

N-Phenyl-3-Substituted 5-Pyrazolone Derivatives as Organic Stabilizers for Rigid Poly(vinyl chloride) Against Photodegradation

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ABSTRACT: N-Phenyl-3-substituted 5-pyrazolone derivatives were investigated as organic photostabilizers for rigid poly(vinyl chloride) (PVC). Their stabilizing efficiency was evaluated by the determination of the weight loss of the polymer after irradiation for different periods and by the determination of the amount of gel formation as well as the intrinsic viscosity of the soluble fraction of the degraded polymer. Moreover, the efficiency was evaluated from the extent of the discoloration of the degraded polymer. This was attributed not only to the radical trapping potency of the pyrazolone derivatives, which intervened with the rad-

ical degradation species in the degradation process of PVC, but also to the blocking of the newly formed radical sites on the polymeric chains. Their stabilizing efficiencies were compared with those of phenyl salicylate and 2-hydroxy-4-(octyloxy)phenyl benzophenone, industrially known UV absorbers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1543–1555, 2006

Key words: degradation; gels; poly(vinyl chloride) (PVC); stabilization; viscosity

INTRODUCTION

The low cost and excellent performance of poly(vinyl chloride) (PVC) make it a very attractive and suitable plastic for a wide variety of applications. With respect to the production and consumption of synthetic materials, it stands third in the world after polyethylene and polypropylene. However, PVC suffers from poor thermal and light stability. It undergoes rapid autocatalytic dehydrochlorination upon exposure to heat^{1,2} and light^{3–6} during its molding and use, respectively. As a result, conjugated polyene sequences are formed from the beginning of the reaction, and they give rise to discoloration of the polymer and seriously change its physical properties.^{1–5} Degradation also causes a drastic change in the mechanical properties of the polymer, which is accompanied by a decrease or increase in its average molecular weight as a result of either chain scission or crosslinking of the polymer molecules, respectively.^{4–7} Various defect sites in the polymer chain are thought to be responsible for this instability. Possible defect structures in PVC chains are allylic chlorine,^{8,9} tertiary hydrogen and chlorine atoms,^{8,10,11} end groups such as double bonds,^{12–14} oxygen-containing groups,^{8,12,13} peroxide residues,^{7,15} and head-to-head

structures.¹⁶ In addition to these abnormalities, the steric order of the monomer units (tacticity) may have some influence on the degradation.^{17,18} The dehydrochlorination most likely proceeds by a chain mechanism involving radical intermediates.^{11,19–21} Recently, scientists have used substituted maleimides and itaconimides^{22,23} as photostabilizers for rigid PVC. They have also used glucoside derivatives as novel photostabilizers for rigid PVC.²⁴ In addition, 5-pyrimidine carbonitrile²⁵ derivatives have been used as photostabilizers for PVC.

N-Phenyl-3-substituted 5-pyrazolone derivatives are organic compounds that have been known since 1883; they are very useful as intermediates for pharmaceuticals and are used as anti-inflammatory agents and allergy inhibitors.²⁶

In our previous work,²⁷ N-phenyl-3-substituted 5-pyrazolone derivatives were investigated as thermal stabilizers for rigid PVC. The results revealed that these compounds are efficient thermal stabilizers and that the stabilizing action is most likely attributable to their ability to act as radical traps. Therefore, it is worth studying the stabilizing efficiency of these compounds against the photodegradation of rigid PVC.

EXPERIMENTAL

Materials

PVC (suspension) with a *K* value (which provides information about the average molecular weight of the

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TABLE I
Code Names, Melting Points, and Elemental Analyses of Various *N*-Phenyl-3-Substituted 5-Pyrazolone Derivatives

Material	Code name	mp (°C)	Elemental analysis					
			Calcd			Found		
			C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
1-Phenyl-3-methyl-2-pyrazolin-5-one	PMP	127	69	5.7	16.1	68.7	5.5	15.9
1-Phenyl-3-amino-2-pyrazolin-5-one	PAP	118	61.7	5.1	24.0	61.6	5.1	23.3
1-Phenyl-3-salicyloyl amino-2-pyrazolin-5-one	PSAP	142	65.1	4.4	14.2	64.9	4.1	14.2
1-Phenyl-3-methyl-4-salicyloyl-2-pyrazolin-5-one	PMSP	148	69.4	4.8	9.5	69.2	4.5	9.3

PVC used) of 70 was supplied by Hüls Co., and phenyl salicylate (salol) was acquired from El-Nasr Co. for Medicinal Chemicals (Cairo, Egypt). Methanone,2-Hydroxy-4-(octyloxy)phenyl benzophenone, was obtained from Linkers Co. (Far East Pte., Ltd., Singapore).

Tetrahydrofuran (THF), used as a solvent, was obtained from Prolabo Co. (Prolabo Co., France; analyt-

ical-grade). It was refluxed over potassium hydroxide pellets for 3 h and then distilled through a very short column. The pure solvent was stored in dark bottles and never used more than 3 weeks after distillation as fresh peroxides might have formed.

Preparation of the organic stabilizers

Various *N*-phenyl-3-substituted 5-pyrazolone derivatives, listed in (Table I), were synthesized by the procedure originally developed by Vogel²⁸ (Scheme 1).

TABLE II
Measurements of the Weight Loss, Soluble Fraction, Gel Content, and Intrinsic Viscosity for Rigid PVC in the Presence of *N*-Phenyl-3-Substituted 5-Pyrazolone Derivatives Acting as Photostabilizers in Comparison with Reference Stabilizers

Material	Weight loss (%)	Gel content (%)	Soluble fraction (%)	Intrinsic viscosity (dL/g) ^a
PVC (3 h)	3.2	13.02	85	3.21
PVC (6 h)	4.53	17.5	82	3.5
PVC (9 h)	5.34	20.77	79	4.17
PVC (15 h)	6.39	25.87	74.05	4.58
PVC + A (3 h)	2.7	10.98	88.77	2.96
PVC + A (6 h)	3.95	15.06	85	3.3
PVC + A (9 h)	4.81	18.89	81.2	3.87
PVC + A (15 h)	5.47	23.83	75.9	4.27
PVC + B (3 h)	2.36	8.77	91	2.74
PVC + B (6 h)	3.43	12.85	86.87	3.12
PVC + B (9 h)	4.38	16.43	83.22	3.6
PVC + B (15 h)	5.13	21.7	78	3.97
PVC + PMP (3 h)	1.52	6.13	92.97	2.25
PVC + PMP (6 h)	2.12	9.53	90	2.7
PVC + PMP (9 h)	2.75	13.28	86.43	2.97
PVC + PMP (15 h)	3.95	17.45	82.45	3.36
PVC + PMSP (3 h)	0.82	3.74	96	2
PVC + PMSP (6 h)	1.24	7.06	92	2.37
PVC + PMSP (9 h)	1.97	10.64	88.7	2.7
PVC + PMSP (15 h)	3.13	13.62	86.8	3
PVC + PAP (3 h)	1.16	7.5	92	2.11
PVC + PAP (6 h)	1.82	11.15	88.5	2.55
PVC + PAP (9 h)	2.42	14.47	85.45	2.86
PVC + PAP (15 h)	3.62	19.32	80.44	3.17
PVC + PSAP (3 h)	0.36	4.77	95	1.84
PVC + PSAP (6 h)	0.77	8.34	91	2.12
PVC + PSAP (9 h)	1.39	11.91	88	2.47
PVC + PSAP (15 h)	2.58	15.4	85	2.81

A = salol; B = methanone.

^a For nonirradiated PVC, the intrinsic viscosity was 1.6 dL/g.

