Stabilization of Isotactic Polypropylene. Problems Bound to the Interactions of Stabilizers with Pigments and Fillers

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ABSTRACT: The efficiency of conventional Hindered Amine Stabilizers (HAS) can be significantly reduced by their adsorption on other additives or fillers present in the polymer. The present article reports on the effect of titanium dioxide, phtalocyanine blue, and talc on the thermal and the photo stabilizations of isotactic polypropylene (iPP) by HAS. The durability of iPP was measured by the length of the induction period preceding the development of carbonyl groups by FTIR spectroscopy. The adsorption of HAS on pigments and fillers was revealed by the precise analysis of the carbonyl band of the ester group of HAS. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 609–615, 1997

INTRODUCTION

Polypropylene is well known for its low resistance to heat and UV radiations.[1-5] Even in smooth conditions like those found in outdoor exposure, a radical oxidation occurs with mechanisms that are now fairly well understood.[6,7]

Fortunately, very efficient stabilizers acting at different levels of the oxidation chain are now available, allowing the use of polypropylene in a large variety of applications including outdoor.

However, polypropylene is very often modified by a lot of compounds with the aim to improve its physical properties and enhance again its application field. It is, for example, possible to increase stiffness, flexural modulus, tensile properties, impact resistance, colorability, or to reduce mold shrinkage, warpage, or simply the material cost by using suitable additives, pigments, and fillers.

It results in very complex formulations in which stabilizers are still compulsory but whose effect can be dramatically reduced by the presence of the added compounds, which are sometimes present in very high concentrations ($\approx 50\%$ w/w in the case of some fillers). Then, some antagonistic effects have been reported between, for example, hindered amines stabilizers (HAS) and sulfur compounds,[8] transition metals,[9] or talc.[10]

We recently completed extensive work[11] on the combined effects of stabilizers/inorganic pigments/organic pigments and fillers on the thermal and the photo aging of isotactic polypropylene. This article reports on typical effects that have been pointed out between HAS and (a) TiO_2, (b) phtalocyanine blue pigment, and (c) talcs, respectively.

EXPERIMENTAL

Isotactic polypropylene (Hoechst France) was issued from Spheripol process; it was characterized by $MFI_5 = 2-3$ g/10 min; % cristallinity = 55; isotactic content 98%, and contained 120 ppm of a conventional processing phenolic antioxidant (Irganox 1010 from Ciba Geigy).

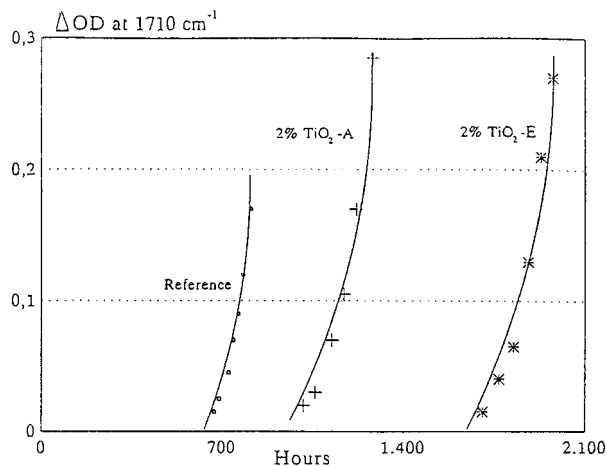The following additives and fillers were used:

Figure 1 Kinetics of photo aging in SEPAP 12–24 at 60°C. Influence of the quality of TiO_2 on the stability of [iPP + 1000 ppm HAS-A].

(a) hindered amine stabilizer: Tinuvin 770 (HAS-A) from Ciba Geigy (Switzerland) and Hostavin N20 (HAS-B) from Hoechst (Germany); (b) inorganic pigments: Rutile titanium dioxide (A, B, C, and D) from Tioxide (France) characterized by different surface treatments; (c) organic pigments: phtalocyanine blue from Hoechst (Germany); four varieties of this organic pigment (A, B, C, and D) characterized both by different cristalline forms (α,β) and flocculating properties (f, n.f) were used; (d) fillers 12 talcs different by

their geological origin, granulometry, and impurities content were provided by Talc de Luzenac (France).

