and the good performance of poly(vinyl chloride) products have increased the utilization of this polymer in building, mainly in exterior application, such as window profiles, cladding structure, and siding.[5] However, ultimate user acceptance of the PVC products for outdoor building applications will depend on their ability to resist photodegradation over long periods of sunlight exposure. To ensure weatherability, the PVC resin needs to be compounded and processed properly using suitable additives, leading to a complex material whose behavior and properties are quite different from the PVC resin by itself.[6] On the other hand, it is important to perform reliable accelerated weathering test methods. In this regard, factors that influence the degradation of PVC-based materials in the service condition, like light and temperature are accelerated.

As part of our on-going research on the photostabilization of PVC, the photostabilization of PVC was studied using 2N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds.

To our knowledge there is no attempt to investigate the photostabilization of PVC films by Schiff bases compounds containing four 1,3,4-thiadiazole rings, therefore, in this article we report the designing of some Schiff bases and studied their use as photostabilizing reagent.
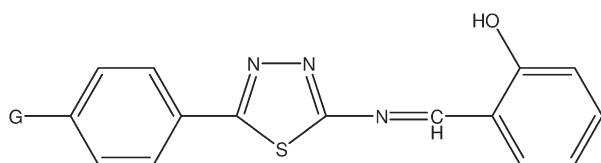
## EXPERIMENTAL

### Materials

The following 2N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds were all prepared by the method previously described[7]

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| 2N-salicylidene-5-( $P$-nitro-phenyl)-1,3,4-thiadiazole | SN |
| 2N-salicylidene-5-( $P$-chloro-phenyl)-1,3,4-thiadiazole | SC |
| 2N-salicylidene-5-( $P$-bromo phenyl)-1,3,4-thiadiazole | SB |
| 2N-salicylidene-5-($P$-iodo-phenyl)-1,3,4-thiadiazole | SI |
| 2N-salicylidene-5-(phenyl)-1,3,4-thiadiazole | SP |



where G = —NO$_2$, —Cl, —Br, —I or —H.

## Experimental techniques

### Films preparation

The polymer matrix used in this study was PVC ($K$ value = 67, degree of polymerization = 800) supplied by Petkim (Turkey) was re-precipitated from THF solution by alcohol several times and finally dried under vacuum at room temperature for 24 h. PVC films were prepared as follows. The best solvent for PVC is THF. The films were prepared by dissolving 5 g of PVC in 100 g of THF under vigorous stirring for 30 min. It was necessary to control the hygrometry and the rate of evaporation of solvent during casting to maintain good optical quality and very limited turbidity. The film transmission should be greater than 80% in the near-UV range. After 3 h, the solution was spread on a slide stainless steel model (250 × 120 × 0.5 mm$^3$) and air-dried for 24 h. After the solvent evaporation, the samples were dried in a vacuum at room temperature for 30 h. The thickness of the resulting PVC film (30 μm) was measured by a micrometer type 2610 A, Germany.

### Irradiation experiments

*Accelerated testing technique.* Accelerated weatherometer Q.U.V. tester (Q. panel, company, USA), was used for irradiation of polymer films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40-W each. These lamps are of the type UV-B 313 giving spectrum range between 290 and 360 nm with a maximum wavelength at 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation

is perpendicular to the samples. The irradiated samples are rotated from time to time to ensure that the intensity of light incident on all samples is the same.

### Photodegradation measuring methods

*Measuring the photodegradation rate of polymer films using infrared spectrophotometery.* The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000–400 cm$^{-1}$ using FTIR 8300 Shimadzu spectrophotometer. The position of carbonyl absorption is specified at 1722 cm$^{-1}$, polyene group at 1602 cm$^{-1}$, and the hydroxyl group at 3500 cm$^{-1}$.[8] The progress of photodegradation during different irradiation time was followed by observing the changes in carbonyl and polyene peaks. Then carbonyl ($I_{co}$), polyene ($I_{po}$), and hydroxyl ($I_{OH}$) indices were calculated by comparison of the FTIR absorption peak at 1722, 1602, and 3500 cm$^{-1}$ with reference peak at 1328 cm$^{-1}$, respectively. This method is called band index method which includes.[8]

$$Is = \frac{As}{Ar} \qquad (1)$$

As = Absorbance of peak under study
Ar = Absorbance of reference peak
Is = Index of group under study