Preparation of *N*-phenyl-3-methyl (or amino)-5-pyrazolone derivatives

Equimolar amounts of ethyl acetoacetate (or ethyl cyanoacetate) were mixed with phenyl hydrazine in a beaker; drops of glacial acetic acid were added, and the mixture was heated in a water bath for 1 h with stirring from time to time. After it cooled, 50 mL of petroleum ether (or diethyl ether) was added.

The mixture was stirred until solidification, filtered with a pump, washed with ether, and dried in an air oven.

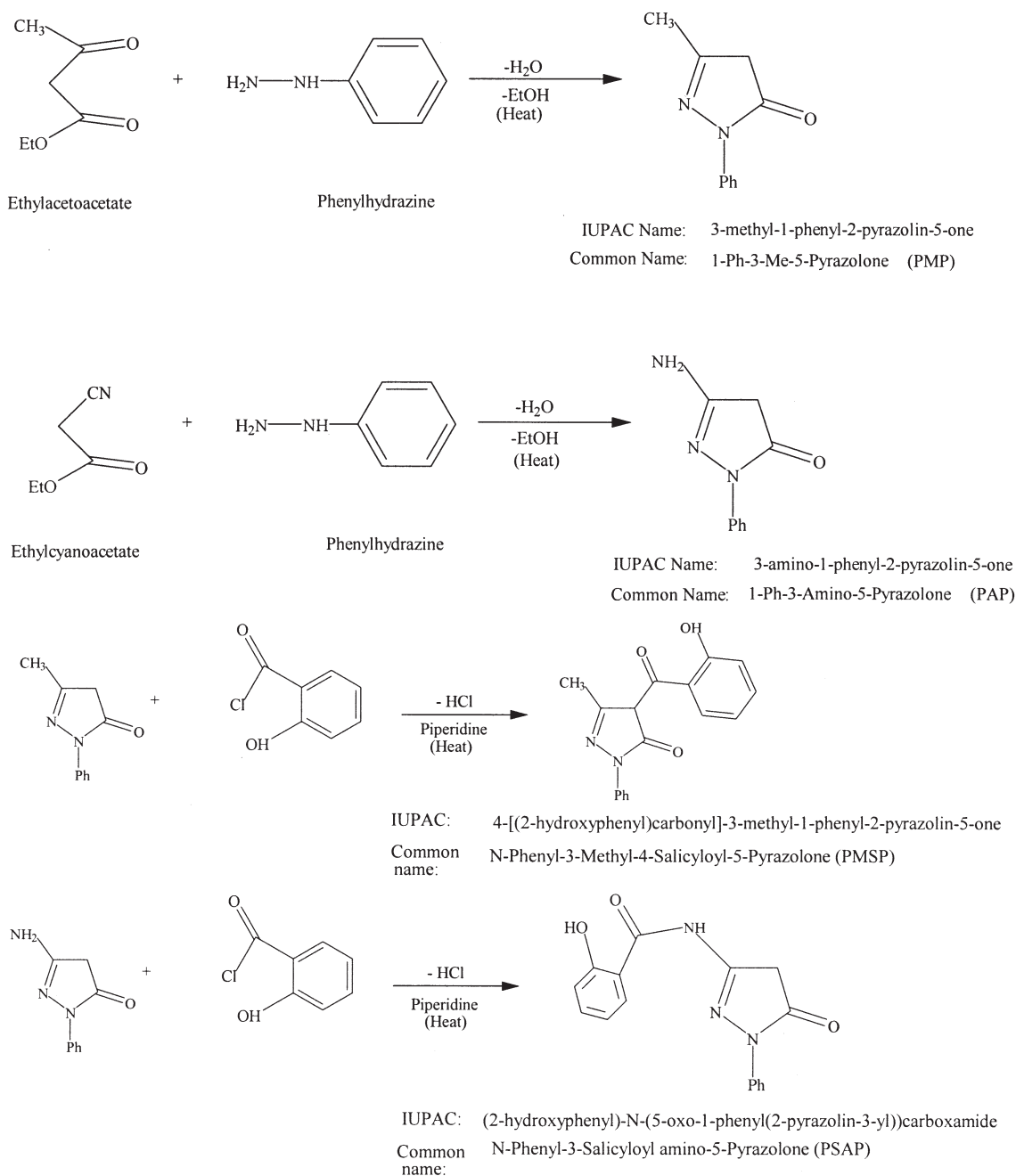
Preparation of *N*-phenyl-3-methyl (or amino)-2-salicyloyl-5-pyrazolone derivatives

N-Phenyl-3-methyl (or amino)-5-pyrazolone was dissolved in cold pyridine, and an equimolar amount of salicyloyl chloride was added with stirring for 3–4 h. Then, the mixture was poured onto crushed ice, stirred with scratching until complete precipitation, filtered with a pump, and washed with ether.

The elemental analyses, ¹H-NMR charts, and characteristic IR peaks of the various *N*-phenyl-3-substituted 5-pyrazolone derivatives agreed well with the theoretical values.

Preparation of the PVC films

Films of PVC containing either the reference stabilizer or the material under investigation were prepared by the polymer and the stabilizer being dissolved separately in THF. After complete dissolution, the two



Scheme 1

solutions were mixed and stirred to attain maximum homogeneity. The resulting solution was then poured into a Petri dish of a known constant diameter.

The films that formed upon complete evaporation of the solvent at room temperature were then immersed in diethyl ether; this was followed by heating in a vacuum oven at 70°C to remove any residual THF.²⁹ The films were 0.10 ± 0.02 mm thick in all cases.

Photodegradation

Photodegradation was affected by a PRK-2M 375-W UV lamp (Russia), from which each sample was held

at a constant distance of 15 cm. The temperature around the sample was kept constant at 70 ± 2°C⁵ (to obtain effective results in a convenient time).

Method of the evaluation of the stabilizing efficiency

Weight-loss measurements were carried out according to the following equation:

$$\text{Weight loss (\%)} = (W_1 - W_2 / W_1) \times 100$$

where W_1 is the weight of the original sample (before irradiation) and W_2 is the weight of the sample (after irradiation).

