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Impact of stabilisers on the thermal catalytic activity of micro- and nano-particulate titanium dioxide in oxidizing condensed mediums

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Abstract

This investigation was undertaken to elucidate an interplay between stabilisers and titanium dioxide nano-particles in oxidizing condensed mediums comprising of the initiatied (initiator is 2,2′-azobisisobutyronitrile, AIBN) oxidation of cumene and ethylbezene and an intercomparison with the thermal oven ageing of high-density polyethylene (HDPE). As a preliminary study, the catalytic influence of different nano and micro-particle sized anatase and rutile titanium dioxide pigments on the uninitiated oxidation of cumene at moderate temperature (60 °C) has been established. The oxidation rates depend linearly on the square root of the concentration of the titanium dioxides over a sufficiently wide range and thereby follow the mechanism of oxidation with recombination of peroxy radicals.

Kinetic measurements of oxidation rates of the model reactions of initiated oxidation of cumene and ethylbenzene in the absence and presence of a hindered piperidine stabiliser, Chimassorb 119 FL, Cyasorb 3529 and sterically hindered Irganox 1010 stabilisers clearly showed that the stabilisers promote over-additional initiating activity of titanium dioxide pigments. This effect was found to be very large, i.e. the values of afforded additional initiation rates are 2–9 times more than those compared with the value of the initial initiation rate induced by titanium dioxides in the system without stabilisers. In the case of hindered amine stabilisers this phenomenon is more pronounced than that for the Irganox phenolic antioxidants. On the basis of susceptibility towards all the examined stabilisers, resulting in a sharp increase of the initial initiating activity, the titanium dioxides can be ordered as nano-rutile untreated > nano-anatase treated hydroxyapatite ≥ nano-anatase untreated ≥ (nano-anatase (75%) + nano-rutile (25%)) untreated > micro-anatase untreated > micro-rutile treated. These additional initiation rates of titanium dioxides which are affected by the stabilisers can be explained in terms of physical absorption of the stabilisers onto the surface of the titanium dioxide particles. The stabilisers being adsorbed onto the surface of titanium dioxides block titania surface-OH groups and thereby prevent the formation of water in the oxidizing system to promote the additional catalytic capacity of the titanium dioxide pigments. Basic amine functionalities of Chimassorb 119 FL and Cyasorb 3529 are energetically more protonated by the titanium dioxides' surface hydroxyls during oxidation than when compared with phenolic hydroxyl and ester groups of Irganox 1010 and thereby the amine functionalities stimulate a relatively higher level of additional initiating activity of the pigments. This explanation is in good accordance with the data of work elsewhere [Allen NS, Edge M, Sandoval G, Ortega A, Liauw CM, Stratton J, et al. Factors affecting the interfacial adsorption of stabilizers on to titanium dioxide particles (flow microcalorimetry, modeling, oxidation and FTIR studies): nano versus pigmentary grades. Dyes Pigments 2006; 70(3):192–203]. Nano-anatase pigment C is shown to exhibit a sensitizing effect at a concentration of 1 and 2% w/w in the model reaction of cumene initiated oxidation whereas it exhibits a different effect in the thermal sensitizing oxidation at 1% w/w to the stabilising at 2% w/w during thermooxidative ageing in HDPE film.

Keywords: Titanium dioxide pigments; Hindered amine stabilisers; Antioxidant; Model oxidation; Oxidation rates; Iinitiation rates; Interfacial adsorption; Thermooxidative degradation

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1. Introduction

The analysis of the behaviour of titanium dioxides in an oxidizing medium showed a tendency to accelerate the liquid phase model reaction of cumene initiated oxidation [1,2]. The catalytic activity was mainly attributed to the capacity of titanium dioxide particles to decompose the cumyl hydroperoxide with concomitant generation of a new additional portion of free radicals leading the oxidation chain. These results obtained in the model reaction have found convincing confirmation of similar titanium dioxide reactions in different polymer materials.

In particular, the results on the ageing of filled polyethylene (PE) showed that rutile pigments exhibit a thermal sensitizing effect on the polymer and a marked autocatalytic effect on the growth in carbonyl formation when compared to that of the control polymer. The higher initial carbonyl index for the pigmented films compared to those of the control film after processing was found to be due to a pro-oxidant effect induced by thermal catalysis of the pigments. The anatase pigments were found to be extremely active catalysts of thermal oxidation such that their activity was found to be comparable only in the presence of an antioxidant. Higher the surface/ambient temperature of exposure greater is the thermal sensitization factor in the rate process. Thus, the thermal activity of the pigments clearly plays an important role in controlling the rate of thermal oxidation of polymers [3] with the nano-particulates being more active.

Chemiluminescence analysis under nitrogen allows one to determine the effect of titanium dioxide pigments and nanoparticles on the thermal stability of a polymer in an oxygen deficient environment such as polymer melt processing. Chemiluminescence studies under nitrogen on monomodal metallocene polyethylene containing nano and micro-titania (0.5 and 2.0%) showed that the pigmented polymers suppress emission (exception is nano-rutile untreated), which correlates well with the lower initially determined hydroperoxide content. This effect is enhanced with pigment content and coated grades. Apparently, a greater surface area pigment allows higher contact with the polymer, and induces more oxidation during processing as measured by hydroperoxide analysis. Much higher intensity of chemiluminescence was observed under oxygen compared to that obtained under a nitrogen atmosphere. Here, the rutile nano-particles exhibit a thermal sensitizing effect. This effect is suppressed for micro-pigmented samples which exhibit longer induction periods than that for unpigmented polymer, and the protective effect is enhanced with coating, as was observed under nitrogen. A similar trend is observed for anatase grade titania, where the oxidation induction time (OIT) is reduced with respect to the micro-particles. For untreated nano-particles the OIT decreased in the order PC-50 > PC-105 > PC-500, which follows the decrease in particle size for Millennium grades (UK, Grimsby). The greater surface area of particles allows greater contact with the polymer, and induces more oxidation. Higher oxidation in all polyethylene samples is observed when the content of pigment is increased. All samples with pigmented rutiles and the anatase treated by hydoxyapatite show higher oxidation rates after an initial induction period [4].

The results of the effect of the titanium dioxides on the rate of the polyethylene (monomodal molar mass distribution) thermal oxidation at 110 °C showed that all nano-particle pigments exhibit a thermal sensitizing effect on the polymer and a marked autocatalytic effect on the growth in carbonyl formation. Of these the nano-particle rutile exhibited the greatest thermal activity. Apart from pigments PC-105 and PC-500 the effect increased with increasing pigment concentration from 0.5 to 2% w/w. For the micro-sized pigments the effect varies with grade and concentration being sensitizing or stabilising. In this case the presence of the antioxidant seems to play an important role since oxidation studies at 90 °C on the micro-pigmented films showed that all the coated rutile grades are sensitizers [5].

The overview of ageing and stabilization of filled polymers underline the problem regarding the filler–polymer and filler–stabiliser interactions where chemical and physical adsorption processes or sensitization reactions can control the nature of both the oxidation and stabilization processes [6]. Rates of carbonyl index formation which are used to monitor the extent of ageing in filled polyethylene films show that as the temperature of ageing is increased the pigment type becomes less important in terms of its catalytic activity on polymer oxidation. At lower oven ageing temperatures the anatase pigments are more thermally active than the rutile pigments and those with heavier coating protection give better stabilization (less sensitization). All the pigments stimulate the formation of hydroperoxide groups during ageing of the polymer at 90 °C compared with the control sample without pigments. Furthermore, prior to oven ageing it was fixed that all the titania pigmented polymer samples exhibit higher hydroperoxide concentrations than that of the control film [6]. Thus, during the processing operation to make the films (twin screw compounding extruder) the titanium dioxide pigments are catalyzing the formation of hydroperoxide groups with both the uncoated anatase and lightly coated rutile pigments being the most active types. At lower oven ageing temperatures, the coated durable rutile types were the least active in this regard followed by the fine crystal grades. The uncoated fine crystal grade rutile was more active than anatase in terms of hydroperoxide formation. The coated anatase pigment was much less active. Thus, the nature of coating treatment appears to be quite important in terms of actual contact between the surface of the titanium dioxide particles and the polymer matrix both during polymer melt processing or/and ageing. Difference between the rates of carbonyl index formation and those related to hydroperoxide formation was also noted. Hydroperoxide concentrations are changeable during ageing of a polymer since hydroperoxides behave as potential initiators and depending upon the temperature of oxidation they will be thermally and also catalytically decomposed by the titanium dioxide pigments to produce carbonyl groups [6].

The thermoxidative (oven ageing) and photooxidative degradation of polypropylene films (200 μm thick) and low density polyethylene (LDPE), linear low density polyethylene (LLDPE) film materials (100 μm thick) containing a range of antioxidants and light stabilisers, together with anatase and rutile titanium dioxide pigments were studied by the carbonyl index method, Fourier transform infrared (FTIR) spectroscopy and hydroperoxide analysis [7–10]. Rates of thermal and photooxidative degradation were determined by measuring the formation of non-volatile carbonyl and hydroperoxide oxidation products which absorb in the infrared region of the spectrum with maxima at 1710 and 3410 $\mathrm{cm^{-1}}$, respectively. On thermal oxidative degradation (50–90 °C) the rates of carbonyl formation increase autocatalytically with most of the pigments acting as thermal (catalytic) sensitizers [8,10]. The behaviour of the pigments as catalysts for the thermooxidative breakdown of the polymer was confirmed by hydroperoxide analysis [9]. Rates of polymer oxidation were found to be closely related to the nature of the surface treatments on the pigment particles [8]. During thermal oxidation of the polymer the hindered piperidine light stabilisers (HAS) (polymeric and non-polymeric) and the benzophenone absorber were strongly antagonistic with rutile while the HAS and benzotriazole stabilisers display weak synergism. The anatase strongly accelerated and catalysed the thermal stabilization effects with all the stabilisers and antioxidants. For the stabiliser combinations, the HAS are more effective in inhibiting oxidative degradation than the absorbers in the presence of both pigment types. The thermal catalytic effects of anatase are strongly suppressed by antioxidant/stabiliser combinations [7].