Actual absorbance, the difference between the absorbance of top peak and base line (A Top Peak–A Base Line) is calculated using the Base Line method.[9]

*Determination of average molecular weight ($\overline{M}_v$) using viscometry method.* The viscosity property was used to determine the average molecular weight of polymer, using the Mark Houwink relation.[10]

$$[\eta] = K\overline{M}_v^{\alpha} \qquad (2)$$

$[\eta]$ = the intrinsic viscosity.
$K$ and $\alpha$ are constants depend upon the polymer-solvent system at a particular temperature.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (g 100 mL$^{-1}$) and the flow times of polymer solution and pure solvent are $t$ and $t_0$, respectively. Specific viscosity ($\eta_{sp}$) was calculated as follows:

$$\eta_{re} = \frac{t}{t_o} \qquad (3)$$

$\eta_{re}$ = Relative viscosity.

$$\eta_{sp} = \eta_{re} - 1 \qquad (4)$$

The single-point measurements were converted to intrinsic viscosities by the relation 2.
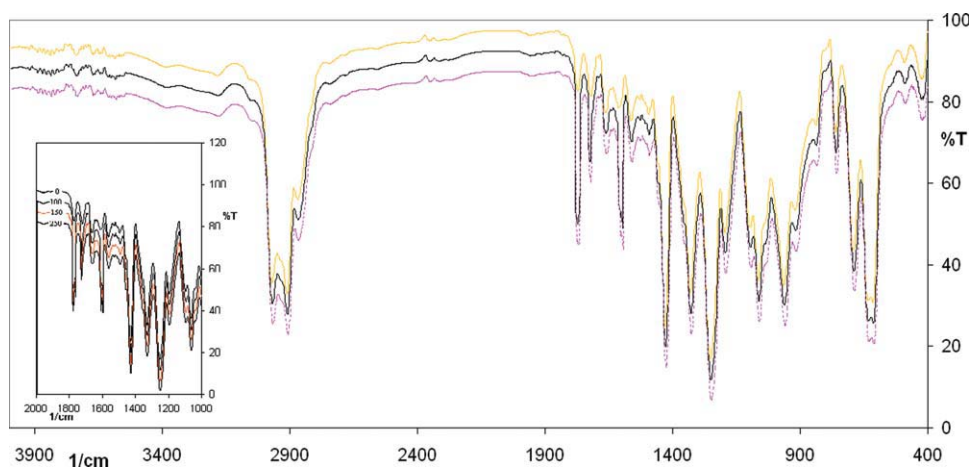
**Figure 1** Change in IR spectrum of PVC film (30 µm) in the presence of SB compound (numbers in spectra are irradiation time in hours). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$[\eta] = (\sqrt{2}/c)(\eta_{sp} - \ln \eta_{re})^{1/2} \quad (5)$$

$C$ = Concentration of polymer solution (g 100 mL$^{-1}$).

By applying eq. (5), the molecular weight of degraded and virgin polymer can be calculated. Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solution using the following equation:

$$[\eta] = 1.38 * \times 10^{-4} M_w^{0.77} \quad (6)$$

The quantum yield of main chain scission $(\phi_{cs})$[11] was calculated from viscosity measurement using the following relation (7).

$$\phi_{cs} = (CA/\overline{M}_{v,0})\left[\left((\eta_o)/[\eta])^1/\alpha - 1\right]\right/I_o t \quad (7)$$

where $C$ = concentration; $A$ = Avogadro's number; $(\overline{M}_{v,0})$ = the initial viscosity-average molecular weight; $[\eta_o]$ = Intrinsic viscosity of PVC before irradiation; $I_o$ = Incident intensity, and $t$ = Irradiation time in second.