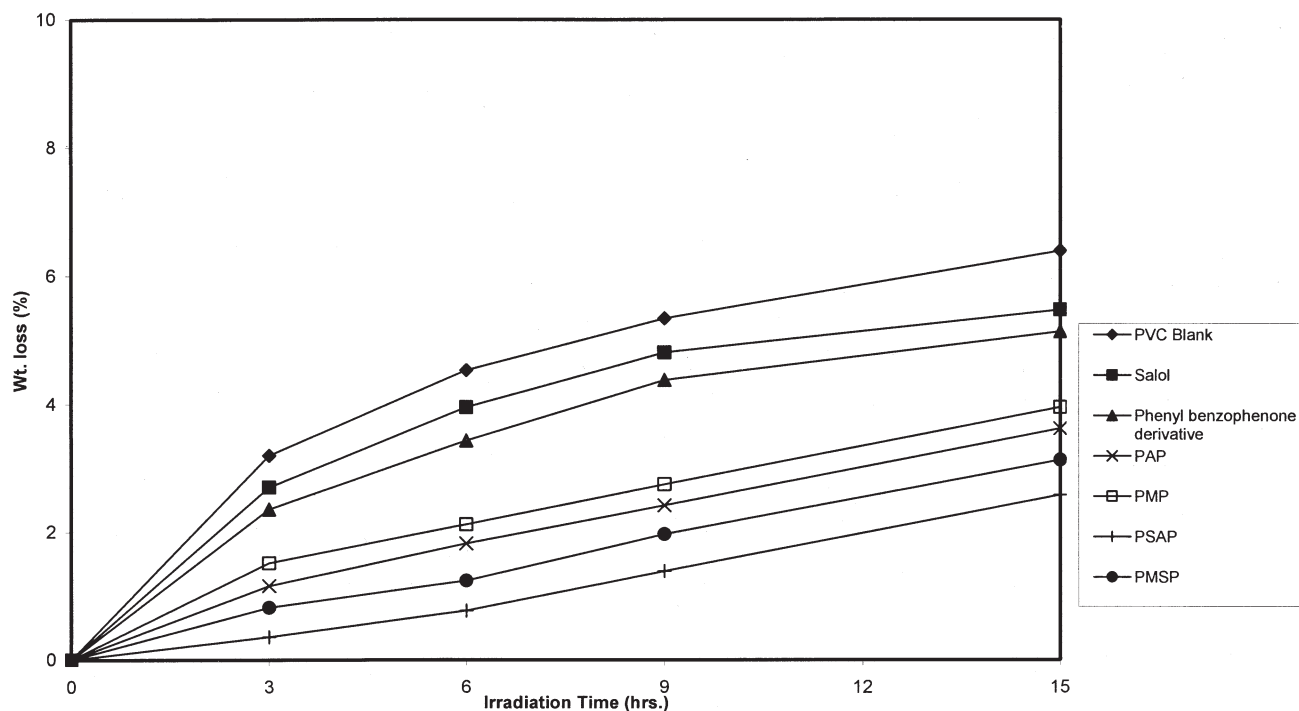


Figure 1 Variation of the weight loss of PVC in the presence of *N*-phenyl-3-substituted pyrazol-5-one derivatives with the irradiation time.

The gel content of the degraded polymer samples was determined by the dissolution of constant weights (0.5 g) of each sample photolyzed for various time intervals in 20 mL of THF at 35°C overnight. The insoluble fractions were then separated by centrifuga-

tion, washed with the solvent, and dried to a constant weight in an air oven. The gel percentage was calculated as follows:

$$\text{Gel}(\%) = W_2/W_1 \times 100$$

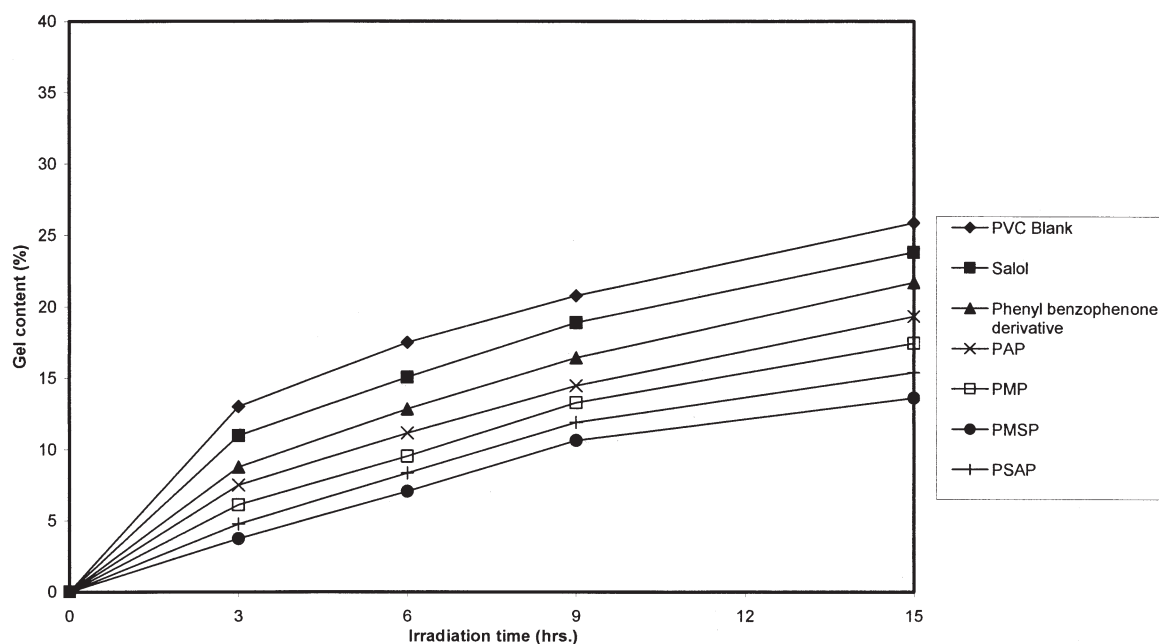


Figure 2 Variation of the gel content of PVC in the presence of *N*-phenyl-3-substituted-5-pyrazolone derivatives with the irradiation time (h).

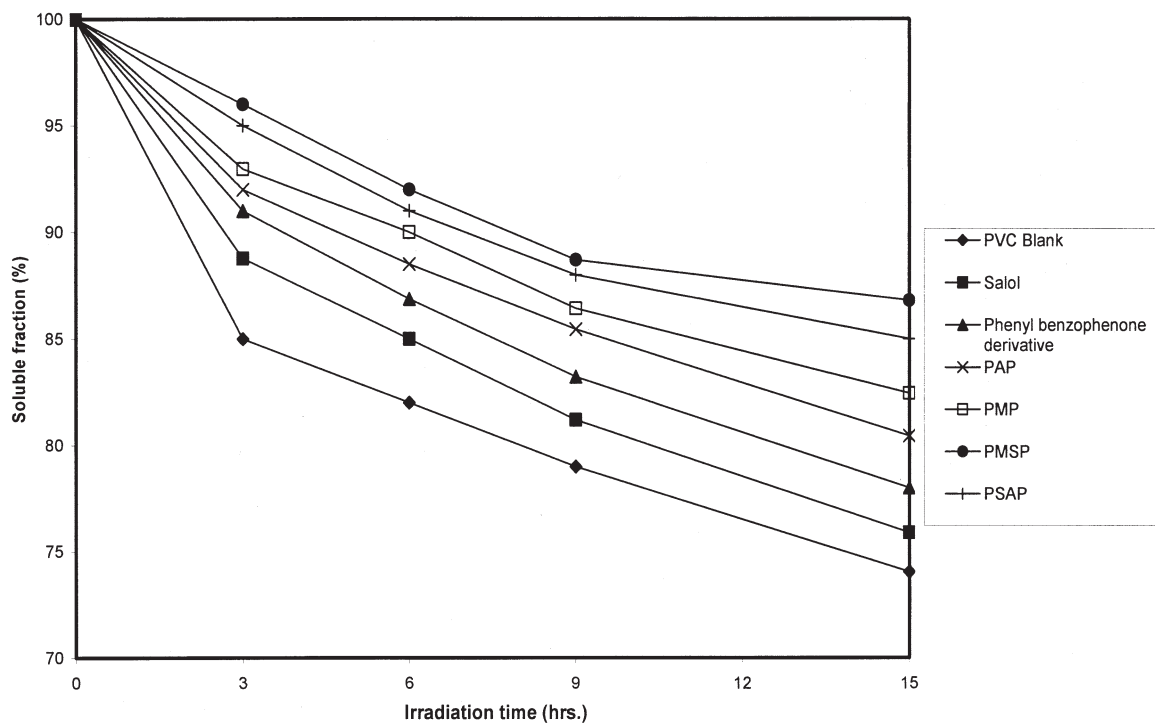


Figure 3 Variation of the soluble fraction of PVC in the presence of *N*-phenyl-3-substituted 5-pyrazolone derivatives with the irradiation time.

