

LIST OF PUBLICATIONS BASED ON PRESENT WORK

1. Studies on antioxidants, 1 "Phenolic antioxidants as stabilizers for polypropylene" in *Die Angewandte Macromolekulare Chemie*. (in press).

A. Raja, V.N.S. Pendyala, S.F. Xavier, A.C. Shah, K.B. Nair*
2. Studies in Antioxidants Part II "Melt Stabilisation of Isotactic Polypropylene with Thiosemi-carbozones" in *Polymer Degradation and Stability* (in press).

Atul. Raja, V.N.S. Pandya, S.F. Xavier, A.C. Shah and K.B. Nair*
3. Studies in Antioxidants Part III "2-[3,5-di-tert-butyl-4-hydroxy phenyl]] hydrazine carbothioamide as melt stabilizer for unstabilised polypropylene "(communicated).
4. Studies in Antioxidants Part III. "Melt Stabilisation of unstabilised IPP with 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene]-N-Phenyl-hydrazine carbothioamide" (Communicated).
5. Studies in antioxidants Part IV, "4,4'-di{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl ether, as melt stabiliser for unstabilised IPP" (Communicated).
6. "Synthesis and Characterisation of some new antioxidants based upon hindered phenols" (Communicated).

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Studies on antioxidants, 1 Phenolic antioxidants as stabilizers for polypropylene

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SUMMARY:

A group of phenolic antioxidants was synthesized, characterized and the performance of these antioxidants in polymer processing was tested in the polymer melt by multiple extrusions. The change in melt flow was observed and compared with the change in melt flow by use of commercially available antioxidants. All the antioxidants examined had the same phenolic stabilization moiety but varied in the size of the substituents in the para-position of the aromatic ring. Increasing length of the side chain considerably influences the behaviour of the antioxidants in the polymer and thus their effectiveness.

ZUSAMMENFASSUNG:

Eine Gruppe neuer phenolischer Antioxidantien wurde synthetisiert und charakterisiert; ihr Einfluß auf die Polymerverarbeitung wurde an Polymerschmelzen bei wiederholter Extrusion untersucht. Die Änderung des Schmelzflusses wurde gemessen und mit dem Verhalten bei Verwendung handelsüblicher Antioxidantien verglichen. Die untersuchten Verbindungen waren alle aus dem gleichen Phenylsegment aufgebaut, unterschieden sich aber in der Länge der para-Substituenten, die das Verhalten der Antioxidantien in Polymeren und somit ihre Wirkung entscheidend beeinflussen.

Introduction

Polypropylene undergoes extensive degradation under commercial processing conditions¹. Hydroperoxides are formed at a significant rate and these

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01 00 reactive intermediates decompose into radicals capable of promoting either
02 00 thermal or photooxidation. A variety of antioxidants has been used to inhibit
03 00 degradation at this critical stage in the life-cycle of thermally sensitive
04 00 polymers².

05 00 In the literature it was found that many of the new Antioxidants synthesized,
06 00 combine a hindered phenol group with another group containing nitrogen,
07 00 sulfur, triazines, phosphates, phosphites etc.³. This combination gives active
08 00 materials, having the advantage of two or more stabilizing moieties.

09 00 Wasser and Smith⁴ reported that tert-butyl groups at the ortho-position
10 00 and alkyl groups at the para-position resulted in the most effective antioxidant
11 00 activity in the alkyl phenolic type of antioxidants of which 2,6-di-
12 00 tert-butyl-4-methylphenol (BHT) is one of the best-known. Among 2,6-di-
13 00 tert-butyl-4-alkylphenols, a variation of the alkyl chain from methyl to n-butyl
14 00 did not cause any significant modification in the antioxidant activity⁵. It was
15 00 reported by Miller⁶ that an electron-donating group at the para-position of
16 00 the alkylphenols would enhance the antioxidant activity. On the other hand,
17 00 an electron-withdrawing group at the same position has been reported to retard
18 00 or completely eliminate the antioxidant activity^{6, 7}. Furthermore, it has been
19 00 observed that the removal of such an electron-withdrawing group from the
20 00 para position of 3,5-di-tert-butyl-4-hydroxybenzaldehyde resulted in the
21 00 recovery of antioxidant activity. 3,5-Di-tert-butyl-4-hydroxybenzaldehyde
22 00 regained antioxidant activity when it was converted into 3,5-di-tert-butyl-
23 00 4-hydroxybenzaldehyde-4'-isonicotinoylhydrazone⁷.