## RESULTS AND DISCUSSION

The 2N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds were used as additives for the photostabilization of PVC films. To study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl and polyene indices were monitored with irradiation time using IR spectrophotometry. The irradiation of PVC films with UV light of wavelength, $\lambda$ = 313 nm led to a clear change in the FTIR spectrum,[2] as shown in Figure 1. Appearance of bands at 1772 and 1724 cm$^{-1}$, were attributed to the formation of carbonyl groups related to chloroketone and to aliphatic ketone,

respectively. A third band was observed at 1604 cm$^{-1}$, related to polyene group. The hydroxyl band appeared at 3500 cm$^{-1}$ was annotated to the OH— of the hydroperoxides group as shown in Scheme 1.

The absorption of the carbonyl, polyene, and hydroxyl groups was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index $(I_{co})$, polyene index $(I_{PO})$, and hydroxyl index $(I_{OH})$. It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. However, in Figure 2, the $I_{co}$ of SP, SI, SB, SC, and SN showed lower growth rate with irradiation time with respect to the PVC control film without additives. Since the growth of carbonyl index with irradiation time is lower than PVC control, as seen in
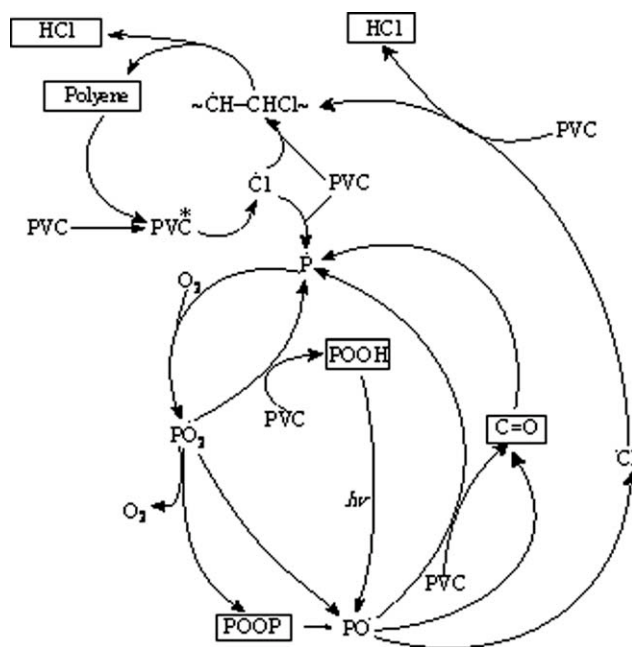
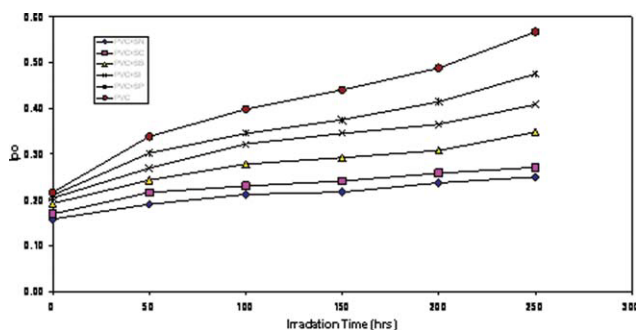