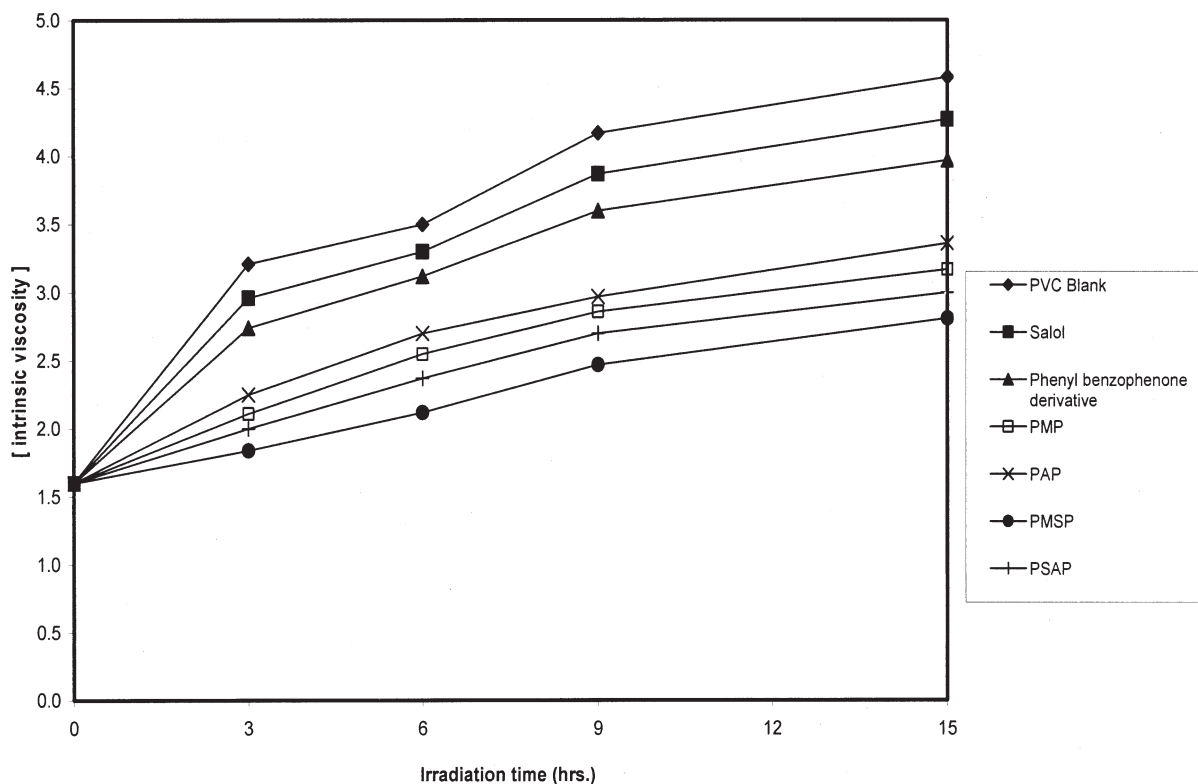


Figure 4 Variation of the intrinsic viscosity of PVC in the presence of *N*-phenyl-3-substituted 5-pyrazolone derivatives with the irradiation time (h).

TABLE III
Extent of the Discoloration of Photodegraded Films of Rigid PVC in the Presence of the Investigated Stabilizers (2 wt %) as a Function of the Irradiation Time

Stabilizer	Irradiation time (h)				
	0	3	6	9	15
PVC (blank)	Colorless	Colorless	Colorless	Pale brown	Brown
PVC + A	Colorless	Colorless	Colorless	Colorless	Yellow
PVC + B	Colorless	Colorless	Colorless	Colorless	Yellow
PVC + PMP	Colorless	Yellow	Yellow	Yellow	Yellow
PVC + PAP	Colorless	Colorless	Colorless	Colorless	Yellow
PVC + PSAP	Yellow	Yellow	Yellow	Yellow	Yellow

A = salol; B = methanone.

where W_1 is the weight of the original sample and W_2 is the weight of the insoluble fraction (the gel fraction).

Moreover, the soluble fractions were precipitated in cold methanol, filtered, and dried in an air oven to a constant weight. The percentages of the soluble fractions were then determined to ensure the amounts of gel previously determined:

$$\text{Soluble fraction (\%)} = W_3/W_1 \times 100$$

where W_1 is the weight of the original sample and W_3 is the weight of the soluble fraction after precipitation in methanol (after complete evaporation of the solvent and complete dryness).

The viscosity measurements for the soluble fractions were carried out in a thermostated water bath with 1% solutions of the soluble fractions of the polymer samples in the solvent dimethylformamide at 30°C with a suspended-level Ubbelohde viscometer (Cairo, Egypt) with negligible kinetic energy correction;^{30,31} dilution was allowed in the viscometer.

The surface morphology was determined with scanning electron microscopy (SEM; magnification = 200×) as a criterion for the photostabilizing efficiency. SEM analyses were performed with a JEOL (Japan) JEM-100S electron microscope. Electric and magnetic lenses were used to focus electrons. The wavelength of the electrons, depending on their energy, was very short (ca. 0.086 Å). The accelerated voltage was 40 kV, and the beam current was 40 μA. The samples were coated with gold with a sputtering technique.

RESULTS AND DISCUSSION

Weight loss and gel formation as criteria for the photostabilizing efficiency

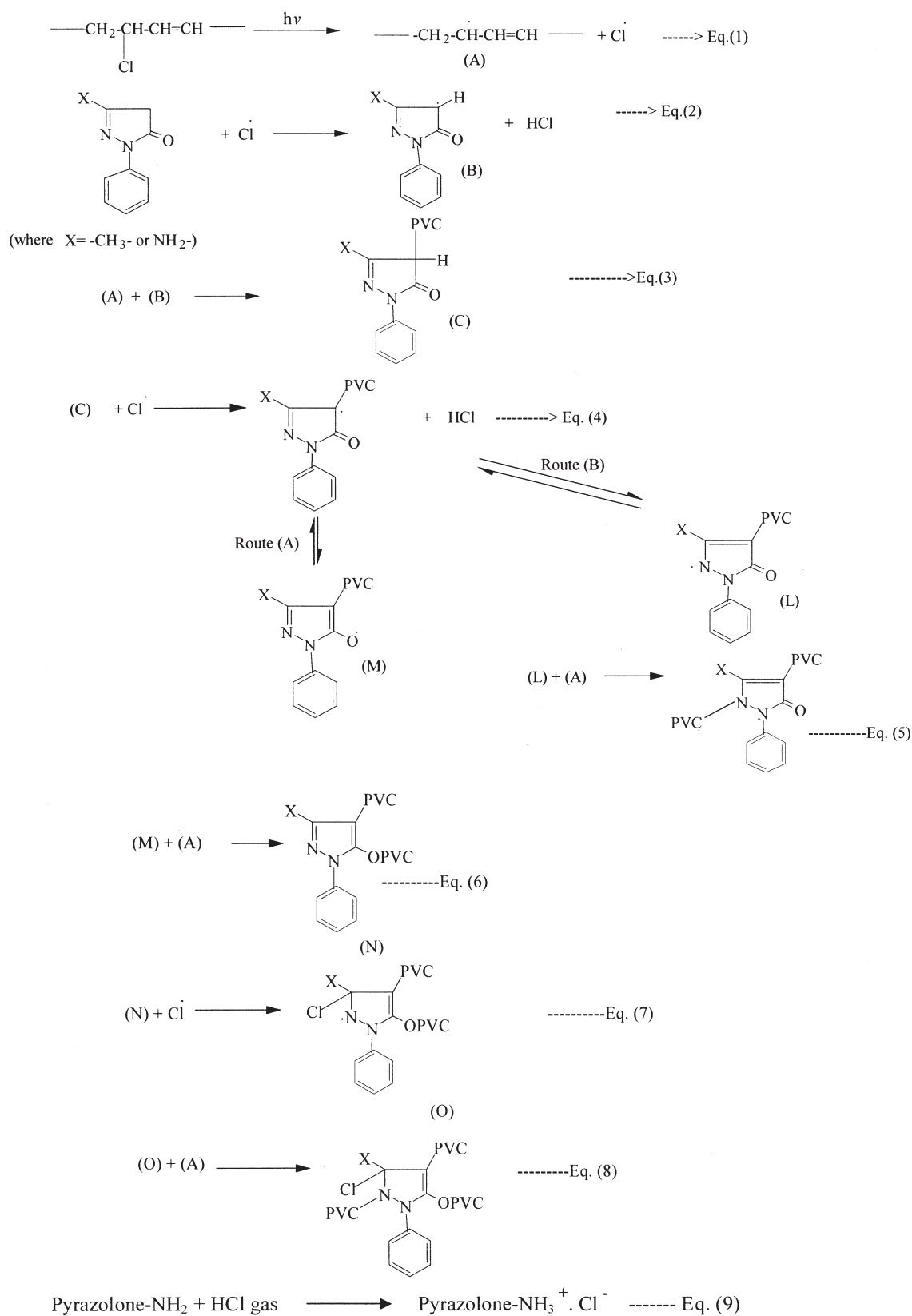
The photodegradation of PVC is commonly known to be accompanied by a dehydrochlorination process (the evolution of HCl gas); consequently, weight loss occurs, which increases with increasing irradiation