Controlled quantities of additives were introduced in polypropylene by using a Henschel mixer; the mixture homogeneity was improved by the addition of 0.5% of a paraffinic oil. After extrusion (T_{max} = 220°C) and granulation, polymers were pressed (Darragon press, P = 200 bars) between two polyester sheets at 180°C for 3 min to obtain 100 μm films. The films were placed on aluminium holders and submitted to thermal and photo aging.

Thermal oxidation were performed at 140°C in an oven aerated by natural convection.

Accelerated photo aging were obtained from a SEPAP chamber[12] (MPC France) at 60°C. The unit has a UV source supplying radiations longer than 300 nm (representative of natural exposure). Samples are rotated at a constant speed and distance from the source. The value of the accelerating factor was approximatively 8, based on Florida exposure of few samples.

The aging was controlled by following the evolution of the carbonyl bands (1710 cm^{-1} for oxidized iPP; 1720–1740 cm^{-1} for HAS) by FT–IR spectroscopy (Nicolet 5SX spectrometer).

RESULTS AND DISCUSSION

The oxidation of polypropylene results in the formation of hydroxyl (mainly hydroperoxide and al-
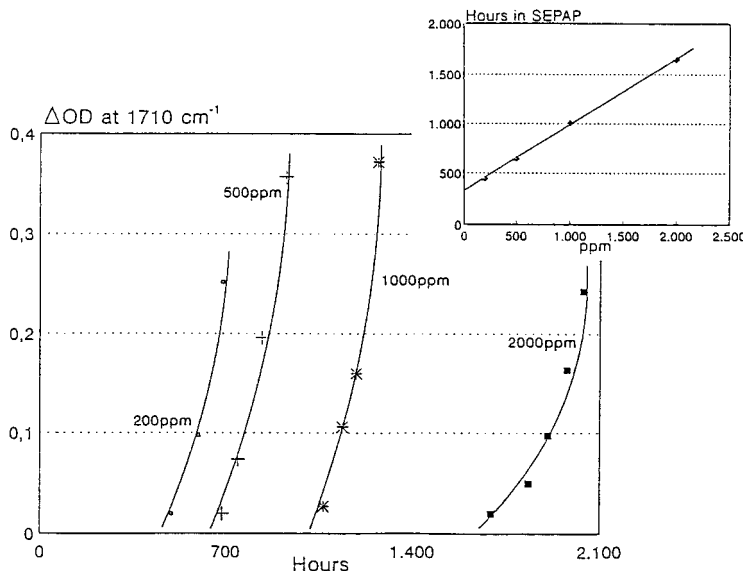

Figure 2 Kinetics of photo aging in SEPAP 12–24 at 60°C. Influence of the concentration in HAS-A on the stability of [iPP + 2% TiO_2-A]. Above, correlation between % HAS and induction period.
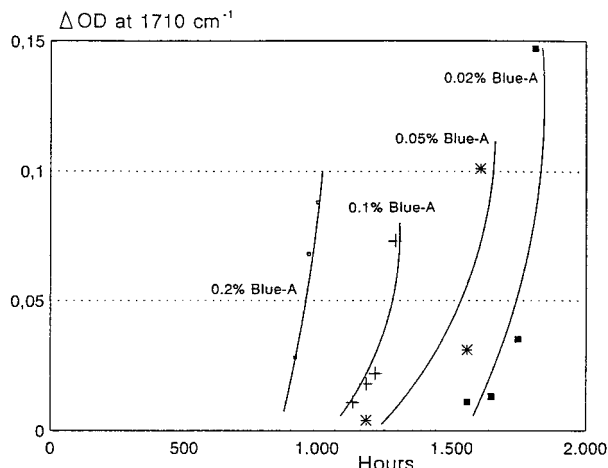
Figure 3 Kinetics of thermal aging at 100°C. Influence of the concentration in Blue-A on the stability of [iPP + 1000 ppm HAS-A].