24 00 Antioxidants intended to provide protection during processing must be
25 00 capable of migrating freely throughout the polymer bulk to reach the large
26 00 number of initiation sites that are generated at elevated temperatures⁸. For
27 00 this reason, low-molecular-weight antioxidants like 2,6-di-tert-butyl-4-
28 00 methylphenol are preferred. However, BHT suffers from a major drawback
29 00 viz. high volatility. 2,6-Di-tert-butylphenol with long aliphatic groups
30 00 replacing the methyl group at the para-position has succeeded in reducing
31 00 volatility, but at the sacrifice of reduction of active —OH on a weight/weight
32 00 basis⁹.

33 00 Taking into account the above-mentioned facts, it was thought worthwhile
34 00 to synthesize new antioxidants by replacing the hydrogen atom of the methyl
35 00 group at the para-position of BHT by a long chain which is electron donating,
36 00 and to investigate the influence of molecular weight on the efficiency of these
37 00 antioxidants in isotactic polypropylene paying special attention to the changes
38 00 in melt flow index (MFI). This was achieved by converting the methyl group
39 00 into an aldehyde by using a method reported by Coppinger and Campbell¹⁰.



The aldehyde was then treated with p-hydroxybenzoic acid hydrazide to get the corresponding hydrazone. The hydroxy group at the 4'-position was replaced by different alkoxy groups. These alkyl derivatives were mixed with isotactic polypropylene (iPP) and were subjected to melt-mixing as well as to multiple extrusion. After multiple extrusion the melt flow behaviour of the extruded sample was studied. All the newly synthesized antioxidants were characterized by elemental analysis, IR and NMR spectral studies.

Experimental

Materials

2,6-Di-tert-butyl-4-methylphenol (BHT) was supplied by HICU, Bombay, ethanol, acetic acid, acetone, and potassium carbonate were obtained from BDH (England), p-hydroxy benzohydrazide, pentyl bromide and decyl bromide were from Aldrich Co. All the solvents used were of reagent grade and were purified by distillation.

3,5-Di-tert-butyl-4-hydroxybenzaldehyde was prepared according to a known procedure¹⁰.

Stabilized isotactic polypropylene (Indian Petrochemical Corporation Ltd., Baroda, India) with MFI grade 10 g/10 min was used for the experiments.

Syntheses

N'-(3,5-di-tert-butyl-4-hydroxybenzylidene)-4-hydroxybenzohydrazide (AO1): To 3,5-di-tert-butyl-4-hydroxybenzaldehyde (1 mmol) in ethanol (50 ml) were added p-hydroxybenzohydrazide (1 mmol) and acetic acid (2 drops). The reaction mixture was refluxed for 12 h and the excess alcohol was then distilled off. The product obtained was crystallized from ethyl alcohol, m. p. 273 °C; yield 76%. TLC (Acmes TLC grade silica gel with 13% CaSO₄ as binder, 0.2 mm on a glassplate; benzene/methanol 90:10 (v/v)) showed a single spot at $R_f = 0.345$.

$C_{22}H_{28}N_2O_3$ (368.48)	Calcd.	C 71.7	H 7.66	N 7.60
	Found	C 71.30	H 8.01	N 7.68

IR spectrum (KBr): ν_{max} 3700 cm^{-1} (OH), 3150–3250 cm^{-1} (NH), 1610 cm^{-1} (C=N), and 1640 cm^{-1} (C=O).

¹H NMR, δ (DMSO-*d*₆): 1.5 (18H, s, C(CH₃)₃), 6.9 (2H, d, ArH), 7.5 (2H, s, ArH), 7.9 (2H, d, ArH), 8.3 (1H, s, CH=N) ppm.