Thus, all the data regarding the behaviour of titanium dioxides in oxidizing condensed mediums obtained to date may be demonstrated/summarised as in Table 1.

It is clearly seen from the data in Table 1 that the titanium dioxide pigments mainly exhibit a thermal sensitizing effect with nano and uncoated forms being the most active. There is an exception for micro-grade highly coated pigments in the presence of antioxidant.

Continuing the investigation in this study we expanded the range of implicated titanium dioxides to elucidate comparative activity and details of mechanisms of filler–stabiliser interaction during the model oxidation of cumene and ethylbenzene initiated by 2,2′-azo-bisisobutyronitrile with a subsequent comparison of this with data of the nano-anatase PC-105 in high density polyethylene (HDPE). The course of liquid phase model oxidation allows one to monitor the contribution of a stabiliser–pigment interaction to the rate of oxidation, having excluded the influence of the polymer–pigment interaction. In this study we applied for the first time the new model reaction of the ethylbenzene initiated oxidation to study the activity of titanium dioxides in the liquid oxidizing medium with a reactive secondary carbon atom.

2. Theoretical considerations

The model reactions of cumene and ethylbenzene initiated (initiator is 2,2′-azo-bis-isobutyronitrile, AIBN) oxidation are obligatory designed to proceed under steady state conditions with fairly long kinetic chains ($\nu > 10$) at moderate temperatures (40–80 °C) [11–13]. The hydroperoxide does not contribute additionally to the initiation of oxidation. The air oxygen pressure is not sufficient to limit the process [$P\mathrm{O_2} = 20$ kPa (10^{-3} mol $\mathrm{O_2\,l^{-1}}$)].

For this case the model oxidation scheme may be represented in the following form:

Chain initiation: generation of $\mathrm{R^{\cdot}}$ radicals (W_{iAIBN} is the initiation rate),

$\mathrm{AIBN} \longrightarrow$ radicals of initiator $\mathrm{r\cdot}$ and $\mathrm{rO_2^{\cdot}}$ (k_i) $\longrightarrow$ hydrocarbon alkyl radicals $\mathrm{R^{\cdot}}$ (k_1) [1]

Chain propagation: $\mathrm{R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}}$ (rate constant k2) [2]

$\mathrm{RH + RO_2^{\cdot} \longrightarrow ROOH + R^{\cdot}}$ (rate constant k_3) [3]

Chain termination: $\mathrm{2\,RO_2^{\cdot}} \longrightarrow$ inactive products(rate constant k_6) [4]

Scheme 1.

The products are RH – hydrocarbon; R• – alkyl radical; $\mathrm{RO_2}$• – peroxy radical; ROOH – hydroperoxide.

The reaction rate derived from this scheme is described as follows:

$$W\mathrm{O_2} = W_{\mathrm{iAIBN}}^{1/2} k_3 k_6^{-1/2} [\mathrm{RH}] \tag{1}$$

where: $W\mathrm{O_2}$ – rate of initiated oxidation; W_{iAIBN} – initiation rate induced by the initiator; k_3 and k_6 – rate constants; [RH] – concentration of hydrocarbon. The involvement of titanium dioxides into the system of model initiated oxidation changes only the stage of chain initiation of Scheme 1[1] as [1,2]:

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[1] Using the currently accepted rate constant numbering for elementary oxidation reactions [14,15].

$$\begin{tikzcd}[column sep=small] \text{AIBN} \longrightarrow r\cdot \longrightarrow R\cdot(\text{initiation rate is } W_{\text{iAIBN}}) \arrow[dr] & \\ & \text{formation of } RO_2^{\cdot} \ (\text{initiation rate is } W_{\text{iAIBN}}+W_{\text{iTiO}_2}) \\ TiO_2 + ROOH \ (\text{initiation rate is} W_{\text{iTiO}_2}) \arrow[ur] & \end{tikzcd}$$

Scheme 2.

The oxidation rate expression (1) is modified accordingly to:

$$WO_{2(\text{i+TiO}_2)} = (W_{\text{iAIBN}} + W_{\text{iTiO}_2})^{1/2} k_3 k_6^{-1/2} [\text{RH}] \qquad (2)$$

where: $WO_{2(\text{i+TiO}_2)}$ — oxidation rate in the simultaneous presence of the initiator and titanium dioxide; W_{iTiO_2} — additional initiation rate induced by the titanium dioxide.

Scheme 1 is supplemented by additional stages of interaction between active species and the antioxidant in the presence of a phenolic antioxidant (InH) acting as a scavenger of peroxy radicals [16–21] (Scheme 3):

Chain termination:

$$\begin{array}{llr} RO_2^{\cdot} + \text{InH} \xrightarrow{k_7} \text{ROOH} + \text{In}^{\cdot} & & [7] \\ RO_2^{\cdot} + \text{In}^{\cdot} \xrightarrow{k_8} \text{inactive products} & & [8] \\ \text{In}^{\cdot} + \text{In}^{\cdot} \xrightarrow{k_9} \text{inactive products} & & [9] \end{array}$$

Scheme 3.

with: InH — phenolic antioxidant (stabiliser); In• — radical of the stabiliser.

This scheme is kinetically described by the following expressions [11–13,16–21]:

$$WO_{2(\text{InH})} = W_{\text{iAIBN}} k_3 [\text{RH}]/fnk_7[\text{InH}] \qquad (3)$$

$$\tau_{(\text{InH})} = fn[\text{InH}]/W_{\text{iAIBN}} \qquad (4)$$

where: $WO_{2(\text{InH})}$ — rate of inhibited oxidation; $\tau_{(\text{InH})}$ — induction period; n — number of functional groups in one molecule of a stabiliser; f — inhibition coefficient, representing the number of RO_2• peroxy radicals deactivated per one antioxidizing functional group of one molecule of stabiliser or how many oxidation chains are terminated by one antioxidizing group of one molecule of stabiliser; [InH] — concentration of a stabiliser; k_7 — rate constant of inhibition (reaction 7).

The additional presence of titanium dioxide pigments (TiO_2) alters the chain initiation stage as well, as shown in Scheme 2 [1].

For this case the reaction rate and induction period are described as follows:

$$WO_{2(\text{InH+TiO}_2)} = \left(W_{\text{iAIBN}} + W_{\text{i(InH+TiO}_2)}\right) k_3[\text{RH}]/fnk_7[\text{InH}] \qquad (5)$$

$$\tau_{(\text{InH+TiO}_2)} = \tau_{(\text{InH})} - \Delta\tau = fn[\text{InH}]/\left(W_{\text{iAIBN}} + W_{\text{i(InH+TiO}_2)}\right) \qquad (6)$$

$$\begin{aligned} \Delta\tau &= fn[\text{InH}]W_{\text{i(InH+TiO}_2)}/W_{\text{iAIBN}}\left(W_{\text{iAIBN}} + W_{\text{i(InH+TiO}_2)}\right) \\ &= \tau_{(\text{InH})} W_{\text{i(InH+TiO}_2)}/W_{\text{iAIBN}} + W_{\text{i(InH+TiO}_2)} \\ &= \tau_{(\text{InH})} W_{\text{i(InH+TiO}_2)}/\left(W_{\text{iAIBN}} + W_{\text{i(InH+TiO}_2)}\right) \\ &= \tau_{(\text{InH+TiO}_2)} W_{\text{i(InH+TiO}_2)}/W_{\text{iAIBN}} \qquad (7) \end{aligned}$$

where: $WO_{2(\text{InH+TiO}_2)}$ — rate of the initiated oxidation in the simultaneous presence of an antioxidant and TiO_2, $W_{\text{i(InH+TiO}_2)}$ — rate of the additional initiation induced by TiO_2 in the presence of an antioxidant, $\tau_{(\text{InH+TiO}_2)}$ — induction period in the simultaneous presence of an antioxidant and TiO_2, $\Delta\tau$ — the period of lowering of initial induction period.

In the presence of hindered amine stabilisers (HAS) based on 2,2,6,6-tetramethylpiperidine derivatives the scheme of the cumene and ethylbenzene initiated oxidation may be represented in the following simple way [2,19,21,22]:

Chain initiation:

$$\text{AIBN} \longrightarrow \text{radicals of the initiator } r\cdot(rO_2\cdot) + \text{RH} \longrightarrow R\cdot(\text{initiation rate is } W_{\text{iAIBN}}) \qquad [1]$$

Chain propagation:

$$R\cdot + O_2 \longrightarrow RO_2^{\cdot} \quad (\text{rate constant } k_2) \qquad [2]$$

$$RO_2\cdot + \text{RH} \longrightarrow \text{ROOH} + R\cdot \ (\text{rate constant } k_3) \qquad [3]$$

Formation of nitroxyl radicals: $R_1\text{-NH} \longrightarrow R_1\text{-NO}\cdot$ + molecular products [4]

Chain termination:

$$R\cdot + R_1\text{-NO}\cdot \longrightarrow R_1\text{-NOR} + \text{inert products}(\text{rate constant } k_5) \qquad [5]$$

$$2\,RO_2^{\cdot} \longrightarrow \text{inactive products (rate constant } k_6) \qquad [6]$$

Scheme 4.

with: R_1-NH — hindered amine stabiliser; R_1-NO• — nitroxyl radical.