**Scheme 1** Photooxidation reaction Scheme of PVC.[9]
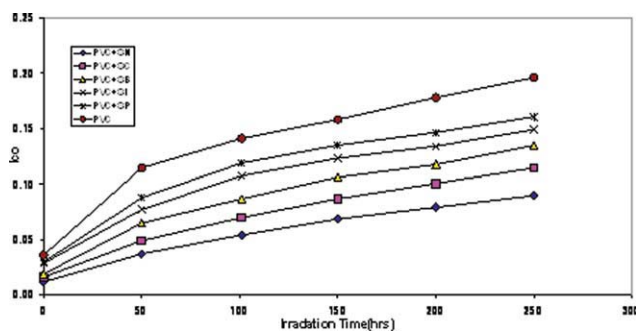
**Figure 2** The relationship between the carbonyl index and irradiation time for PVC films (30 μm thickness) containing different additives. Concentration of additives is fixed at 0.5% by weight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 4** The relationship between the hydroxyl index and irradiation time for PVC films (30 μm thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2, it is suitable to conclude that these additives might be considered as photostabilizers of PVC polymer. Since efficient photostabilizer shows a longer induction period, therefore, the SN is considered as the most active photostabilizer, followed by SC, SB, SI, and SP which is the least active. Just like carbonyl, polyene compounds are also produced during photodegradation of PVC. Therefore, polyene index ($I_{PO}$) could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Figure 3.
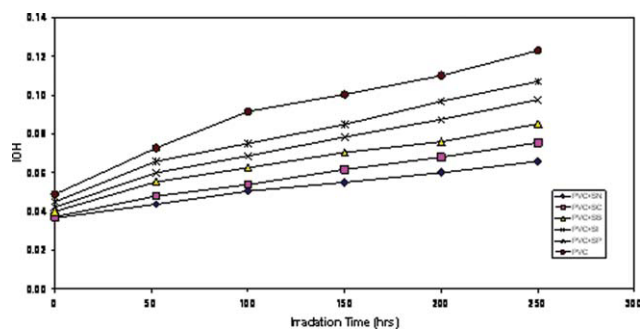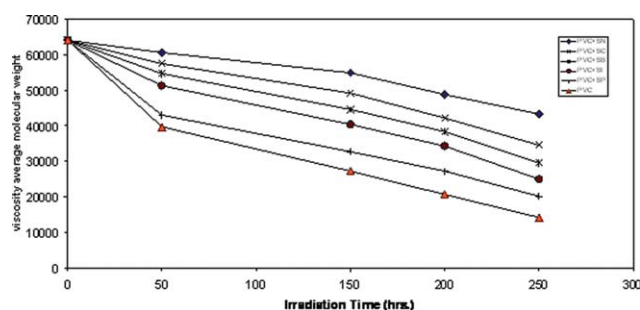
Hydroxyl species were produced during photodegradation of PVC. Therefore, hydroxyl index ($I_{OH}$) was monitored with irradiation time for PVC and with additives. From Figure 4 the SP, SI, SB, SC, and SN showed lower growth rate of hydroxyl index with irradiation time compared to PVC blank.

**Variation of PVC molecular weight during photolysis in the presence of 2N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds**

Analysis of the relative changes in viscosity average molecular weight ($\overline{M}_v$), has been shown to provide a versatile test for random chain scission. Figure 5

shows the plot of $\overline{M}_v$ versus irradiation time for PVC film with and without 0.5% (wt/wt) of the selected additives, with absorbed light intensity of $1.052 \times 10^{-8}$ ein dm$^{-3}$ s$^{-1}$. $\overline{M}_v$ is measured using eq. (4) with THF as a solvent at 25°C.

It is worth mentioning that traces of the films with additives are not soluble in THF indicating that crosslinking or branching in the PVC chain does occur during the course of photolysis.[12] For better support of this view, the number of average chain scission (average number cut per single chain) (S)[13] was calculated using the relation (8):

$$S = \frac{\overline{M}_{v,o}}{\overline{M}_{v,t}} - 1 \qquad (8)$$

where $\overline{M}_{v,0}$ and $\overline{M}_{v,t}$ are viscosity average molecular weight at initial (o) and $t$ irradiation time, respectively. The plot of $S$ versus time is shown in Figure 6. The curve indicates an increase in the degree of branching such as that might arise from crosslinking occurrence. It is observed that insoluble material was formed during irradiation which provided an additional evidence to the idea that crosslinking does occur.[8]