time. Thus, the weight-loss percentage as a function of the irradiation time can be a good measure of the degree of degradation and consequently can measure the stabilizing potency of the stabilizer and how long that stabilizer would protect the polymer.

The results of the weight loss as a function of the irradiation time are shown in Table II and Figure 1. The results clearly show the low extent of weight loss (i.e., the low extent of dehydrochlorination as evolved HCl is the main degradative product) of photodegraded PVC stabilized by pyrazolone derivatives in comparison with the weight loss of photodegraded unstabilized PVC or PVC stabilized by the two reference UV absorbers used in this study: salol and methanone. The stabilizing efficiency of the investigated photostabilizers was found to follow this order: 1-phenyl-3-salicyloyl amino-2-pyrazolin-5-one (PSAP) > 1-phenyl-3-methyl-4-salicyloyl-2-pyrazolin-5-one (PMSP) > 1-phenyl-3-amino-2-pyrazolin-5-one (PAP) > 1-phenyl-3-methyl-2-pyrazolin-5-one (PMP). The stabilizing efficiency of the investigated stabilizers was so pronounced that, in the case of the PSAP stabilizer (which yielded the least weight loss), the weight loss of PVC degraded after 3 h of irradiation was only 11% of that of the blank PVC, ~13% of that of PVC stabilized with salol, and ~15% of that of PVC stabilized with the benzophenone derivative stabilizer. After 15 h of irradiation, the weight loss of PVC degraded in the presence of PSAP was equal to 40.3% of that of the blank, ~47% of that of salol, and ~50.3% of that of the hydroxy benzophenone derivative UV absorber.

Preliminary studies of photodegraded blank PVC and PVC stabilized with the investigated stabilizers have proven the formation of gels; the extent to which gels are formed as a result of the photoirradiation of the polymer in the presence of different stabilizers can be taken as a measure of the extent of degradation and consequently as a measure of the efficiency of stabilization.

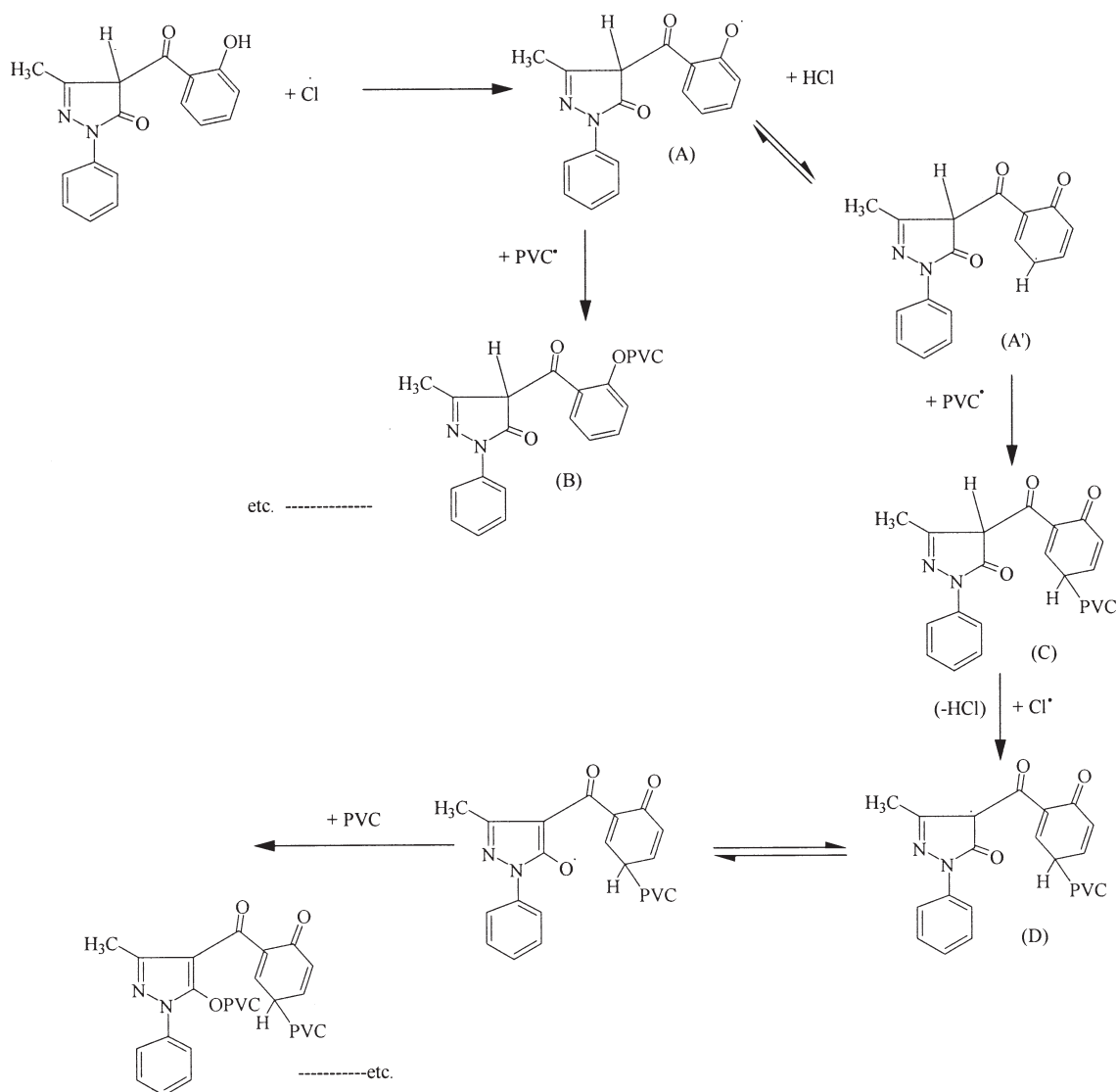
The results for the gelation of the photodegraded PVC blank and for PVC stabilized with the investi-



Scheme 2

gated stabilizers are presented in Table II and Figure 2. The results for the gelation of PVC photodegraded in the presence of the two reference stabilizers are given

for comparison. The results for both the weight loss and gel content represent the average of three comparable experiments for each stabilizer.



Scheme 3

The results clearly reveal the lower extent of gelation for all the investigated pyrazolone derivatives in comparison with the blank and the two reference stabilizers, and the order of magnitude in the lower extent of gelation for the investigated stabilizers is quite remarkable (Table II). Moreover, the stabilizing efficiency of the investigated stabilizers as measured by the amount of gel formation followed this order: PMSP > PSAP > PMP > PAP. In addition, the data obtained for the percentage of the soluble fraction for photodegraded blank PVC or for PVC photodegraded in the presence of reference stabilizers or in the presence of the investigated pyrazolone derivatives as a function of the irradiation time agreed well with the data obtained for the gelation percentage (Table II and Fig. 3). This was additional proof for the results obtained for the amount of gel formation.