Figure 4 Kinetics of thermal aging at 100°C. Influence of phtalocyanine blues (0.2%) on the stability of [iPP + 1000 ppm HAS-A].

cohols) and carbonyl groups (mainly ketones and acids) easily detectable by FT–IR spectroscopy in the 3200–3600 cm^{-1} and the 1600–1800 cm^{-1} regions, respectively. In polypropylene, the appearance of these oxidized groups upon aging is very fast comparatively with the induction period (due to stabilizers as residual processing antioxidants). In addition we have recently checked[11,13] that the sharp jump shown by infrared spectroscopy (a nondestructive method) can be correlated with the loss of mechanical properties (tensile strength) (see also, ref. 1), which is, of course, a destructive method consumming a lot of time and samples. So infrared spectroscopy appears to be a fast and reliable technique to check the stability of numbers of formulations. Then, the long-term stability of stabilized polypropylene can be simply correlated with the length of the induction period preceding the beginning of the oxidation.

Competitive Effects of HAS and TiO$_2$ upon iPP Photo Aging

Titanium dioxide is a photoactive pigment able to protect the polymer from the photo aging by its UV-filter effect (2% w/w of TiO$_2$ in a 100 μm PP film absorb more of 95% of the UV light below 380 nm) but, conversely, is also able to initiate the polymer oxidation by the photogeneration of high oxidizing species (=OH, ···).[14–21] In the case of pigments used for polymer applications, this protocatalytic effect is generally strongly reduced by efficient surface treatments by silica or alumina.

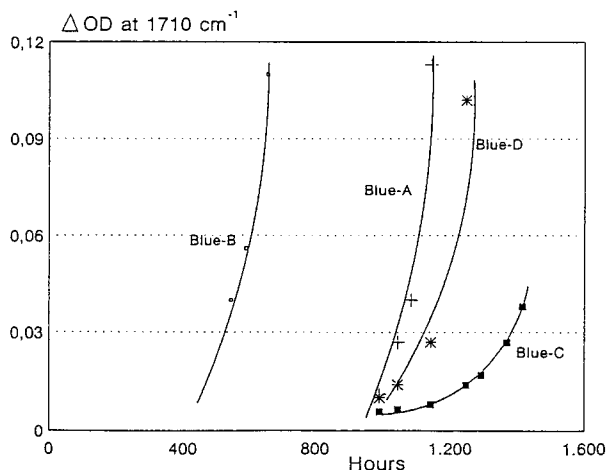In our case, only a small protective effect (the

induction period length shifts from 40 to 100 h) was detected in formulation containing surface-treated TiO$_2$ alone; that probably corresponds to the protection of the phenolic antioxidant present in low content in the basic formulation. However, the protective (filter) effect of TiO$_2$ is obvious in the case of polypropylene containing HAS (Fig. 1). The most efficient TiO$_2$ (E) allows increase of the polymer lifetime by a factor 3. TiO$_2$ (E) has received a more important mineral treatment based on alumine. In addition, Figure 2 shows the linear relationship between the HAS content and the lifetime of polypropylene containing 2% of TiO$_2$ (A).
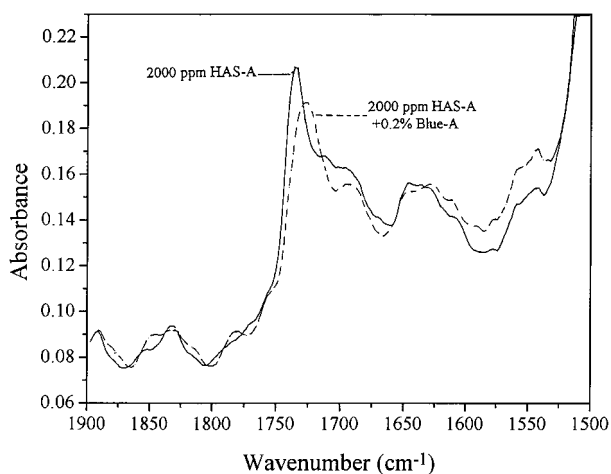