According to this scheme, the HAS-stabilisers play a retarding role in the oxidation to reduce the initial initiation rate due to the interaction with the R• alkyl radicals [2,21].

For this scheme the rate of oxidation and rate of retardation caused by HAS are described as follows:

$$WO_{2\mathrm{HAS}} = (W_{\mathrm{iAIBN}} - W_{5\mathrm{HAS}})^{1/2} k_3 k_6^{-1/2} [\mathrm{RH}] = W^{1/2}_{\mathrm{i(HAS+AIBN)}} k_3 k_6^{-1/2} [\mathrm{RH}] \quad (8)$$

$$W_{5\mathrm{HAS}} = k_{5\mathrm{HAS}} [R\bullet][\mathrm{HAS}(-\mathrm{NO}\bullet)] = W_{\mathrm{iAIBN}} - W_{\mathrm{i(HAS+AIBN)}} = W_{\mathrm{iAIBN}} - WO^2_{2\mathrm{HAS}} k_3^{-2} k_6 [\mathrm{RH}]^{-2} \quad (9)$$

where: $WO_{2\mathrm{HAS}}$ – rate of the retarded oxidation in the presence of HAS; W_{iAIBN} – initiation rate induced by the initiator in the absence of HAS; $W_{5\mathrm{HAS}}$ – rate of interaction between R• and R_1-NO• radicals; $W_{\mathrm{i(HAS+AIBN)}}$ – rate of initiation in the simultaneous presence of the initiator and HAS.

In the additional presence of a titanium dioxide the initiation stage of Scheme 4[2] is modified as [2] follows:

The rate of apparent oxidation derived from Scheme 5 is described as follows:

Chain initiation:

AIBN $\rightarrow$ r ·(rO_2·)+ RH $\rightarrow$ R·+O_2 $\rightarrow$ RO_2·(initiation rate is W_{iAIBN})

TiO_2+ ROOH $\rightarrow$ $RO_2^{\cdot}$ + Ti^{+3} + H^+ (initiation rate is $W_{\mathrm{i\,(HAS+TiO_2)}}$)

joint formation of peroxy radicals $RO_2^{\cdot}$(initiation rate is W_{iAIBN}+$W_{\mathrm{i\,(HAS+TiO_2)}}$)

Scheme 5.

$$WO_{2(\mathrm{HAS+TiO_2})} = WO_{2(\Sigma)} = k_3[\mathrm{RO_2}\bullet][\mathrm{RH}] = \left(W_{\mathrm{iAIBN}} + W_{\mathrm{i(HAS+TiO_2)}} - W_{5\mathrm{HAS}}\right)^{1/2} \times k_3 k_6^{-1/2}[\mathrm{RH}] = W^{1/2}_{\mathrm{i}(\Sigma)} k_3 k_6^{-1/2}[\mathrm{RH}] \quad (10)$$

where $WO_{2(\Sigma)} = WO_{2(\mathrm{HAS+TiO_2})}$ and $W_{\mathrm{i}(\Sigma)} = W_{\mathrm{iAIBN}} + W_{\mathrm{i(HAS+TiO_2)}} - W_{5\mathrm{HAS}}$ are the rate of oxidation and the rate of initiation in the simultaneous presence of the initiator, HAS and TiO_2.

3. Experimental

3.1. Materials

The titanium dioxides used in this investigation were all experimental grades prepared in the laboratories of Millennium Inorganic Chemicals, Grimsby, UK. The titania codes and characteristics are given in Table 2.

The stabilisers used were hindered piperidine stabilisers (HAS) Chimassorb 119 FL, Cyasorb 3529 and phenolic antioxidants Irganox 1010. Structures and details of the stabilisers are shown in Table 3:

3.2. Methods

3.2.1. Model reaction of cumene oxidation

The model reaction of cumene oxidation was conducted with and without initiator. 2,2′-azobisisobutyronitrile (AIBN) was employed as initiator. The initiated oxidation was undertaken at the initiation rate $W_i = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}), temperature (60 ± 0.02) °C and oxygen pressure $PO_2 = 20$ kPa (air). Employed cumene was 98% purity (Fluka Chemika) and 99% purity (Alfa Aesar). The volume of the reaction mixture was 10 cm^3 (25 °C). For the given initiation rates 2.5 mg of AIBN had to be added, respectively [23]. The rate constants for the cumene oxidation at 60 °C are: $k_3 = 1.75 \times 10^5$ l mol^{-1} s^{-1}, $k_6 = 1.84 \times 10^5$ l mol^{-1} s^{-1}, and the concentration of cumene [RH] = 6.9 mol/l.

The rate of oxidation was evaluated from the amount of oxygen consumed, which was measured volumetrically with the simple equipment as described in [12,18,21]. Oxidation rates were assessed from slopes of kinetic curves of oxygen consumption. Experiments were carried out at least in triplicate and the accuracy of the oxidation rate values determined was within the range 1–4%.

The induction period τ was evaluated from the kinetic curves of oxidation as described in Refs. [11–13,16,18]. Error in determination of the induction period was ±1 min.

The cumene hydroperoxide content was assessed by a standard iodometric method using Perkin Elmer Lambda UV/vis spectrophotometer monitored at 420 nm to avoid any interference form additive absorptions at the 357 nm maximum for I^{3-}. The hydroperoxide concentration in original cumene measured before starting the experiments was found to be 4.9×10^{-4} mol/l [2].

3.2.2. Model reaction of ethylbenzene oxidation

The model reaction of ethylbenzene oxidation was undertaken with the initiator 2,2′-azobisisobutyronitrile (AIBN). The assigned parameters were as follows: initiation rate $W_i = 3.4 \times 10^{-7}$ mol l^{-1} s^{-1} (3.9×10^{-7} mol kg^{-1} s^{-1}), temperature (80 ± 0.02) °C and oxygen pressure $PO_2 = 20$ kPa (air). Employed ethylbenzene was of 99% purity (Sigma–Aldrich). The volume of the reaction mixture was 10 cm^3 (25 °C). For the given initiation rate 3.6 mg of AIBN had to be added [23].

The rate constants for the ethylbenzene oxidation at 80 °C are $k_3 = 5.37$, $k_6 = 2.0 \times 10^7$ l mol^{-1} s^{-1}, and the concentration of ethylbenzene [RH] = 7.8 mol/l.

The rate of oxidation was evaluated from the amount of oxygen consumed fixed manometrically as well as for the cumene initiated oxidation [12,13]. Each of experimental measurements was done in triplicate and the error in determination of oxidation rates was ±5%.

3.2.3. Polyethylene oven ageing

HDPE film samples with additives and titania were prepared by processing in a Brabender Plasticorder (7 min) at 170 °C and

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[2] Using the accepted rate constant numbering for elementary reactions of the retarded oxidation [2,21].

Table 1
Polymer–pigment–stabiliser interaction: influence of the titanium dioxide pigments on the thermal oxidative ageing of polymers and the rate of cumene initiated model oxidation

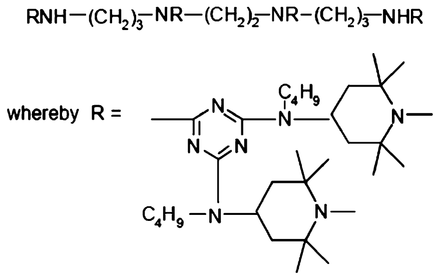
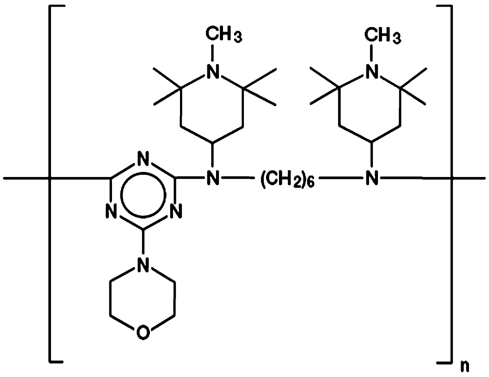
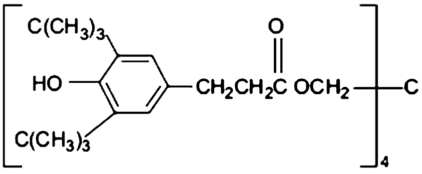
Oxidizing medium	Effects of TiO_2 pigments	T (°C)	A	Monitoring	Reference
PE-M (films of 100–200 μm thickness)	All micro-grade rutile samples are thermal sensitizers with most active the least coated at 2% w/w	90	−	CI	[3]
	Micro-grade anatase sample AT-1 is a thermal sensitizer, whereas for the micro-sized rutiles effect varies with grade and concentration being either stabilising or accelerating. All nano-grade anatases and rutiles exhibit powerful thermal sensitizing effect with most active PC-500 at 1% w/w	110	+	CI	
PE-M (melt condition)	Untreated nano-rutile exhibits the thermal sensitizing effect. Micro-sized rutiles exhibit a protective effect which is enhanced with coating. The similar trend was observed for the anatases	170	+	CL	[4]
PE-M (films of 100–200 μm thickness)	All nano-particle anatase and rutile pigments exhibit a thermal sensitizing effect with untreated rutile and anatase PC-500 being most active at 0.5 and 1% w/w, respectively. For the micro-sized pigments the effect varies with grade and concentration being either initiating or stabilising	110	+	CI	[5]
	All micro-grade coated rutile pigments exhibit thermal sensitizing effect with most active the least Al coated at 2% w/w	90	−		
LDPE (films of 100 μm thickness)	All anatase and rutile pigments coated and uncoated, with fine and medium crystal sizes sensitise the thermal oxidative ageing. As the temperature of ageing is increased the pigment type becomes less important in terms of its catalytic activity	60	−	CI	[6]
	All the pigments sensitise the formation of hydroperoxide groups during ageing. The most active is uncoated rutile type pigment with fine crystal size	90	−	HA	
PP (films of 200 μm thickness)	A polysiloxane coated rutile exhibits powerful thermal sensitizing effect whereas uncoated anatase is indifferent to oven ageing	130	−	CI	[7]
	Both the polysiloxane coated rutile and the uncoated anatase exhibit almost equal thermal sensitizing effect		+ (0.1% w/w)		
	The uncoated anatase exhibits thermal sensitization			HA	
LDPE and LLDPE (films of 100 μm thickness)	Most of the pigments acting as thermal catalysts stimulating oxidative breakdown of the polymer	50–90	−	FTIR CI HA	[8–10]
CM (liquid phase initiated oxidation)	Anatase and rutile pigments are catalysts to a greater or lesser extent. On the sensitizing activity they can be ordered as nano-rutile > nano-anatase treated hydroxyapatite > nano-anatase untreated > micro-anatase > micro-rutile	60	+ (0.002% w/w)	OU	[1]