Intrinsic viscosity measurements as criteria for the photostabilizing efficiency

An additional proof of the potency of the pyrazolone derivatives for intervening with the free-radical chain degradation mechanism during photoirradiation comes from the lower viscosities of the soluble fractions of the degraded polymer in the presence of the investigated organic stabilizers in comparison with those of either the blank or PVC samples stabilized with the two reference UV stabilizers (Table II and Fig. 4).

These results can be taken as evidence that pyrazolone stabilizers protect the degraded polymeric chains at least partially by blocking the odd electron sites created on the PVC chains as a result of photodegradation and consequently minimize the possibility of the recombination of macroradicals. This recom-

bination of macroradicals, especially if the radicals are at the chain ends, is responsible for the increase in the viscosity as a function of the irradiation time.

A mechanism for the stabilizing mode of action of pyrazolone derivatives based on the aforementioned explanation implies that the ability of these compounds to be incorporated into the body of the polymeric chain is to be expected, and factors favoring this ability will accordingly lead to better efficiencies. This has been experimentally proven on the basis of the following observations:

1. When the organic stabilizer PMP alone was subjected to a stream of HCl gas under a UV lamp for 30 min, the elemental analysis showed the absence of Cl (0%). These results indicate that the aforementioned derivatives cannot interact with the evolved HCl gas.
2. The elemental analysis of PVC films photodegraded in the presence of the PAP derivative after extensive washing with hot ethanol to get rid of the unreacted stabilizer indicated the presence of 0.5% N at 9 h and 0.6% N at 15 h. This implied the incorporation of the stabilizer moiety into the body of the polymeric chain. The IR spectrum of a PVC film in the presence of PAP (irradiated for 3 h) showed two bands at 3332 and 3591 cm^{-1} attributable to the —NH_2 group, and the IR spectrum of a PVC film in the presence of PAP (irradiated for 9 h) showed two bands at 3391 and 3603 cm^{-1} attributable to the —NH_2 group. The IR spectrum of a PVC film in the presence of PAP (irradiated for 3 h) showed a band at 1724 cm^{-1} attributable to the imide carbonyl group, whereas it appeared at 1713 cm^{-1} in the presence of PAP (irradiated for 9 h).
3. To examine the efficiency of PMP as a radical trap, the organic stabilizer was dissolved in carbon tetrachloride (CCl_4), a solvent that produced chlorine atoms upon photolysis. The solution was subjected to a low-pressure UV lamp for 120 min, and benzophenone was added in a catalytic amount to enhance the radical decomposition of CCl_4 . The elemental analysis proved the presence of chlorine in the irradiated sample (3.5% Cl). The IR spectrum showed a band at 702 cm^{-1} attributable to C—Cl . Thus, pyrazolone derivatives can act as radical traps.
4. Another experimental proof for the high stabilizing efficiency of the investigated stabilizers, in comparison with the reference stabilizers, was the lower rate of discoloration of samples (irradiated films) stabilized with PMP, PAP, and PSAP with respect to the blank sample and PVC samples stabilized with any of the reference stabilizers (Table III).

On the basis of these experimental findings, we can suggest a probable radical mechanism for the stabilizing efficiency of the investigated stabilizers during the photodegradation of PVC. The mechanism of the pyrazolone derivative is outlined by the equations in Scheme 2. When X is a —NH_2 group (i.e., the amino pyrazolone derivatives), the stabilization reaction goes one step further: the interaction between the basic amino group and the HCl that has evolved from the PVC degradation (Scheme 3). The mechanism was evidenced by the IR spectrum of a PVC film in the presence of PAP irradiated for 3 h and 9 h, which showed a band at 1601 cm^{-1} attributable to aromatic —C=C— stretching. This which implied that the investigated stabilizer was chemically bonded to the degraded polymeric chains during the stabilization process because of the ability of the investigated stabilizer to be chemically incorporated into the polymeric chains, thus disrupting the chain degradation process.

Surface morphology via SEM (magnification = 200 \times) as a criterion for the photostabilizing efficiency

The surface morphology of films of the nonirradiated PVC blank, PVC irradiated for 15 h, and PVC in the presence of PAP and PSAP (irradiated for 15 h) was



Figure 5 PVC (nonirradiated).



Figure 6 PVC (irradiated for 15 h).

studied with SEM (Figs. 5–8). The PVC (blank) film surface was smooth and empty of any white spots indicating degradation, whereas the PVC film surface irradiated for 15 h was full of white spots indicating the holes or grooves in which HCl evolved. In the case of PVC in the presence of either PAP or PSAP (irradiated for 15 h), the surface was almost smooth, and fewer white spots appeared; this indicated the great stabilizing efficiency of the investigated organic stabilizer and how much it protected the polymer surface from deterioration via dehydrochlorination.

Effect of the mixed stabilizers on the stabilization efficiency of photodegraded rigid PVC

Because of the efficiency of PMSP and PSAP as radical trappers for radical species that might result from photoirradiation and salol and hydroxyphenyl benzophenone derivatives that act as UV absorbers, this study was extended to investigate the effect of blending PMSP and PSAP stabilizers with both reference stabilizers on the stabilization. This most likely would lead to a combination of their mechanisms of action.

Mixing was performed in the range of 0–100% of the investigated stabilizer with respect to either of the reference stabilizers. The overall mixed stabilizer concentration was taken as 2 g/100 g of PVC, and the

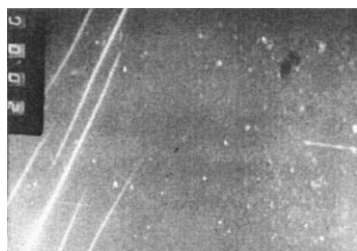


Figure 7 PAP (irradiated for 15 h).

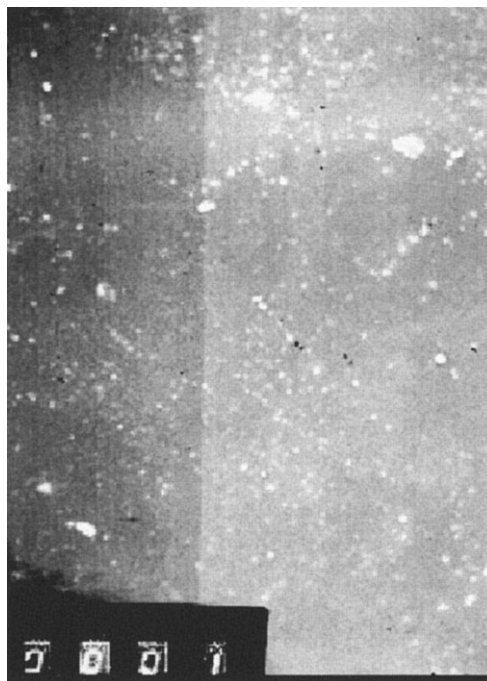


Figure 8 PSAP (irradiated for 15 h).