Figure 5 IR absorption of the ester band for HAS-A. Influence of Blue-A.
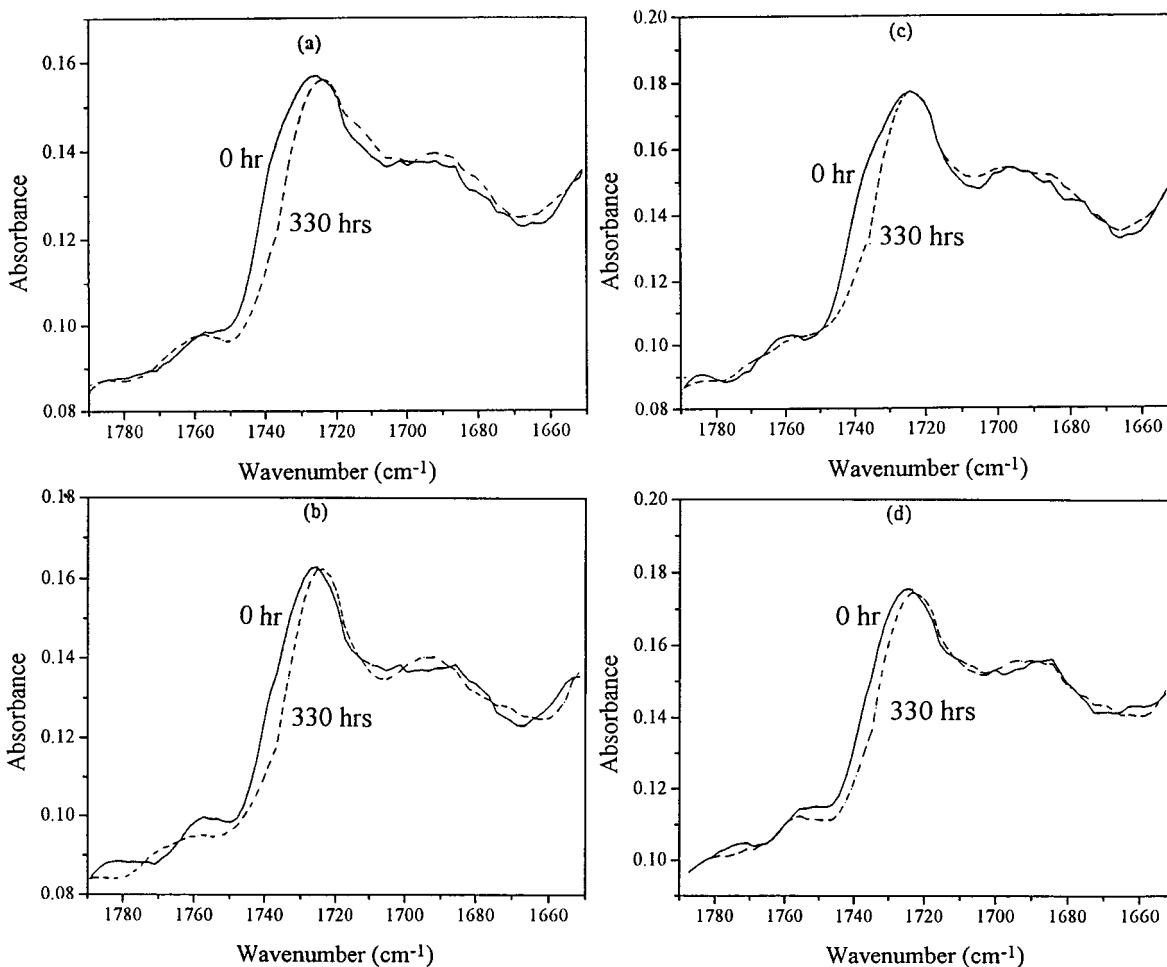
Figure 6   Absorption IR of the ester band for HAS-A in the presence of phtalocyanine. Evolution during thermal aging at 100°C. (a) With 0.02% Blue-A; (b) with 0.2% Blue-A; (c) with 0.2% Bluc-C; (d) with 0.2% Blue-B.