A – antioxidant Irganox 1010 (0.05% w/w); CI – carbonyl index; CL – chemiluminescence; HA – hydroperoxide analysis; FTIR – Fourier transform infrared spectroscopy; OU – oxygen uptake; PE-M – metallocene polyethylene; LDPE – low-density polyethylene; PP – polypropylene; LLDPE – linear low-density polyethylene; CM – cumene. The polymer films were aged in an hot air fan oven at 90 and 110 °C (T (°C) – temperature of the exposure). Concentrations of the pigments added were 0.5, 1 and 2% w/w.

Table 2
Properties of pigments used in this work

Sample	BET surface area (m^2/g)	Particle size	Surface treatment	% Surface treatment
A – anatase normal	10.1	0.24 μm	None	–
B – rutile normal	12.5	0.29 μm	Al	3.4
C – nano-anatase	77.9	15–25 nm	None	–
D – nano-anatase	329.1	5–10 nm	None	–
E – nano-anatase	52.1	70 nm	Hydroxyapatite	5
F – nano-rutile	140.9	25 nm	None	–
G – nano-anatase 75% + nano-rutile 25% (mixed morphology)	50	25–30 nm	None	–

Table 3
Structures of stabilisers

Trade name and nomenclature	Molar mass	Chemical structures, supplier
Chimassorb 119 FL: 1,3,5-triazine-2,4,6,-triamine-*N*,*N*‴-[1,2-ethane-diyl-bis [[[4,6-bis-[butyl (1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2yl-]imino]-3,1-propanediyl]]bis [*N*′,*N*″-dibutyl-*N*′,*N*″-bis (1,2,2,6,6-pentamethyl-4-piperidinyl)	2286	 Ciba Speciality Chemicals
Cyasorb 3529, 1,6-hexanediamine, *N*,*N*′-bis(2,2,6,6-tetramethyl-4-piperidinyl)-, polymers with morpholine-2,4,6,-trichloro-1,3,5,-triazine	1700 ± 10%	 Cytec Industries Inc.
Irganox 1010: tetrakis[methylene-3-(3′,5′-di-*tert*-butyl-4-hydroxyphenyl) propionate]methane	1178	 Ciba Speciality Chemicals

then compression moulded for 2 min at 150 °C. High-density polyethylene (HDPE) films were oven aged in the air at 110 °C.

In infrared spectroscopy, IR radiation is passed through a sample when the resulting spectrum is related to vibrations of specific functional groups and this creates a spectral fingerprint of the sample. Carbonyl groups are easily detected in the broad infrared region at 1800–1680 wave numbers for oxidised polyethylene film. Carbonyl growth in this region of the spectrum was determined by the carbonyl index defined as follows [24–27]:

$$\text{Carbonyl index} = A/D \times 100$$

where: A = absorbance and D = film thickness (μm). Embrittlement time is defined as the ageing time related to a carbonyl index value of 0.1. Three replicates were studied in each combination. Spectra were recorded and analysed using a Nicolet Nexus FTIR spectrometer.

4. Results and discussion

4.1. Cumene oxidation

The micro- and nano-grade titanium dioxides were first examined to determine their direct influence on the uninitiated oxidation of cumene. Fig. 1 represents kinetic curves of the oxygen uptake for the cumene oxidation in the presence of different titanium dioxides.

The profiles of oxidation kinetic curves exhibit appreciable oxidation rates in the presence of nano-grade samples having advantage over the micro-sized titanium dioxides. The latter accelerates the oxidation after a certain short induction period. The nature of the induction period can be attributed to the time of the hydroperoxide accumulation, after which the process accepts a stationary state and proceeds with the steady rate during the measuring period. However, the induction periods are very negligible for the titanium dioxides with relatively strong catalytic activity (pigments D, E, F, G). In these cases,

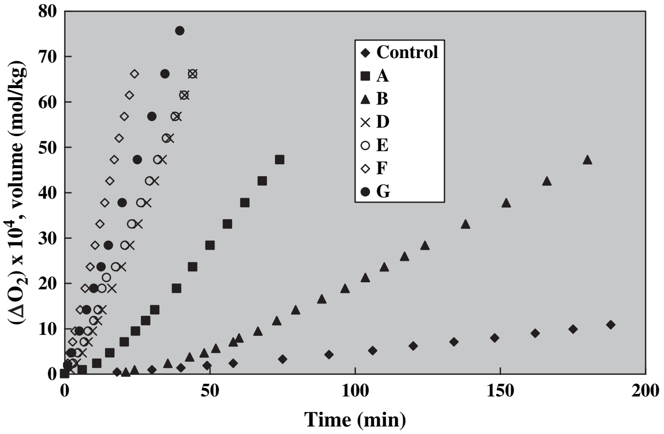


Fig. 1. Kinetic dependencies of oxygen uptake for cumene oxidation in the presence of titanium dioxide pigments (TiO_2). Reaction mixture volume, 10 ml; oxygen pressure, 20 kPa (air); temperature, 60°C. Concentration of the titanium dioxides, $[TiO_2] = 5.4 \times 10^{-2}$ mol/l (6.25×10^{-2} mol/kg, 0.5 wt%, 43.2 mg/10 ml).

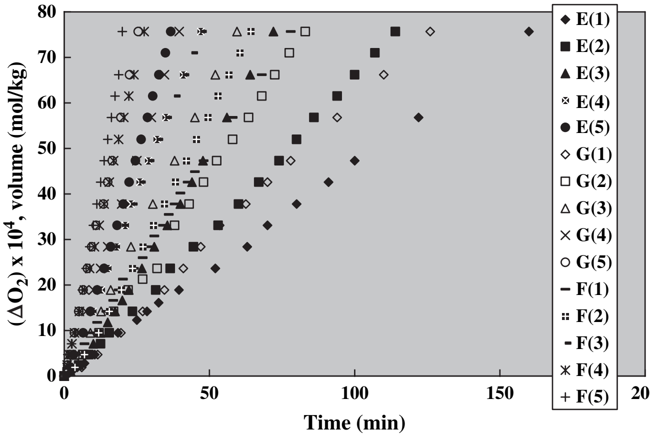


Fig. 2. Kinetic dependencies of oxygen consumption for cumene oxidation in the presence of titanium dioxide pigments (TiO_2). Reaction mixture volume, 10 ml; oxygen pressure, 20 kPa (air); temperature, 60 °C. Concentration of the titanium dioxides $[TiO_2] = (1)$: 5×10^{-3} mol/l (5.8×10^{-3} mol/kg, ~0.05 wt%, 4 mg/10 ml); (2): 1×10^{-2} mol/l (1.2×10^{-2} mol/kg, ~0.1 wt%, 8 mg/10 ml); (3): 2×10^{-2} mol/l (2.3×10^{-2} mol/kg, ~0.2 wt%, 16 mg/10 ml); (4): 5.4×10^{-2} mol/l (6.25×10^{-2} mol/kg, 0.5 wt%, 43.2 mg/10 ml); (5): 1.0×10^{-1} mol/l (1.2×10^{-1} mol/kg, ~1 wt%, 80 mg/10 ml).

the oxidation starts at the steady state conditions immediately after the first few minutes. Fig. 2 represents the profiles of the oxidation kinetic curves for the active titanium dioxides taken at different concentrations.

According to the profiles of the kinetic curves in Fig. 2 the oxidation proceeds with steady rates during the measuring period. The greater the concentration of titanium dioxides the greater are the oxidation rates which are changed according to the law represented in Fig. 3. The dependencies of the data in Fig. 3 show quite good linearization between experimentally observed oxidation rates and the square root of the titanium dioxide concentrations over the range 5×10^{-3}–1×10^{-1} mol/l at 60 °C, i.e. $WO_{2(TiO_2)} \sim W_{iTiO_2}^{1/2}$.

