

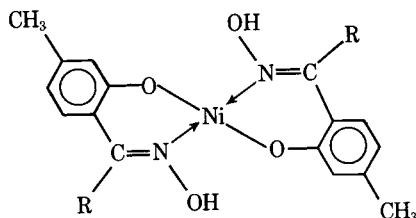
# Photostabilizing Effect of Nickel(II) Chelates in Polymers. III. Effect of *In Situ* Stabilizer Synthesis in Polypropylene

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## INTRODUCTION

The ultraviolet stabilizing effectiveness of certain nickel chelates in commercial polyolefins has been known for some time, but as yet the precise mechanism of their stabilizing action has been the subject of considerable controversy.<sup>1,2</sup> For example, it has been suggested that nickel chelates operate by processes of energy transfer,<sup>3-10</sup> ultraviolet screening, and ultraviolet stable antioxidant action.<sup>11-13</sup> Indeed, it is possible that they may even act by several different mechanisms, and this could account for the high stabilizing activity of certain types.<sup>2</sup>

In this paper, we have investigated for possible photostabilization and triplet quenching action the two main components constituting nickel oxime chelates of the structure



where R = alkyl groups. These components were the parent ligand of the chelate, 2-hydroxy,4-methylacetophenone oxime (HMAO), and a nickel compound of an inert long-chain carboxylic acid, nickel nonanoate.

## EXPERIMENTAL

All components were solvent blended at stoichiometric quantities into polypropylene powder (supplied by I.C.I. (Plastics Division) Ltd., containing no commercial additives). The solvent, dichloromethane, was then removed using a rotary evaporator and the polymer powder pressed into film (200  $\mu$  thick) at 190°C for 1 min. All samples were irradiated under sunlight-simulated conditions using a Xenotest-150 Weatherometer.<sup>8</sup> The rate of photo-oxidation of the polymer was measured by means of a carbonyl index at 1710  $\text{cm}^{-1}$  using a Perkin-Elmer 157G infrared spectrophotometer:

$$\text{Carbonyl Index} = [(\log I_0/I_t)/d] \times 100$$

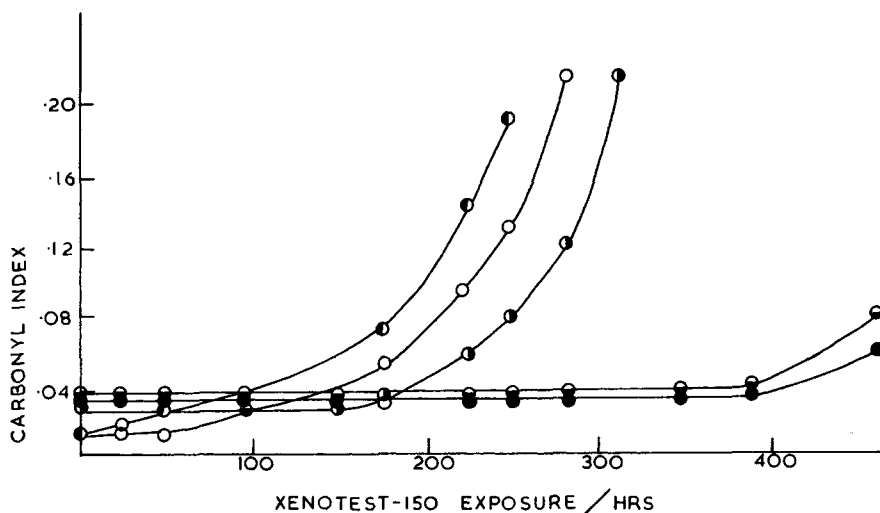


Fig. 1. Rate of photo-oxidation of commercial polypropylene film ( $200 \mu$  thick) containing (O) no additives, (●) 0.25% HMAO, (⊙) 0.1% nickel nonanoate, (⊖) 0.25% HMAO + 0.1% nickel nonanoate, and (●) 0.25% nickel chelate as measured by carbonyl index.

where  $I_0$  = intensity of incident light,  $I_t$  = intensity of transmitted light, and  $d$  = film thickness in microns.