Antagonism between HAS and Phtalocyanines upon iPP Thermal Aging

Organic pigments used in plastic engineering are not generally expected to have a particular effect on the thermal aging of polymers at moderate temperature. This point was checked for most of the pigments tested by our group,[11] however, phtalocyanine blue was showing an unusual behavior when it was in the presence of HAS-A. The presence of this pigment dramatically reduces the efficiency of HAS, as it can be seen in Figure 3 for a thermal aging at 100°C. Complementary experiments were performed with several phtalocyanine pigments differing both by their cristalline form (α or β) and their flocculating properties; this pigment is usually flocculating (f), i.e., it is not well dispersed and forms aggregates in the polymer matrix. By an appropriate physical treatment, it

is possible to improve the dispersion to get so-called "nonflocculating" (n.f) pigment. The influence of the four pigments [A(β, f); B(β, n.f); C(α, f), and D(α, n.f)] is reported in Figure 4.

The thermal stability at 100°C in the presence of HAS (1000 ppm) decreases as follows: C > D > A > B . Both the cristalline form β and the nonflocculating treatment decrease the efficiency of HAS.

It is also shown in Figure 3 that this antagonist effect was increasing with the pigment (A) content from 0 to 0.2%. These results are consistent with a negative interaction (antagonism) between HAS and phtalocyanine. The more the pigment is abundant and dispersed the stronger the inhibition of HAS. This observation was supported by the detailed FT–IR analysis of the HAS ester band.

As it can be seen in Figure 5, the maximum of the HAS ester band initially at 1736 cm^{-1} (without pigment) is shifted to 1730 cm^{-1} in the presence of the pigment according a probable interaction between HAS and phtalocyanine A.

Figure 6(a) and (b) report the expanded ester region for both HAS-A 0.02% and HAS-A 0.2% before and after a short oven aging (100°C, 330 h), i.e., prior to the development of carbonyl groups from the oxidized iPP. Two remarks can be pointed out: (1) the shoulder corresponding to the free HAS form (1736 cm^{-1}) is more important when the pigment content is low; and (2) the thermal oxidation concerns first the free HAS form, the associated form (1730 cm^{-1}), which probably corresponds to an adsorption of HAS on the pigment being some or not at all reactive.

The same remarks can be true for the other pigments B and C [Fig. 6(c) and (d)] and very similar results were obtained with another type of HAS (HAS-B).

Then, HAS stabilizers can be adsorbed on organic pigments as phtalocyanine blue; this adsorption is increased by increasing the content and the dispersion of the pigment and finally results in an inhibition of the stabilizing activity of the piperidine group, probably by reducing its mobility in the polymer matrix.

Such behavior was recently reported in the case of polypropylene containing talc (or chalk) as filler,[10] so it was particularly interesting to test our infrared method in the case of such fillers.

Antagonism between HAS and Talcs upon Photo and Thermal Aging of iPP

Figure 7 reports on the photo (a) and the thermal (b) aging of iPP containing 3000 ppm of HAS-A in the presence of several kinds of talc (30% w/w).

In the case of photo aging, all the talcs drastically reduce the induction period, for example, the best talc (A) reduces the photo aging resistance from 2000 to 1100 h. Other talcs have a worst effect on the iPP/HAS durability (A > B > D ≥ C).