The signal for the aldehydic proton of 3,5-di-tert-butyl-4-hydroxybenzaldehyde appears at $\delta = 9.8$ ppm; that particular signal disappears in the case of 3,5-di-tert-butyl-4-hydroxybenzaldehyde-4'-hydroxybenzoylhydrazone and the new signal for —CH=N appears at $\delta = 8.3$ ppm.



N'-(3,5-di-tert-butyl-4-hydroxybenzylidene)-4-alkoxybenzohydrazides (AO₂, AO₃):
To AO₁ (1 mmol) in dry acetone (50 ml), pentyl or decyl bromide (1 mmol) was
added. The reaction mixture was refluxed for 32 h, poured into ice-cold water and
recrystallized from petroleum ether, to yield 3a and 3b, respectively.

N'-(3,5-di-tert-butyl-4-hydroxybenzylidene)-4-pentyloxybenzohydrazide (AO₂),
m. p. 186 °C, yield 55%.

C ₂₇ H ₃₈ N ₂ O ₃ (438.61)	Calcd.	C 73.94	H 8.73	N 6.39
	Found	C 73.45	H 8.21	N 6.40

¹H NMR, δ (CDCl₃): 1.4 (27H, s, C(CH₃)₃, C₄H₉), 4.0 (2H, t, CH₂), 5.4 (1H, s, OH) 6.9 (2H, d, ArH), 7.4 (2H, s, ArH), 7.9 (2H, d, ArH) ppm.

N'-(3,5-di-tert-butyl-4-hydroxybenzylidene)-4-decyloxybenzohydrazide (AO₃), m. p.
80 °C, yield 62%.

C ₃₂ H ₄₈ N ₂ O ₃ (508.74)	Calcd.	C 75.55	H 9.51	N 5.51
	Found	C 75.29	H 9.26	N 5.45

¹H NMR, δ (CDCl₃): 1.3 (37H, s, C(CH₃)₃, C₉H₁₉), 3.9 (2H, t, CH₂), 5.4 (1H, s, OH), 6.8 (2H, d, ArH), 7.4 (2H, s, ArH), 7.9 (2H, d, ArH) ppm.

Characterization

IR spectra were run on a Shimadzu-IR 4108 spectrophotometer. ¹H NMR spectra
were measured on a 90 MHz Perkin Elmer-50 spectrophotometer with tetramethyl-
silane as the reference. Elemental analysis were carried out at our micro-analytical
laboratory using Coleman analyser models 29 and 33.

Results and discussion

From 3,5-di-tert-butyl-4-hydroxybenzaldehyde, novel antioxidants
N'-(3,5-di-tert-butyl-4-hydroxybenzylidene)-4-hydroxybenzohydrazide(AO₁),
N'-(3,5-di-tert-butyl-4-hydroxybenzylidene)-4-pentyloxybenzohydrazide
(AO₂), and N'-(3,5-di-tert-butyl-4-hydroxybenzylidene)-4-decyloxybenzo-
hydrazide (AO₃) were prepared. Their ¹H NMR spectra are shown in Fig. 1.