This implies that the titanium dioxides operate in the oxidation as radical generating initiator and thereby suggest the following Scheme 6 proposed with recombination of cumylperoxy radicals given below:

$TiO_2 + ROOH \rightarrow$ generation of the of peroxy radicals $RO_2^{\cdot}$ (initiation rate is W_{iTiO2}) [1']

Chain propagation: $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ (rate constant k_2) [2]

$RH + RO_2^{\cdot} \rightarrow ROOH + R^{\cdot}$ (rate constant k_3) [3]

Chain termination: $2\,RO_2^{\cdot} \rightarrow$ inactive products(rate constant k_6) [4]

Scheme 6.

The oxidation rate derived from Scheme 6 may be represented by the following expression:

$$WO_{2(TiO_2)} = W_{i(TiO_2)}^{1/2} k_3 k_6^{-1/2} [RH] \quad (11)$$

Thus we can state the thermal catalytic effect of titanium dioxides on the uninitiated oxidation of cumene. In terms of the degree of the thermal sensitizing action the titanium dioxides can be ordered as nano-rutile untreated > nano-anatase treated hydroxyapatite ≥ nano-anatase untreated ≥ (nano-anatase (75%) + nano-rutile (25%)) untreated > micro-anatase untreated > micro-rutile treated.

4.1.1. Cumene initiated oxidation

It has been observed during these experiments that the catalytic power of titanium dioxides depends significantly on the structure of stabiliser present. Therefore, in this work the inverse task has been setup to ascertain the influence of the nature of the stabiliser on the initiating activity of the titanium dioxides.

Fig. 4 illustrates the influence of titanium dioxides on the initiated oxidation of cumene. The kinetic curves clearly showed the catalytic effect of the pigments. The oxidation proceeds according to Scheme 2, and the rate of the additional initiation $W_{i(TiO_2)}$ can be calculated from Eqs. (1) and (2) as the ratio of the experimentally observed oxidation rates and assigned value of the rate of initiation in the presence of AIBN:

$$WO_{2(i+TiO_2)}/WO_2 = (W_{iAIBN} + W_{iTiO_2})^{1/2} W_{iAIBN}^{-1/2} \quad \text{and}$$
$$W_{iTiO_2} = WO_{2(i+TiO_2)}^2 W_{iAIBN} WO_2^{-2} - W_{iAIBN} \quad (12)$$

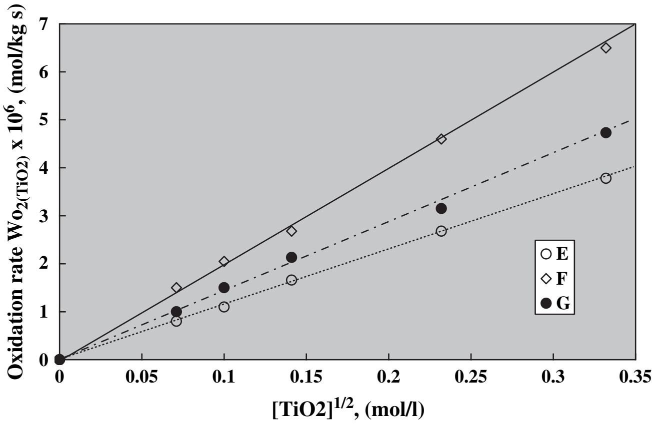


Fig. 3. Oxidation rate for cumene versus concentration of titanium dioxides (TiO_2). Reaction mixture volume, 10 ml; oxygen pressure, 20 kPa (air); temperature, 60 °C.

The obtained values of $W_{i(TiO_2)}$ as well as the accompanying kinetic data are given in Table 4.

Fig. 5 shows the effect of the titanium dioxides on the initiated oxidation of cumene in the presence of an antioxidant Irganox 1010 (Ciba–Geigy, Switzerland). The oxidation proceeds according to the scheme of the initiated oxidation of cumene in the simultaneous presence of titanium dioxides and Irganox 1010 [1]. The system exhibits a permanent reduction in the induction periods in the presence of titanium dioxides according to the above-mentioned sequence of their catalytic activity.

The shortening of induction periods occurs as result of an increase in the initiation rate in accordance with Eq. (6). In this case the additional initiation rate induced by titanium dioxides in the presence of Irganox 1010 $W_{i(Irg.+TiO_2)}$ may be derived from Eq. (7) as follows:

$$\begin{aligned} W_{i(Irg.+TiO_2)} &= \Delta\tau W_{iAIBN}/\tau_{(Irg.+TiO_2)} \\ &= \left(\tau_{(Irg.)} - \tau_{(Irg.+TiO_2)}\right) W_{iAIBN}/\tau_{(Irg.+TiO_2)} \end{aligned} \qquad (13)$$

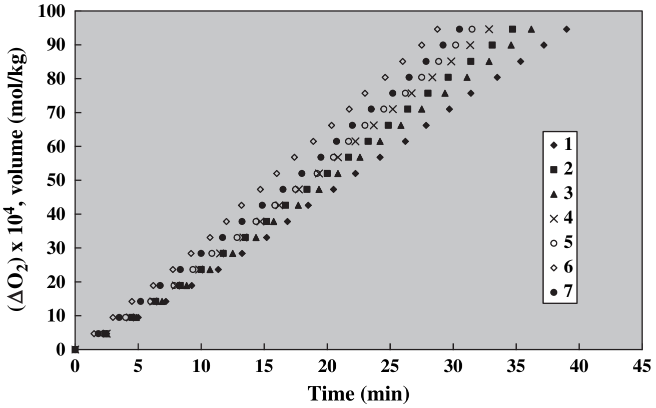


Fig. 4. Kinetic dependencies of oxygen consumption for cumene initiated oxidation in the presence of various titanium dioxide additives (TiO_2). $[TiO_2] = 1.1 \times 10^{-1}$ mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.4 mg/10 ml); initiator = 2,2′-azobisisobutyronitrile (AIBN); initiation rate, $W_{iAIBN} = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}); reaction mixture volume, 10 cm^3; oxygen pressure, 20 kPa (air); temperature, 60 °C. (1): $[TiO_2] = 0$; (2): A; (3): B; (4): D; (5): E; (6): F; (7): G.

Table 4
Initiated oxidation of cumene in the presence of different titanium dioxides

TiO_2 type	$WO_{2(i+TiO_2)} \times 10^6$, mol l^{-1} s^{-1}	$W_{iTiO_2} \times 10^9$, mol l^{-1} s^{-1}	$WO_{2(i+TiO_2)} \times 10^6$, mol kg^{-1} s^{-1}	$W_{iTiO_2} \times 10^9$, mol kg^{-1} s^{-1}
–	3.47	17	4.02	20
A	4.0	2.2 ± 0.1	4.6	2.6 ± 0.1
B	3.75	2.0 ± 0.1	4.33	2.3 ± 0.1
D	4.15	2.4 ± 0.1	4.81	2.8 ± 0.1
E	4.36	2.7 ± 0.1	5.04	3.1 ± 0.1
F	4.77	3.2 ± 0.1	5.52	3.7 ± 0.1
G	4.5	2.9 ± 0.1	5.2	3.3 ± 0.1

Reaction mixture volume, 10 ml; initiator = 2,2′-azobisizobutyronitrile (AIBN); starting initiation rate, $W_{iAIBN} = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}); concentration of pigments $[TiO_2] = 1.1 \times 10^{-1}$ mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.4 mg/10 ml); temperature, 60 °C.

Using the experimentally observed induction periods and an assigned value of W_{iAIBN} the values of $W_{i(Irg.+TiO_2)}$ may be calculated. These data and accompanying kinetic parameters of the model reaction of cumene initiated oxidation in the simultaneous presence of antioxidant Irganox 1010 and the titanium dioxide pigments are tabulated in Table 5.

The data in Table 5 shows the significant increase in the rate of initiation $W_{i(Irg.+TiO_2)}$ induced by titanium dioxides in comparison with the rate $WO_{2(i+TiO_2)}$ induced at the same conditions but without Irganox 1010 (Table 4). The order for the foregoing initiating activity of the titanium dioxides is maintained in the presence of Irganox 1010.

Fig. 6 illustrates the kinetic dependencies of oxygen consumption on the cumene initiated oxidation system, containing a hindered piperidine stabiliser, Chimassorb 119 FL and the titanium dioxide pigments.

The reduction in the retarding activity of the Chimassorb stabiliser caused by the titanium dioxides occurs according

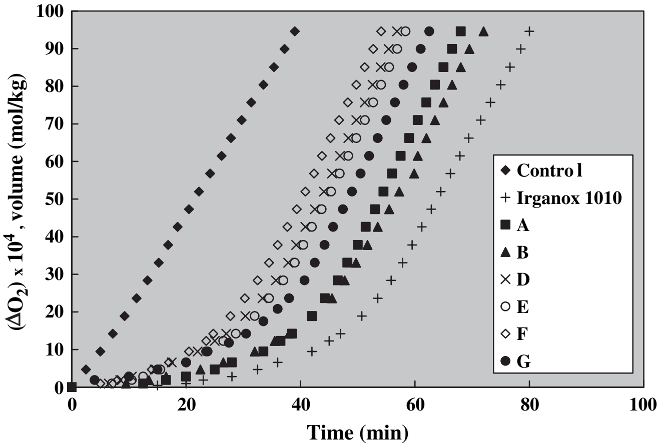


Fig. 5. Kinetic curves of oxygen consumption for the model reaction of cumene initiated oxidation in the simultaneous presence of antioxidant Irganox 1010 and different types of titanium dioxide pigments (TiO_2). Initiator = 2,2′-azobisizobutyronitrile (AIBN); starting initiation rate, $W_{iAIBN} = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}); concentration of the antioxidant [Irganox 1010] $= 6.0 \times 10^{-6}$ mol/l (6.9×10^{-6} mol kg^{-1}, 0.07 mg/10 ml); concentration of pigments $[TiO_2] = 1.1 \times 10^{-1}$ mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.4 mg/10 ml); reaction mixture volume, 10 cm^3; oxygen pressure, 20 kPa (air); temperature, 60 °C.