In the case of thermal aging [Fig. 7(b)], we received the same result between talcs (A > B > D > C); however, contrary to photo aging, all the talcs seem to improve the thermal stability of polypropylene (the induction period in the absence of talc is about 40–50 days only). This phenomenon is probably due to the superposition of a second effect related to the low volatility of HAS-A. All the talcs have a lamellar structure able to
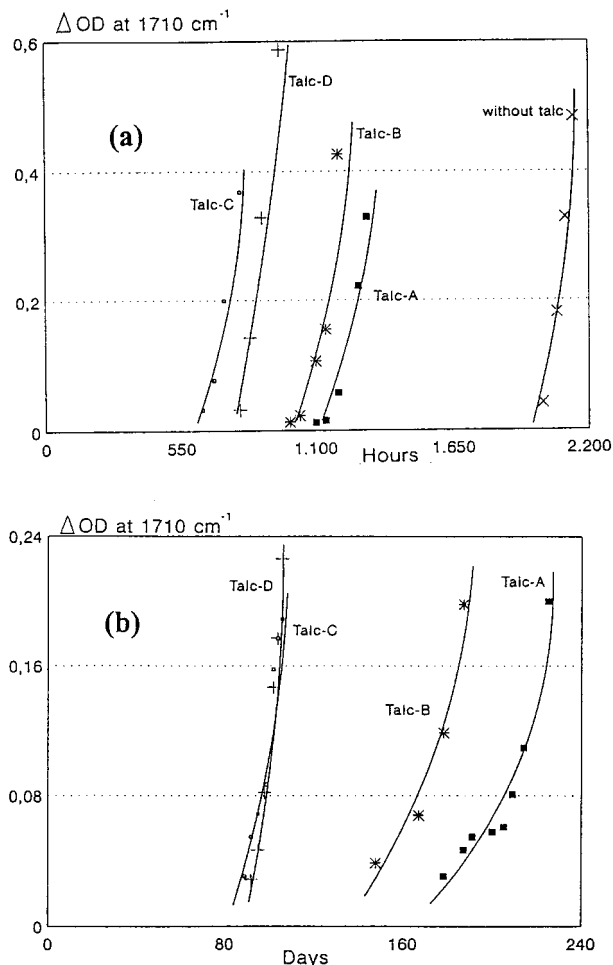

Figure 7 Influence of different talcs (30%) w/w on the stability of [iPP + 1000 ppm HAS-A]. (a) Kinetics of photo aging in SEPAP 12–24 at 60°C; (b) kinetics of thermal aging at 100°C.

act as a physical barrier reducing or avoiding the evaporation of HAS-A; very probably such a phenomenon would disappear in the presence of high molecular weight HAS.