**Figure 3** The relationship between the polyene index and irradiation time for PVC films (30 μm thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5** Changes in the viscosity-average molecular weight ($\overline{M}_v$) during irradiation of PVC films (30 μm) (control) and with 0.5 wt % of additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
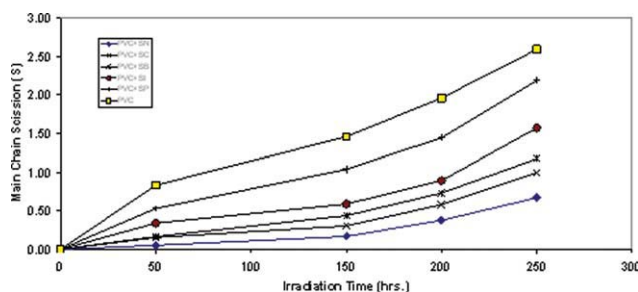
**Figure 6** Changes in the main chain scission (S) during irradiation of PVC films (30 μm) (control) and with 0.5 wt % of additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For randomly distributed weak bond links, which break rapidly in the initial stages of photodegradation, the degree of deterioration α is given as:

$$\alpha = \frac{m.s}{\overline{M}_v} \qquad (9)$$

where $m$ is the initial molecular weight.

The plot of α as a function of irradiation time is shown in Figure 7.

The values of α of the irradiated samples are higher when additives are absent and lower in the presence of additives compared to the corresponding values of the additive free PVC. In the initial stages of photodegradation of PVC, the value of α increases rapidly with time, this indicates a random breaking of bonds in the polymer chain.

Another way of degradation reaction characterization is the measurement of the quantum yield of the chain scission ($\Phi_{cs}$). The quantum yield for chain scission was calculated for PVC films with and without 0.5% (wt/wt) of additive mentioned above using relation (5). The $\Phi_{cs}$ values for complexes are tabulated in Table I.

The $\Phi_{cs}$ values for PVC films in the presence of additive are less than that of additive free PVC (control), which increase in the order:

$$\overrightarrow{SN, SC, SB, SI, SP \text{ and } PVC.}$$
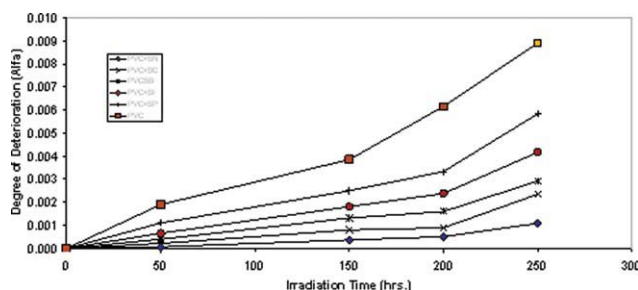


**Figure 7** Changes in the degree of deterioration (α) during irradiation of PVC films (30 μm) (control) and with 0.5 wt % of additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**TABLE I**
**Quantum Yield ($\Phi_{cs}$) for the Chain Scission for PVC Films (30 μm) Thickness with and Without 0.5 (wt/wt) Additive After 250-h Irradiation Time**

| Additive (0.5 wt %) | Quantum yield of main chain scission ($\Phi_{cs}$) |
|---|---|
| PVC+SN | 4.72E-08 |
| PVC+SC | 5.24E-08 |
| PVC+SB | 6.64E-08 |
| PVC+SI | 7.55E-08 |
| PVC+SP | 8.96E-08 |
| PVC(blank) | 8.54E-05 |

The explanation for low values of $\Phi_{cs}$ is that in macromolecule of PVC, the energy is absorbed at one site, and then the electronic excitation is distributed over many bonds so that the probability of a single bond breaking is small, or the absorbed energy is dissipated by non reactive processes.[8]

It is well established that the quantum yield ($\Phi_{cs.}$) increases with increasing temperature[14] around the glass transition temperature, ($T_g$) of the amorphous polymer, and around the melting temperature of crystalline polymers. In the study presented in this work, the photolysis of PVC film is carried out at a temperature 35–45°C well below the glass transition temperature ($T_g$ of PVC = 80°C). Therefore, the $\Phi_{cs}$ dependency on temperature is not expected to be observed.