TABLE IV
Weight Loss, Soluble Fraction, Gel Content, and Intrinsic Viscosity for the Blends of Some Representative Examples of the Investigated Materials with Different Ratios of the Two Reference UV Absorbers Irradiated for 9 h

Material	Weight loss (%)	Gel content (%)	Soluble fraction (%)	Intrinsic viscosity (dL/g) ^a
A (100%)	4.81	18.89	81.2	3.87
PMSP (25%)/A (75%)	1.81	9.54	90.5	2.87
PMSP (50%)/A (50%)	1.76	8.95	91	2.11
PMSP (75%)/A (25%)	1.71	7.64	92.36	1.98
PMSP (100%)	1.97	10.64	88.7	2.7
B (100%)	4.38	16.43	83.22	3.6
PMSP (25%)/B (75%)	1.9	10	90	2.4
PMSP (50%)/B (50%)	1.83	9.32	90.7	2
PMSP (75%)/B (25%)	1.76	8.45	91.5	1.78
PMSP (100%)	1.97	10.64	88.7	2.7
A (100%)	4.81	18.89	81.2	3.87
PASP (25%)/A (75%)	1.24	10.23	89.7	2.2
PASP (50%)/A (50%)	1.17	9.56	90.5	1.97
PASP (75%)/A (25%)	1.25	7.89	92.11	1.76
PASP (100%)	1.39	11.91	88	2.47
B (100%)	4.38	16.43	83.22	3.6
PASP (25%)/B (75%)	1.29	10	90	2.12
PASP (50%)/B (50%)	1.11	9.64	90.5	1.98
PASP (75%)/B (25%)	0.98	7.65	92.5	1.76
PASP (100%)	1.39	11.91	88	2.47

A = salol; B = methanone.

^a For nonirradiated PVC, the intrinsic viscosity was 1.6 dL/g.

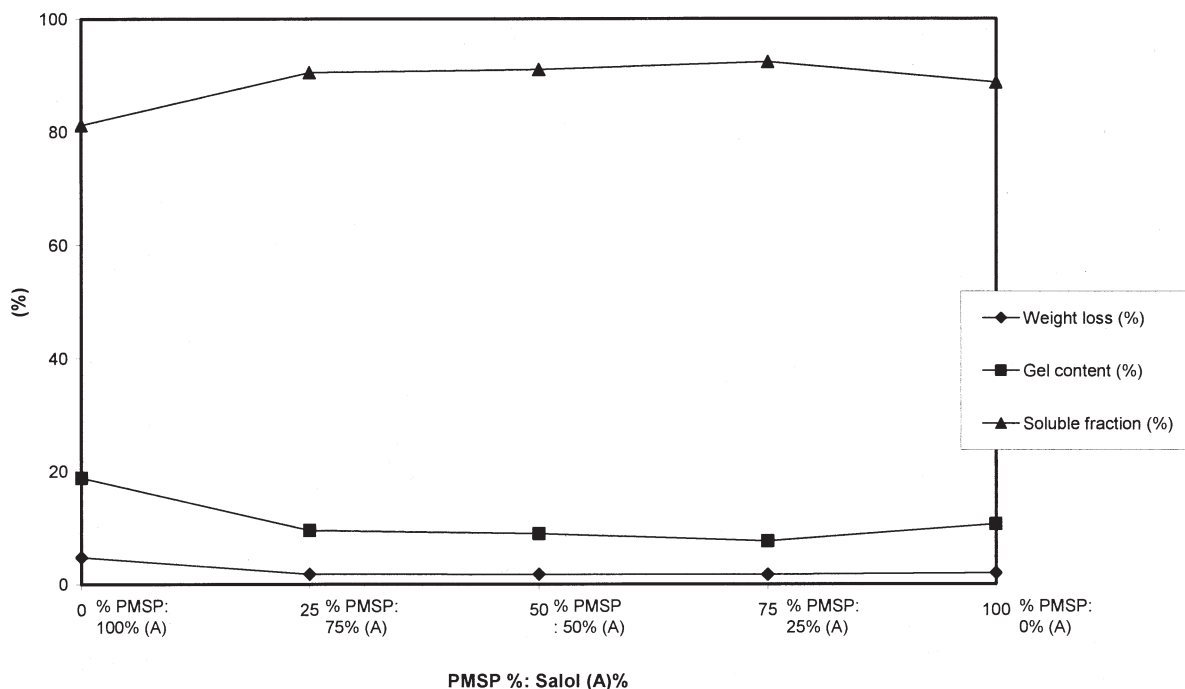


Figure 9 Variation of the weight loss, gel content, and soluble fraction for blends of PMSP and salol irradiated for 9 h.

results represent the average of three comparable experiments for each stabilizer mixture. The results for the weight loss, gel content, soluble fraction, and intrinsic viscosity for each combination irradiated for 9 h are illustrated in Table IV and Figures 9–12.

The results revealed the existence of a true synergistic effect resulting from the combination of either organic stabilizer (PMSP or PSAP) with either of the two reference stabilizers. The maximum synergism was achieved when the PMSP or PSAP stabilizer was

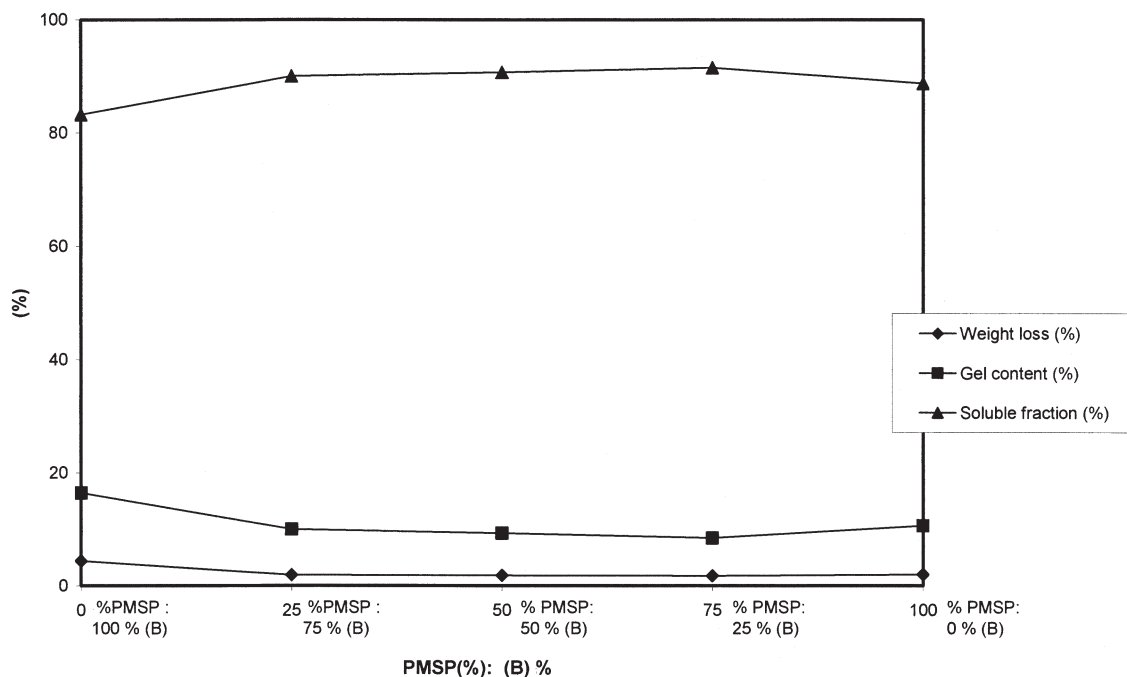


Figure 10 Variation of the weight loss, gel content, and soluble fraction of a mixed stabilizer [PMSP and a phenyl benzophenone derivative (B)] irradiated for 9 h.