Talcs A, B, C, and D were different in many aspects (geological origin, granulometry, impurities nature, etc.), making it difficult to reveal which factors were really prodegrading. A complementary study based on eight talcs having well-defined physical and chemical properties made it possible differenciate the influence of morphology, granulometry, and impurity content. The best result (minimum prodegrading effect) was obtained with talc containing a large content of lamellar structure (in relation with its geological story), a low content in oxydo-reducing impurities as Fe^{+++} or Cu^{++} (complex-
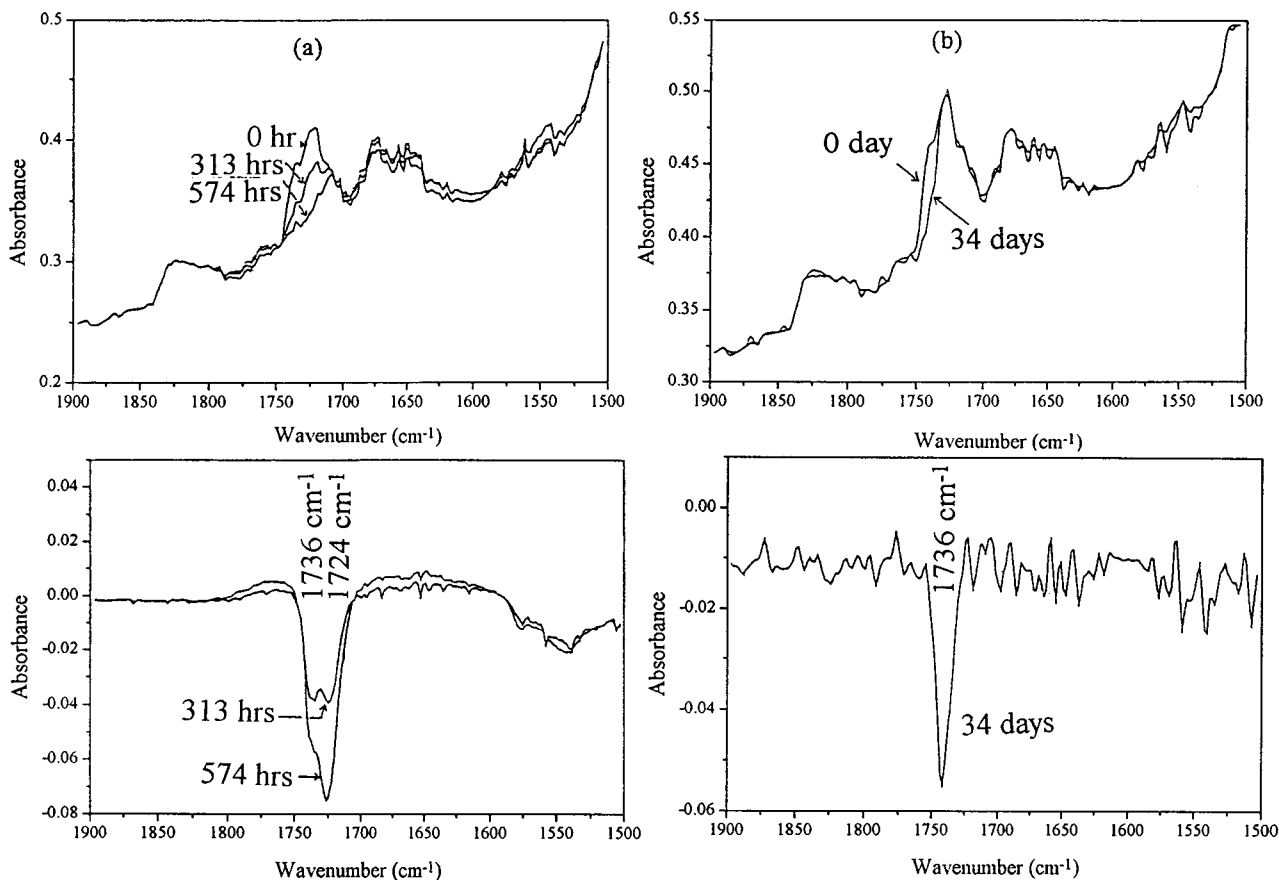
Figure 8 IR absorption ot the ester band for HAS-A with Talc-A. (a) Evolution during irradiation in SEPAP 12–24 at 60°C; (b) evolution during thermal aging at 100°C. Above: direct spectra, and below: difference with initial spectrum.

ation of HAS ?), and a large granulometry (minimizing the adsorption of HAS).

The infrared analysis of the HAS ester group was again consistent with the presence of two types of bands with different reactivities upon aging (see Fig. 8): (1) one absorption at 1736 cm^{-1} corresponding to the free form (active) of the stabilizer, and (2) one absorption at 1724 cm^{-1} corresponding to an associated (adsorbed, inactive) form of HAS on the filler.

In thermal aging [Fig. 8(a)] at 100°C, we received a similar result as in the case of phtalocyanine; only the free band decreased during the first 34 days.