## Suggested mechanisms of photostabilization of PVC by 2N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounnds

Through the overall results obtained, the efficiency of thiadiazole-derived Schiff base complexes as photostabilizers for PVC films can be arranged according to the change in the carbonyl and polyene concentration as a reference for the comparison as shown in Figures 1–7.

$$SN > SC > SB > SI > SP$$

Schiff base stabilize PVC by different mechanisms such as UV absorber, screener or by radical scavenger.

These stabilizers provide very good long-term stability and are usually referred to these mechanisms.

The most probable mechanism involved in a photostabilization is the change energy of absorbed photon to the intramolecular proton transfer. This reaction may occur by two proposed cycles, Schemes 2 and 3, the first passes by intersystem crossing (ICS) process to the excited triplet state, while the second is referred to internal conversion (IC) process to the ground state.

Other mechanism explains the use of this compound as photostabilizer is by charge separated species which could be a form of the excited state such a structure would allow dissipation of energy
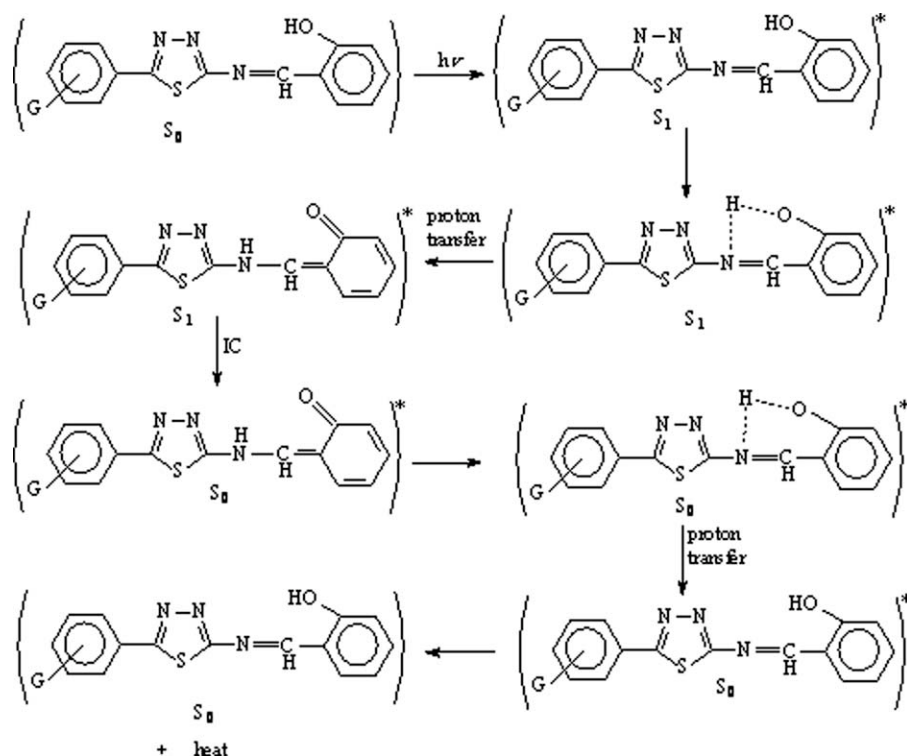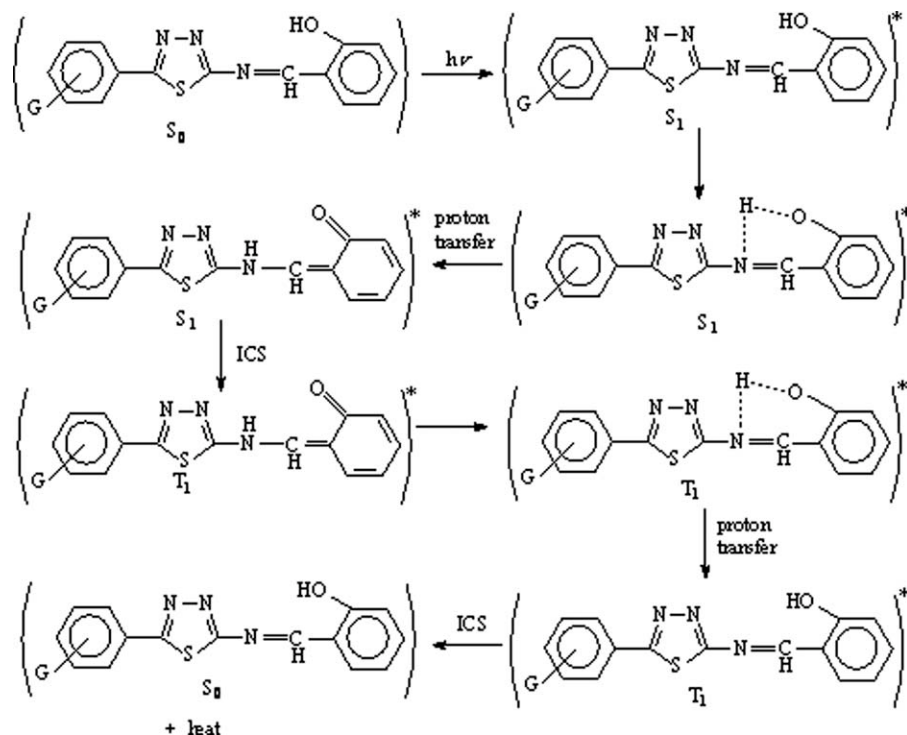
**Scheme 2**  The suggested mechanism of photostabilization of PVC by SE, SN, SE, and SP compounds through absorption of UV light and dissipation light energy as heat.