Table 5
Kinetic parameters of the model reaction of the initiated oxidation of cumene in the simultaneous presence of antioxidant Irganox 1010 and different type of titanium dioxide pigments

TiO_2 type	Induction time $\tau_{(Irg.+TiO_2)}$, min	$W_{i(Irg.+TiO_2)} \times 10^9$, mol l^{-1} s^{-1}	$W_{i(Irg.+TiO_2)} \times 10^9$, mol kg^{-1} s^{-1}
–	55	17	20
A	45	3.8 ± 0.3	4.4 ± 0.4
B	47	2.9 ± 0.3	3.4 ± 0.4
D	37	8.3 ± 0.7	9.6 ± 0.8
E	36	9.0 ± 0.7	10.4 ± 0.8
F	31	13.2 ± 1.0	15.3 ± 1.2
G	39	7.0 ± 0.6	8.1 ± 0.7

Reaction mixture volume is 10 ml. Initiator = 2,2′-azobisizobutyronitrile (AIBN); starting initiation rate, $W_{iAIBN} = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}); concentration of the antioxidant [Irganox 1010] = 6.0×10^{-6} mol/l (0.07 mg/10 ml); concentration of pigments $[TiO_2] = 1.1 \times 10^{-1}$ mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.4 mg/10 ml); temperature, 60 °C.

to the activity order starting from the most inert treated micro-nano-rutile to the most active untreated nano-rutile. The oxidation proceeds according to Scheme 5 and is fitted by the oxidation rate expression of Eq. (10) [2].

The additional initiation rate induced by the titanium dioxides $W_{i(Chim.+TiO_2)}$ leading to an increase in the retardation may be derived and calculated from Eqs. (9) and (10) as follows:

$$\begin{aligned} & W_{iAIBN} + W_{i(Chim.+TiO_2)} - W_{5Chim.} \\ & = WO^2_{2(Chim.+TiO_2)} k_6 k_3^{-2} [RH]^{-2} W_{i(Chim.+TiO_2)} \\ & = WO^2_{2(Chim.+TiO_2)} k_6 k_3^{-2} [RH]^{-2} + W_{5Chim.} - W_{iAIBN} \\ & = WO^2_{2(Chim.+TiO_2)} k_6 k_3^{-2} [RH]^{-2} - WO^2_{2Chim.} k_3^{-2} k_6 [RH]^{-2} \\ & = k_3^{-2} k_6 [RH]^{-2} \left(WO^2_{2(Chim.+TiO_2)} - WO^2_{2Chim.} \right) \\ & = 1.26 \times 10^3 \left(WO^2_{2(Chim.+TiO_2)} - WO^2_{2Chim.} \right) \qquad (14) \end{aligned}$$

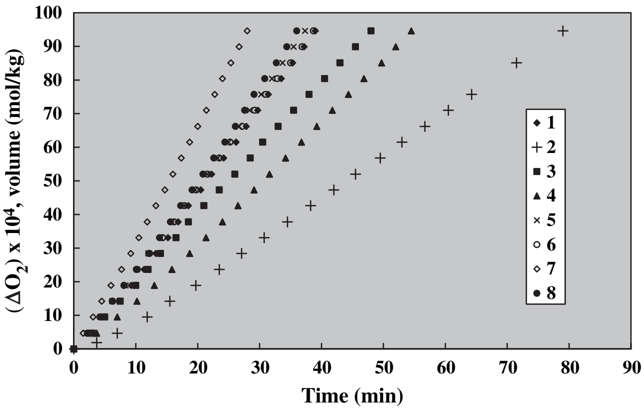


Fig. 6. Kinetic dependencies of oxygen consumption for cumene initiated oxidation in the simultaneous presence of the hindered piperidine stabiliser Chimassorb 119 FL and various titanium dioxide additives (TiO_2). [Chimassorb 119 FL] = 1.0×10^{-4} mol/l (1.2×10^{-4} mol/kg); $[TiO_2] = 1.1 \times 10^{-1}$ mol/l (1.25×10^{-1} mol/kg; 1 wt%; 86.4 mg/10 ml). Initiator = 2,2′-azobisisobutyronitrile (AIBN); initiation rate, $W_{iAIBN} = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}), reaction mixture volume, 10 cm^3, oxygen pressure, 20 kPa (air), 60 °C. (1): $[TiO_2] = 0$, [Chimassorb 119 FL] = 0; (2): $[TiO_2] = 0$; (3): A; (4): B; (5): D; (6): E; (7): F; (8): G.

The obtained values of the $W_{i(Chim.+TiO_2)}$ and the concomitant parameters of the initiated oxidation of cumene in the simultaneous presence of Chimassorb 119 FL and titanium dioxides are given in Table 6.

As can be seen from the data in Tables 4–6 the values of the initiating activity of titanium dioxides in the absence and presence of the antioxidant and the hindered piperidine stabiliser are considerably different. Obtained initiation rates are summarized in the diagram of Fig. 7.

Thus, the stabilisers influence the titanium dioxide pigments and promote an additional contribution to the initial initiation activity of TiO_2 in the model reaction of cumene initiated oxidation. Nano-grade titanium dioxides exhibit more sensitivity to the presence of stabilisers when compared to those of the micro-grade samples. The nano-anatase untreated rutile was found to be most active whereas treated micro-anatase was least active in terms of additional initiation rates. In the case of the hindered piperidine stabiliser, Chimassorb, this phenomenon was more pronounced than that for the Irganox. The titanium dioxides are affected by the stabilisers and thus, reveal an additional catalytic capacity and afford the additional initiation rates which are 2–9 times higher than the initial initiation rate induced by the pigments in the system without stabilisers.

4.2. Ethylbenzene initiated oxidation

The experiments were undertaken using of the model reaction of ethylbenzene initiated oxidation. This study had the aim to check the behaviour of titanium dioxides in oxidizing hydrocarbon with the presence of a reactive secondary carbon atom. Oxygen adsorption resulting from the initiating activity of the initiator AIBN and titanium dioxides in the presence of different stabilisers is shown in Fig. 8.

It can be observed from the profiles of the kinetic curves in Fig. 8 that titanium dioxide E exhibits an additional initiation effect. The treatment of the kinetic curves and calculation of kinetic parameters of the ethylbenzene initiated oxidation have been fulfilled as well as for the cumene initiated oxidation. These following relationships have been used for the calculation of $W_{i(TiO_2)}$:

$$W_{iE} = WO^2_{2(i+E)} W_{iAIBN} WO_2^{-2} - W_{iAIBN} \qquad (15)$$

$$\begin{aligned} W_{i(Irg.+E)} &= \Delta\tau W_{iAIBN} / \tau_{(Irg.+E)} \\ &= \left(\tau_{(Irg.)} - \tau_{(Irg.+E)} \right) W_{iAIBN} / \tau_{(Irg.+E)} \end{aligned} \qquad (16)$$

$$W_{i(Cyas.3529+E)} = 1.14 \times 10^4 \left(WO^2_{2(Cyas.3529+E)} - WO^2_{2Cyas.3529} \right) \qquad (17)$$

Results of the calculation are summarized in Table 7.

Thus the data in Table 7 is further a strong evidence invoking the additional strength of titanium dioxide E under the influence of stabilisers as well as that observed for the model cumene initiated oxidation. These additional contributions to

Table 6
Kinetic parameters of the cumene model initiated oxidation in the simultaneous presence of the Chimassorb 119 FL and different types of titanium dioxides

TiO_2 type	$WO_{2(\mathrm{Chim.+TiO_2})} \times 10^6$ mol l^{-1} s^{-1}	$W_{\mathrm{i(Chim.+TiO_2)}} \times 10^9$ mol l^{-1} s^{-1}	$WO_{2(\mathrm{Chim.+TiO_2})} \times 10^6$ mol kg^{-1} s^{-1}	$W_{\mathrm{i(Chim.+TiO_2)}} \times 10^9$ mol kg^{-1} s^{-1}
A	2.93	7.6 ± 0.6	3.4	8.8 ± 0.7
B	2.52	4.5 ± 0.3	2.92	5.2 ± 0.4
D	3.54	13.2 ± 1.0	4.1	15.3 ± 1.2
E	3.47	12.5 ± 1.0	4.02	14.5 ± 1.2
F	4.77	27.5 ± 2.0	5.52	31.8 ± 2.3
G	3.75	15.3 ± 1.2	4.33	17.7 ± 1.4

Reaction mixture volume is 10 ml. Initiator = 2,2′-azobisizobutyronitrile (AIBN); starting initiation rate $(W_{\mathrm{iAIBN}} - W_{\mathrm{5Chim.}}) = 4.4 \times 10^{-9}$ mol l^{-1} s^{-1} (5.1×10^{-9} mol kg^{-1} s^{-1}); starting oxidation rate, $WO_{2\mathrm{Chim.}} = 1.77 \times 10^{-6}$ mol l^{-1} s^{-1} (2.05×10^{-6} mol kg^{-1} s^{-1}); concentration of the stabiliser [Chimassorb 119 FL] = 1.0×10^{-4} mol/l (2.3 mg/10 ml); concentration of pigments $[TiO_2] = 1.1 \times 10^{-1}$ mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.4 mg/10 ml); temperature, 60 °C.

the initiation rates of titanium dioxides promoted by stabilisers can be explained in terms of physical absorption of stabilisers onto the titanium dioxide particles. It has been shown in Ref. [28] that there is a significant adsorption capacity for the hindered piperidine Tinuvin 770 and antioxidant Irganox 1010. As we have used hindered piperidine stabilisers of the same nature and Irganox 1010 we can similarly approximate our data obtained to the processes of adsorption and to explain the nature of the additional initiating capacity of titanium dioxides.