In photo aging [Fig. 8(b)], both bands disappear, the difference spectra (photo-oxidized−unoxidized) show that the free band disappears first but that associated form seems to act as a reservoir and can be fast converted into the active, free form.

In conclusion, the stability of polypropylene upon aging (thermal or photo) can be largely improved by the use of HAS, but the efficiency of this stabilizer and probably also a numbers of others can be drastically modified by the presence of other additives and fillers.

Large contents of fillers as talc or small contents of organic pigments as phtalocyanine blue adsorb significant amounts of the stabilizer and dramatically reduce the time life of the material; comparatively, this phenomenon seems to be more active in the case of thermal aging.

The adsorption of HAS on the filler or the pigment can be revealed by a detailed analysis of the ester band of the stabilizer (if any) during the short period preceding the development of the carbonyl absorption of the oxidized polypropylene.

However, no significant adsorption of HAS on titanium dioxide was detected, and this inorganic pigment can play a positive role in the photoprotection of PP by HAS.

REFERENCES

1. J. H. Adams, *J. Polym. Sci. A1,* **8,** 1279 (1970).
2. D. J. Carlsson and D. M. Wiles, *J. Macromol. Sci., Rev. Macromol. Chem.,* **C-14,** 65 (1976).
3. C. Decker and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.,* **11,** 2847 (1973).
4. J. M. Ginhac, J. L. Gardette, R. Arnaud, and J. Lemaire, *Makromol. Chem.,* **182,** 1017 (1981).
5. F. Severini, R. Gallo, and S. Ipsale, *Polym. Degrad. Stabil.,* **22,** 185 (1988).
6. J. Lacoste, D. Vaillant, and D. J. Carlsson, *J. Polym. Sci., Polym. Chem.,* **31,** 715 (1993).
7. D. Vaillant, J. Lacoste, and G. Dauphin, *Polym. Degrad. Stabil.,* **45,** 355 (1994).
8. K. Kikkawas, Y. Nakahara, and Y. Ohkatsu, *Polym. Degrad. Stabil.,* **18,** 237 (1987).
9. S. Fairgrieve and J. R. MacCallum, *Polym. Degrad. Stabil.,* **15,** 81 (1986).
10. B. Klingert, Fillers and additives for thermoplastics and rubber. Intertech conferences, Berlin, 1994.
11. D. Vaillant, Thèse d'Université, Université Blaise Pascal of Clermont–Ferrand (1993).
12. G. Penot, R. Arnaud, and J. Lemaire, *Angew. Makromol. Chem.,* **117,** 71 (1983).
13. J. Lemaire, ACS Chicago Meeting (1994) and ACS Symposium Series, to appear.
14. J. Lacoste, R. P. Singh, J. Boussand, and R. Arnaud, *J. Polym. Sci.,* **25,** 2799 (1987).
15. C. Naccache, P. Meriaudeau, and M. Che, *Trans. Faraday Soc.,* **67,** 506 (1971).
16. S. Bourrasseau, J. R. Martin, F. Juillet, and S. J. Teichner, *J. Chim. Phys.,* **71,** 122 (1974).
17. J. M. Hermann, J. Disdier, M. N. Mozagena, and P. Pichat, *J. Catal.,* **60,** 369 (1979).
18. S. J. Pappas and R. M. Fisher, *J. Paint Technol.,* **46,** 65 (1974).
19. H. G. Völz, G. Kaempf, H. G. Fitzky, and A. Klaeren, in ACS Symposium Series, No. 151, American Chemical Society, Washington, DC, 1981, p. 163.
20. R. I. Bickley and R. K. Jayanti, *Faraday Discuss. Chem. Soc.,* **58,** 194 (1974).
21. E. M. Ceresa, L. Burlamacchi, and M. Visca, *J. Mater. Sci.,* **18,** 289 (1983).