through rotation on increased vibration about the central bond[15] as shown in Scheme 4.

The 1,3,4-thiadiazole ring has two different atoms of different electronegativty such as nitro-

gen and sulfur. The polarity of this ring explains the attraction between the stabilizer and PVC Scheme 5. This mechanism can lead to the conclusion that crosslinking could take place upon UV



**Scheme 3**  The suggested mechanism of photostabilization of PVC by SE, SN, SE, and SP compounds through absorption of UV light and dissipation light energy as heat.
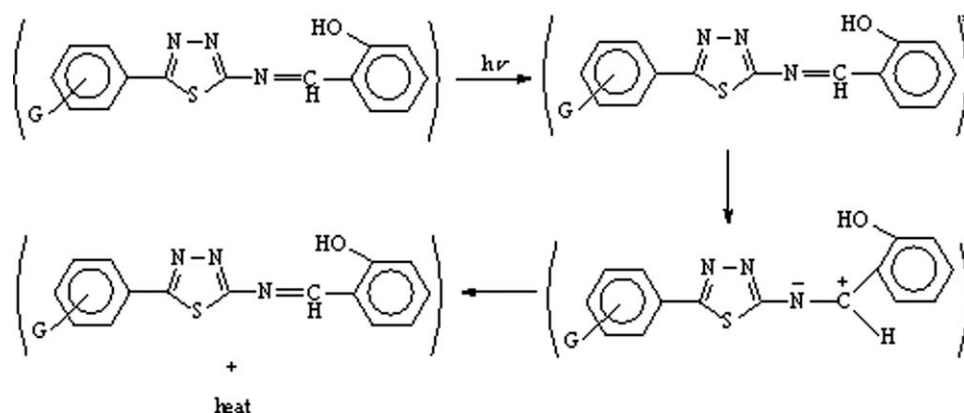
**Scheme 4** The suggested mechanism of photostabilization of PVC by SE, SN, SE, and SP compounds through absorption of UV light and dissipation light energy as heat.
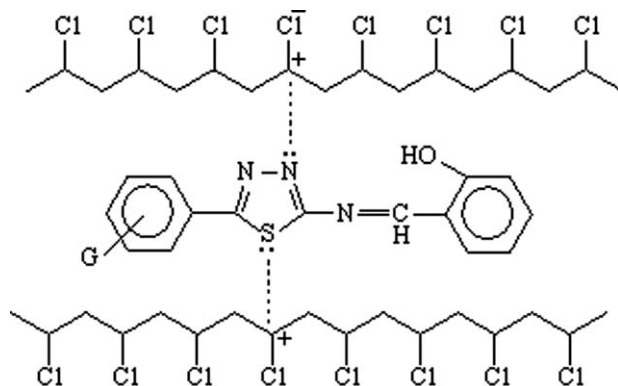
irradiation, which may be correct for all compounds.