It is proposed that the stabilisers being adsorbed onto the surface of titanium dioxides are able to block titania surface-OH groups and thereby promote the additional initiating activity of titanium pigments. In fact these –OH groups play a negative role in oxidation since they induce the formation of water in the system. It has been established by our control experiments that the presence of water leads to a marked suppression of the cumene and ethylbenzene oxidation. The amine functionalities of Chimassorb 119 FL and Cyasorb 3529 are energetically protonated by the surface hydroxyls of titanium dioxides during the oxidation process. The adsorption of the amines can also occur by hydrogen bond formation with surface hydroxyl species. The adsorption of Irganox 1010 onto pigments is much less energetic than that of hindered amine stabilisers and it is a reflection of the reduced interaction of the hindered phenolic hydroxyl group and the ester groups of Irganox 1010 with Ti-OH groups relative to the much more basic piperidine amine groups of Chimassorb 119 FL and Cyasorb 3529. As a result of this the induced additional initiating effect of titanium dioxides in the presence of Irganox 1010 is less than that for the case of hindered amine stabilisers.

Thus, we have established the experimental fact of additional accelerating capacity of titanium dioxides in the initiated oxidation of cumene and ethylbenzene promoted by the presence of stabilisers with amine, hydroxyl and ester functionalities. This effect can totally demolish the initial high level of inhibiting activity of stabilisers and can lead to the intense lability of an oxidizing system. On the basis of

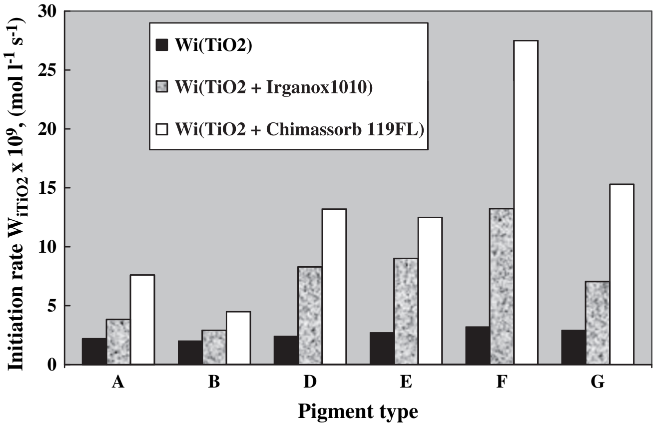


Fig. 7. Rates of initiation induced by titanium dioxides (TiO_2) for the model cumene initiated oxidation in the absence and presence of stabilisers. $[TiO_2] = 1.1 \times 10^{-1}$ mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.4 mg/10 ml). Initiator = 2,2′-azobisisobutyronitrile (AIBN); initiation rate, $W_{\mathrm{iAIBN}} = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}); reaction mixture volume, 10 cm^3; oxygen pressure, 20 kPa (air); temperature, 60 °C.

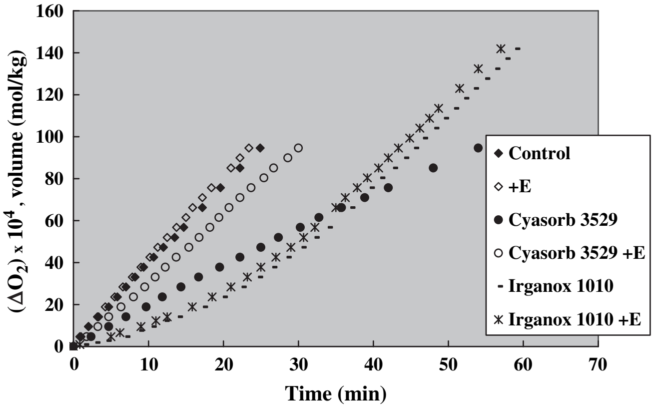


Fig. 8. Kinetic dependencies of oxygen consumption for model ethylbenzene initiated oxidation in the absence and presence of various stabilisers and the titanium dioxide E. Initiator = 2,2′-azobisisobutyronitrile (AIBN); initiation rate, $W_{\mathrm{iAIBN}} = 3.4 \times 10^{-7}$ mol l^{-1} s^{-1} (3.9×10^{-7} mol kg^{-1} s^{-1}); reaction mixture volume, 10 cm^3; oxygen pressure, 20 kPa (air); temperature, 80 °C. [E] = 1.1×10^{-1} mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.7 mg/10 ml); [Cyasorb 3529] = 5.0×10^{-4} mol/l (5.8×10^{-4} mol/kg, 8.5 mg/10 ml); [Irganox 1010] = 7.6×10^{-5} mol/l (8.8×10^{-5} mol/kg, 0.9 mg/10 ml).

Table 7
Rates of initiation induced by titanium dioxide E in the model reaction of ethylbenzene initiated oxidation in the absence and presence of different stabilisers

Stabiliser type	$W_{iE} \times 10^8$ mol l^{-1} s^{-1} (kg/s)	$W_{i(Irg.+E)} \times 10^8$ mol l^{-1} s^{-1} (kg/s)	$W_{i(Cyas.3529+E)} \times 10^8$ mol l^{-1} s^{-1} (kg/s)
–	4.0 ± 0.3 (4.6 ± 0.3)	–	–
Irganox 1010	–	8.0 ± 0.6 (9.2 ± 0.7)	–
Cyasorb 3529	–	–	15 ± 1.0 (17.3 ± 1.2)

Initiator = 2,2′-azobisisobutyronitrile (AIBN); initiation rates, $W_{iAIBN} = 3.4 \times 10^{-7}$ mol l^{-1} s^{-1} (3.9×10^{-7} mol kg^{-1} s^{-1}), ($W_{iAIBN} - W_{5Cyas.}$) = 8.1×10^{-8} mol l^{-1} s^{-1} (9.3×10^{-8} mol kg^{-1} s^{-1}); reaction mixture volume, 10 cm^3; oxygen pressure, 20 kPa (air); temperature, 80 °C. [E] = 1.1×10^{-1} mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.7 mg/10 ml); [Irganox 1010] = 7.6×10^{-5} mol/l (8.8×10^{-5} mol/kg, 0.9 mg/10 ml); [Cyasorb 3529] = 5.0×10^{-4} mol/l (5.8×10^{-4} mol/kg, 8.5 mg/10 ml); oxidation rates: $WO_2 = 5.58 \times 10^{-6}$ mol l^{-1} s^{-1} (6.46×10^{-6} mol kg^{-1} s^{-1}); $WO_{2(i+E)} = 5.86 \times 10^{-6}$ mol l^{-1} s^{-1} (6.78×10^{-6} mol kg^{-1} s^{-1}); $WO_{2Cyas.3529} = 2.72 \times 10^{-6}$ mol l^{-1} s^{-1} (3.15×10^{-6} mol kg^{-1} s^{-1}); $WO_{2(Cyas.3529+E)} = 4.56 \times 10^{-6}$ mol l^{-1} s^{-1} (5.28×10^{-6} mol kg^{-1} s^{-1}); induction times, $\tau_{(Irg.)} = 32$ min; $\tau_{(Irg.+E)}) = 26$ min.

susceptibility towards all the used stabilisers, leading to the sharp increasing of the initial initiating activity, titanium dioxides in the model oxidative reactions can be ordered as nano-rutile untreated > nano-anatase treated hydroxyapatite ≥ nano-anatase untreated ≥ (nano-anatase (75%) + nano-rutile (25%)) untreated > micro-anatase untreated > micro-rutile treated.

4.3. Polyethylene oven ageing

The model data obtained in this study may be qualitatively carried over to polymer systems, although, the polymer matrixes have many specific peculiarities. Such a specificity of polymer system can be evidenced by experiments with nano-grade titanium dioxide C involved in the liquid phase cumene oxidation and in the thermooxidative degradation of high-density polyethylene (HDPE). The Figs. 9 and 10 illustrate the behaviour of titanium dioxide C in these different condensed oxidizing mediums containing Irganox 1010.