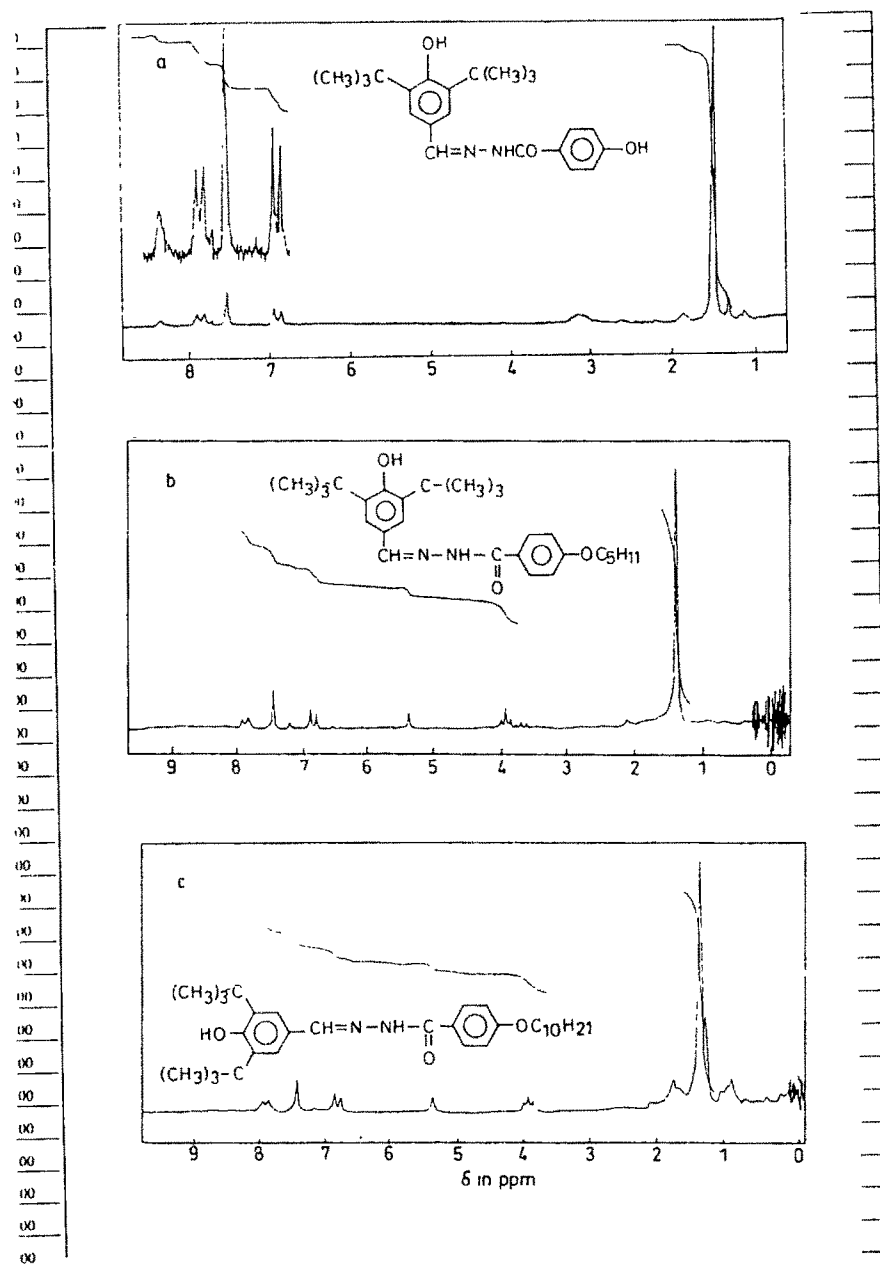


Fig. 1. ^1H NMR spectra of synthesized antioxidants; a) AO_2 , b) AO_3 , c) AO_4 .

01 00 *Testing of polypropylene with the synthesized antioxidants AO₁–AO₃*

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The performance of antioxidants in polymer processing was tested in the polymer melt and assessed by multiple extrusion. The multiple extrusion of isotactic polypropylene was carried out with the suitable concentration of the commercially available antioxidants as well as synthesized antioxidants. To find out the suitable concentration of the antioxidants, melt-mixing of isotactic polypropylene was carried out initially by using commercially available antioxidants and synthesized antioxidants. The stability of a polymer melt viscosity was controlled by the measurement of torque as a function of time and temperature in a Brabender plastograph.

To 50 g of stabilized isotactic polypropylene (iPP) in powder form (MFI 9.6 g/10 min), 0.05 g (0.1 wt.-%) of calcium stearate, 0.025 g (0.05 wt.-%) of Irganox 1010 and 0.015 to 0.045 g (0.03 to 0.09 wt.-%) of synthesized antioxidant AO₁ in various proportions were added. These mixtures were melt-mixed at 230 °C at a screw speed of 15 r.p.m. for 1 min and then at a screw speed of 60 r.p.m. for 5 min. The melt material was taken out, cooled, and the mixing process was repeated four times under similar conditions. The torque values were recorded for all the five mixing cycles.

Similarly, melt-mixing was carried out with available antioxidants like Ultrinox, Weston, butylated hydroxytoluene (BHT). Torque values were recorded for T₁, T₆ and T_{max}. Torque values for T_{max} were plotted against the number of mixing cycles for different antioxidants as shown in Fig. 2.