Absorption spectra were obtained using a Unicam SP800 spectrophotometer. Phosphorescence lifetimes were obtained using a Baird atomic spectrofluorometer Model SF-100E coupled to a fast-response oscillograph recorder Model 3006 (S.E. Laboratories Ltd.). Mean phosphorescence lifetimes were taken as

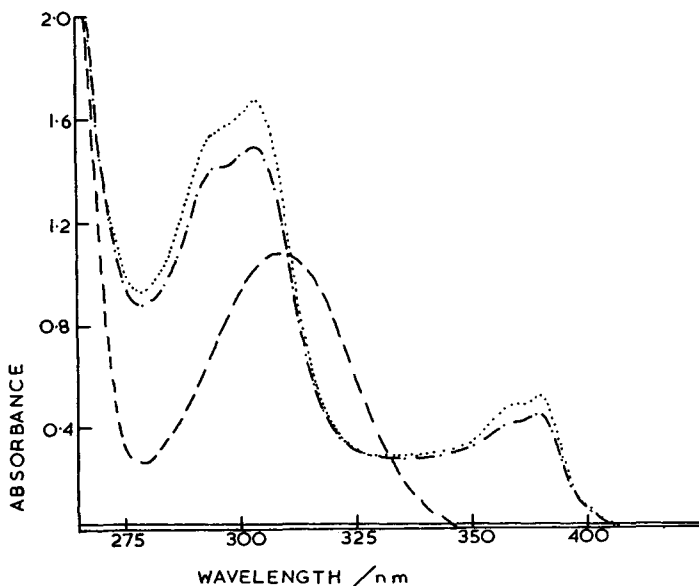


Fig. 2. Ultraviolet absorption spectra of polypropylene films ( $200 \mu$  thick) containing (—) 0.1% nickel nonanoate, (- - -) 0.25% HMAO, (- · - ·) 0.25% HMAO + 0.1% nickel nonanoate, and (· · ·) 0.25% nickel chelate. Polypropylene film ( $200 \mu$  thick) was used as reference.

the time for the phosphorescence to decay to  $1/e$  (where  $e = 2.718$ ) of its initial intensity.

## RESULTS AND DISCUSSION

It is seen from Figure 1 that neither of the compounds had any significant stabilizing action. It is interesting to note that HMAO acted as a weak photosensitizer. However, when both compounds were present, a strong stabilizing action did occur. Indeed, the stabilizing effect was comparable to that of the chelate ( $R = CH_3$ ) itself.

An explanation for this interesting behavior of the mixture is demonstrated in Figures 2 and 3. First, in Figure 2 it is seen that as a result of processing, a chemical reaction occurred between the two compounds and that the absorbance matches that of an authentic sample of the chelate ( $R = CH_3$ ). Also, from Figure 3 it is seen that the chelate quenches the phosphorescence emission from photoreactive impurity  $\alpha, \beta$ -unsaturated carbonyl species present in the polymer.<sup>14,15</sup> Again, the effectiveness of the quenching is similar to that of the chelate ( $R = CH_3$ ). It would appear from this evidence, therefore, that during processing of the polymer, the compounds react to form the nickel oxime chelate.

Thus, the results here show quite clearly that neither component acts as a stabilizer or as a triplet quencher. For them to act in this capacity, it is essential that they react to form the nickel chelate. This conclusion could be of some

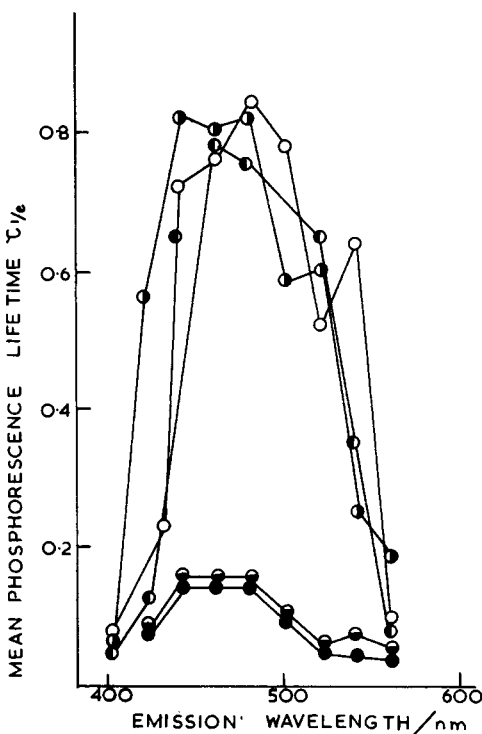


Fig. 3. Mean phosphorescence emission lifetimes in the wavelength region of 400–600 nm for commercial polypropylene film (200  $\mu$  thick) containing (O) no additives, (●) 0.1% nickel nonanoate, (◐) 0.25% HMAO, (◑) 0.25% HMAO + 0.1% nickel nonanoate, and (◒) 0.25% nickel chelate. Excitation wavelength = 270 nm.

interest in technological applications where the in situ preparation of the stabilizer could have advantages over direct methods of stabilizer addition to the polymer.

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