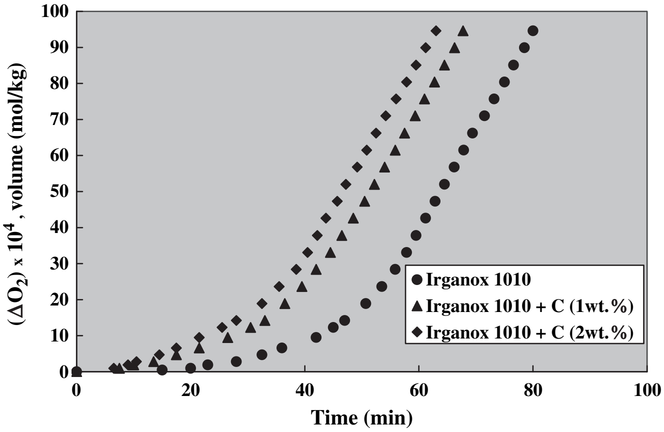


Fig. 9. Kinetic dependencies of oxygen consumption for the model cumene initiated oxidation in the absence and presence of Irganox 1010 and the titanium dioxide pigment C. Initiator = 2,2′-azobisisobutyronitrile (AIBN); initiation rate, $W_{iAIBN} = 1.7 \times 10^{-8}$ mol l^{-1} s^{-1} (2.0×10^{-8} mol kg^{-1} s^{-1}); reaction mixture volume, 10 cm^3; oxygen pressure, 20 kPa (air); temperature, 60 °C. [C] = 1.1×10^{-1} mol/l (1.25×10^{-1} mol/kg, 1 wt%, 86.7 mg/10 ml) and [C] = 2.2×10^{-1} mol/l (2.5×10^{-1} mol/kg, 2 wt%; 172.8 mg/10 ml); [Irganox 1010] = 6.0×10^{-6} mol/l (6.9×10^{-6} mol/kg, 0.07 mg/10 ml).

The kinetic curves shown in Fig. 9 and curves of carbonyl index growth in Fig. 10 compare the effect of the nano-anatase C on both the processes of model cumene initiated oxidation and thermooxidative exposure of HDPE in the presence of Irganox 1010. For the former, a shortening of the initial induction period with an increase in the concentration of nano-anatase C from 1 to 2 wt% is observed, whereas for the latter case along with 1 wt% of C in HDPE exhibiting a thermal sensitizing effect. The 2 wt% addition however, affords an opposite stabilising effect. This is evidence of the complex interplay between the polymer and fillers and additives requiring repeated experiments to reach precise and reproducible results, while the use of model reactions is proposed as an effective tool since it allows one to obtain an ideal pattern of performance on a quantitative level.

5. Conclusions

The interactions of titanium dioxide pigments with stabilisers in condensed mediums involve a complex inter-play of phenomena. The surface area, functionality and hydrophilicity of the pigments may often appear to be crucial in the performance of polymer materials.

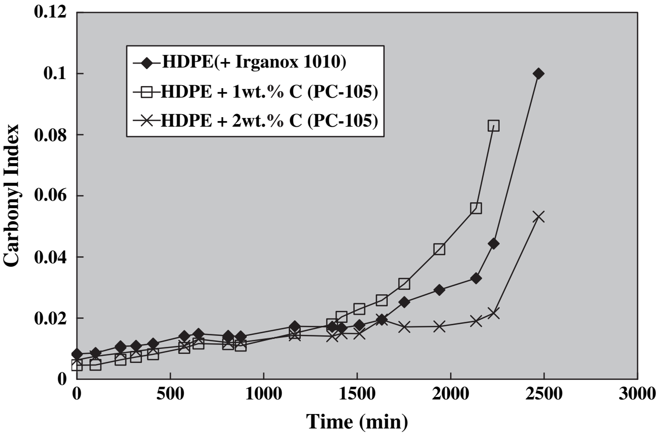


Fig. 10. Carbonyl index versus thermal ageing time at 110 °C in an hot air oven for high-density polyethylene films containing nano-particle grade titania pigment C at 1.0 and 2.0% w/w concentrations with antioxidant Irganox 1010.

References

[1] Zeynalov EB, Allen NS. An influence of micron and nano-particle titanium dioxides on the efficiency of antioxidant Irganox 1010 in a model oxidative reaction. Polym Degrad Stab 2004;86(1):115–20.

[2] Zeynalov EB, Allen NS. Effect of micron and nano-grade titanium dioxides on the efficiency of hindered piperidine stabilizers in a model oxidative reaction. Polym Degrad Stab 2006;91(4):931–9.

[3] Allen NS, Edge M, Ortega A, Sandoval G, Liauw CM, Verran J, et al. Degradation and stabilization of polymers and coatings: nano versus pigmentary titania particles. Polym Degrad Stab 2004;85(3):927–46.

[4] Corrales T, Peinado C, Allen NS, Edge M, Sandoval G, Catalina F. A chemiluminescence study of micron and nanoparticle titanium dioxide: effect on the thermal stability of metallocene polyethylene. J Photochem Photobiol A Chem 2003;156(1–3):151–60.

[5] Allen NS, Edge M, Sandoval G, Ortega A, Liauw CM, Stratton J, et al. Interrelationship of spectroscopic properties with the thermal and photochemical behaviour of titanium dioxide pigments in metallocene polyethylene and alkyd based paint films: micron versus nanoparticles. Polym Degrad Stab 2002;76(2):305–19.

[6] Allen NS, Edge M, Corrales T, Childs A, Liauw CM, Catalina F, et al. Ageing and stabilization of filled polymers: an overview. Polym Degrad Stab 1998;61(2):183–99.

[7] Allen NS, Edge M, Corrales T, Catalina F. Stabiliser interactions in the thermal and photooxidation of titanium dioxide pigmented polypropylene films. Polym Degrad Stab 1998;61(1):139–49.

[8] Allen NS, Katami H. Comparison of various thermal and photoageing conditions on the oxidation of titanium dioxide pigmented linear low density polyethylene films. Polym Degrad Stab 1996;52(3):311–20.

[9] Allen NS, Katami H, Thompson F. Influence of titanium dioxide pigments on the thermal and photochemical oxidation of low density polyethylene film. Eur Polym J 1992;28(7):817–22.

[10] Allen NS, Katami H. Influence of titanium dioxide pigments on thermal and photochemical oxidation and stabilization of polyolefin films Polymer durability. In: Advances in chemistry series, vol. 249; 1996. p. 537-54.

[11] Tsepalov VF, Kharitonova AA, Gladyshev GP, Emanuel NM. Determination of rate constants and inhibition coefficients of inhibitors using a model chain reaction. Kinet Catal 1977;18(6):1142–8.

[12] Zeynalov EB, Vasnetsova OA. Kinetic screening of inhibitors of radical reactions. Baku: Elm; 1993.

[13] Gladyshev GP, Tsepalov VF. Testing of chemical compounds as stabilizers for polymeric materials. Usp Khim 1975;44(10):1830–50.

[14] Emanuel NM, Denisov ET, Maizus ZK. Liquid phase oxidation of hydrocarbons. New York: Plenum Press; 1967.

[15] Scott G. Atmospheric oxidation and antioxidants. London: Elsevier; 1993.

[16] Tsepalov VF, Kharitonova AA, Gladyshev GP, Emanuel NM. Determination of the rate constants and inhibition coefficients of phenol antioxidants with the aid of model chain reactions. Kinet Catal 1977;18(5): 1034–9.

[17] Zeinalov EB, Kossmehl G, Kimwomi RRK. Synthesis and reactivity of antioxidants based on vernolic acid and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionic acid. Angew Makromol Chem 1998;260:77–81.

[18] Zeinalov EB, Schroeder HF, Bahr H. Determination of phenolic antioxidant stabilizers in PP and HDPE by means of an oxidative model reaction, paper 3. In: proceedings of the sixth international plastics additivies and modifiers conference – Addcon World 2000.

[19] Schroeder HF, Zeynalov EB, Bahr H, Rybak Th. A quantitative study of sterically hindered phenol and amine stabilisers in PP materials, paper 20. In: proceedings of the seventh international plastics additives and modifiers conference – Addcon World 2001. Berlin; 2001.

[20] Kimwomi RRK, Koβmehl G, Zeinalov EB, Gitu PM, Bhatt BP. Polymeric antioxidants from vernonia oil. Macromol Chem Phys 2001; 202(13):2790–6.

[21] Zeynalov EB, Allen NS. Simultaneous determination of the content and activity of sterically hindered phenolic and amine stabilizers by means of an oxidative model reaction. Polym Degrad Stab 2004;85(2):847–53.

[22] Schroeder HF, Zeynalov EB, Bahr H, Rybak Th. Analysing the content of antioxidants in PP materials. Polym Polym Compos 2002; 10(1):73–82.

[23] Van Hook JP, Tobolsky AV. The thermal decomposition of 2,2′-azo-bis-isobutyronitrile. J Am Chem Soc 1958;80(4):779–82.

[24] Allen NS. Degradation and stabilisation of polyolefins. In: Allen NS, editor. London: Elsevier Science Publishers Ltd; 1983. p. 337 [chapter 8].

[25] Allen NS, McKellar JF. Photochemistry of dyed and pigmented polymers. London: Applied Science Publishers Ltd; 1980. p. 247.

[26] Rabek JF. Photostabilisation of polymers: principles and applications. London: Elsevier Applied Science Publishers; 1990.

[27] Allen NS, Edge M. Fundamentals of polymer degradation and stabilisation. Chichester: Chapman and Hall; 1992.

[28] Allen NS, Edge M, Sandoval G, Ortega A, Liauw CM, Stratton J, et al. Factors affecting the interfacial adsorption of stabilizers on to titanium dioxide particles (flow microcalorimetry, modeling, oxidation and FTIR studies): nano versus pigmentary grades. Dyes Pigments 2006; 70(3):192–203.