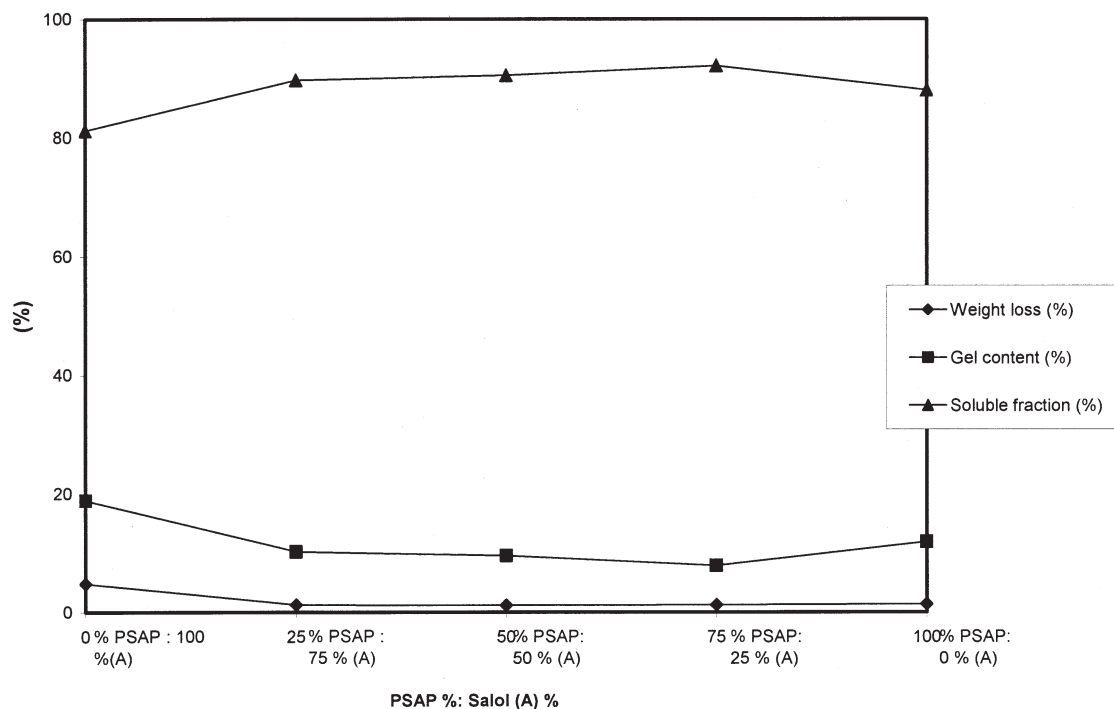


Figure 11 Variation of the weight loss, gel content, and soluble fraction of a mixed stabilizer (PSAP and salol) irradiated for 9 h.

mixed with both reference stabilizers in a weight ratio of 75 : 25.

Moreover, the results also showed a low extent of discoloration of degraded PVC in the presence of the mixed stabilizers (PMSP and PSAP) with both refer-

ence stabilizers in different ratios, especially with 75% investigated stabilizer and 25% reference stabilizer (Table V).

The results imply that the different mechanisms by which the investigated and reference stabilizers work

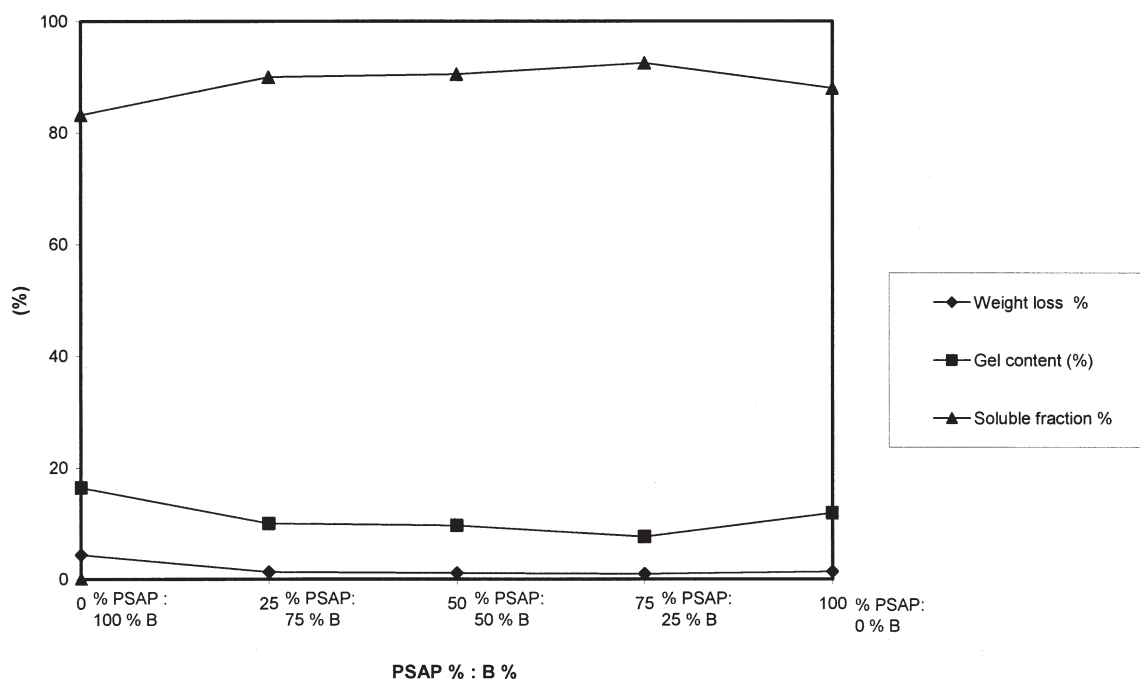


Figure 12 Variation of the weight loss, gel content, and soluble fraction of a mixed stabilizer [PSAP and a phenyl benzophenone derivative (B)] irradiated for 9 h.

TABLE V
Extent of the Discoloration of Photodegraded Films of Rigid PVC for 9 h in the Presence of Some Representative Examples of Mixed Photostabilizers

Colorless PASP (0%)/A (100%)	Yellow PASP (25%)/A (75%)	Colorless PASP (50%)/A (50%)	Colorless PASP (75%)/A (25%)	Orange PASP (100%)/A (0%)
Colorless PASP (0%)/B (100%)	Yellow PASP (25%)/B (75%)	Yellow PASP (50%)/B (50%)	Colorless PASP (75%)/B (25%)	Orange PASP (100%)/B (0%)
Colorless PMSP (0%)/A (100%)	Colorless PMSP (25%)/A (75%)	Colorless PMSP (50%)/A (50%)	Colorless PMSP (75%)/A (25%)	Yellow PMSP (100%)/A (0%)
Colorless PMSP (0%)/B (100%)	Colorless PMSP (25%)/B (75%)	Colorless PMSP (50%)/B (50%)	Colorless PMSP (75%)/B (25%)	Yellow PMSP (100%)/B (0%)

A = salol; B = methanone.

are beyond the obtained synergistic effect that leads to the great improvement in the stabilization of PVC against photodegradation achieved by the mixing of PMSP or PSAP with either of the two reference stabilizers commonly used in industry.

CONCLUSIONS

N-Phenyl-3-substituted 5-pyrazolone derivatives were investigated as efficient photostabilizers for rigid PVC in comparison with two reference stabilizers: salol and hydroxyphenyl benzophenone derivative UV absorbers. This was well illustrated by the lower extent of weight loss, lower extent of discoloration, and lower extent of crosslinking during the later stages of polymer photodegradation in the presence of both *N*-phenyl-3-substituted 5-pyrazolone derivatives in comparison with either salol or the hydroxyphenyl benzophenone derivative; this implied a greater ability for preventing the properties of the polymer from being drastically changed.

When one of the hydrogen atoms of the methylene group in position 4 in the pyrazolone ring was substituted by a salicyloyl group, more active centers were added, and so the photostabilizing efficiency was also improved.

The results revealed that blending both PMSP and PSAP with the two reference stabilizers lowered both the weight loss and the extent of crosslinking of the polymer. Also, blending lowered the degree of discoloration of the polymer during the later stages of degradation. This synergistic effect attained its maximum with 75% organic investigated stabilizer and 25% reference stabilizer (either one).

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