The hydroxyl group of the additive might act as radical scavenger for photostabilization process. Therefore this Schiff bases, besides acting as UV absorber they may also act as radical scavenger additives, Scheme 6.

The rings of 1,3,4-thiadiazole play a role in the mechanism of the stabilizer process by acting as UV absorber.[16] The UV light absorption by these additives containing 1,3,4-thiadiazole dissipates the UV energy to harmless heat energy (Scheme 7). Furthermore, this ring plays a role in resonating structures conjugation of radical in peroxide decomposer Scheme 7, which sport it function as a photostabilizer.

## CONCLUSIONS

In the work described in this article, the photostabilization of poly(vinyl chloride) films using 2*N*-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds were studied. These additives behave successfully as photostabilizer for PVC films. The additives take the following order in photostabilization activity accord-

ing to their decrease in carbonyl, polyene, and hydroxyl indices for PVC films.

$$SN > SC > SB > SI > SP$$

These additives stabilize the PVC films through UV absorption or screening, peroxide decomposer, and radical scavenger mechanisms. The SN compound was found to be the most efficient in photostabilization process according to the photostability



**Scheme 6** The suggested mechanism of photostabilization of PVC by SE, SN, SE, and SP compounds as radical scavenger.
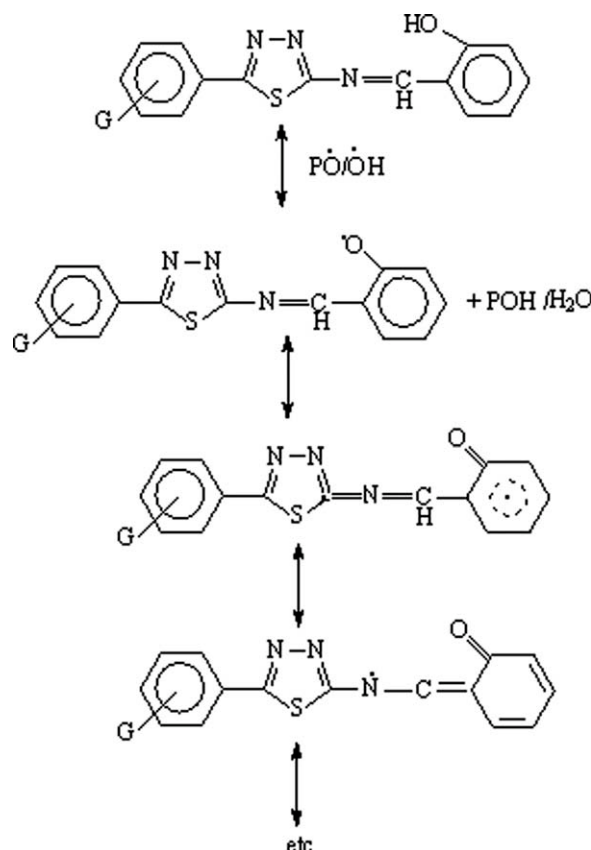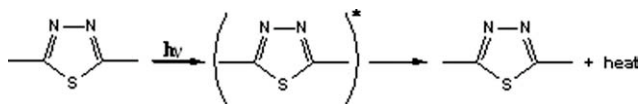


**Scheme 5** The suggested mechanism of photostabilization of PVC by SE, SN, SE, and SP compounds through the interaction between PVC and Schiff base compounds.

**Scheme 7** Suggested mechanism of photostabilization of 1,3,4-thiadiazole as UV absorber.

and mechanisms mentioned above. These mechanisms support the idea of using 2*N*-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds as commercial stabilizer for PVC.

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