Different antioxidants, commercially available like BHT, ULTRANOX, and newly synthesized antioxidants (AO₁), (AO₂) and (AO₃) were used for stabilized PP and simple iPP (without antioxidant). Using each antioxidant together with calcium stearate and Irganox 1010, the iPP was extruded on Brabender Plasticoder at 210 °C. With each antioxidant the extrusion was repeated six times in order to see the stability of the basic polymer.

The degradation studies of iPP were carried out by measuring the melt flow behaviour of the extruded sample. The MFI was determined according to ASTM standard (D 1238–88).

From Fig. 2, it has been observed that the synthesized as well as the standard antioxidants have shown reasonable activity against the degradation of iPP which is indicated by a reasonable retention of the torque values. Among the four concentrations studied, the torque value was found to be maximum in case of 0.025 wt.-% content of the synthesized antioxidant. Based on this observation, the concentration of 0.025 wt.-% was selected for further studies.

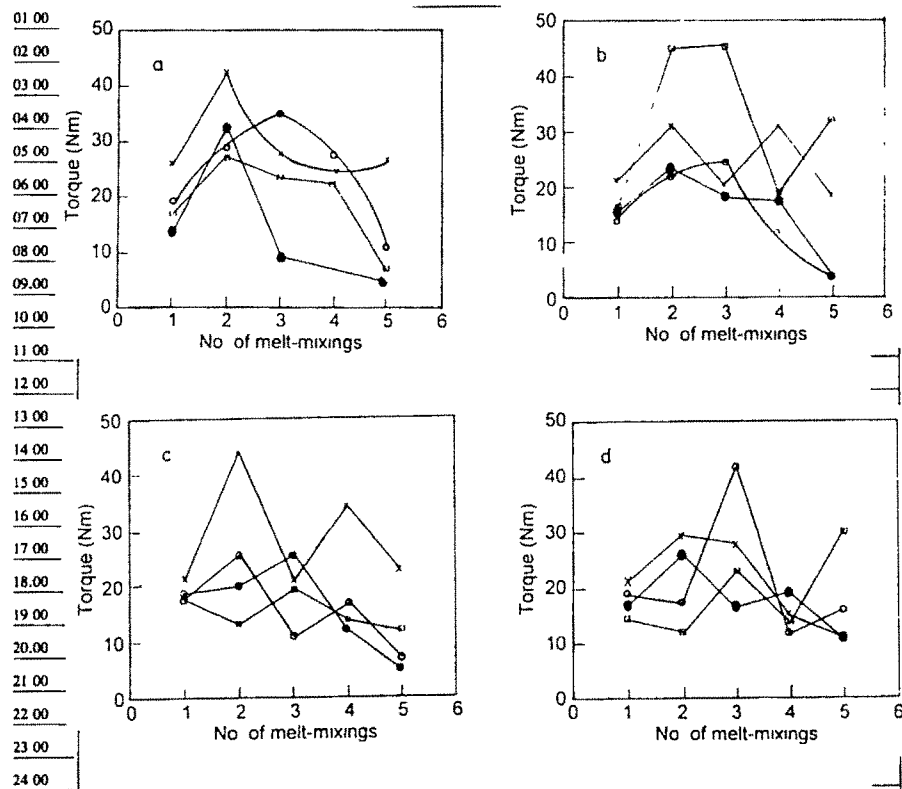


Fig. 2. Torque values plotted against the number of melt mixings for iPP stabilized with (●) BHT, (×) Weston, (○) Ultrinox, and (□) AO₁; stabilizer concentration: a) 0.015, b) 0.025, c) 0.035, d) 0.045 wt.-%.

The melt flow behaviour of all the extruded samples was determined on a Devenport instrument at 230°C.

In Fig. 3, the MFI of the extruded sample was plotted against the number of extrusion.

From Tab. 1 and Fig. 3, it can be seen that MFI of the extruded sample iPP increases as the number of extrusions increases from 1 to 6, both with the commercially available antioxidant and the synthesized antioxidants. When simple iPP without any antioxidants was subjected to multiple extrusion, the MFI values increase rapidly from the 1st to the 6th extrusion to, i.e. 10.2 to

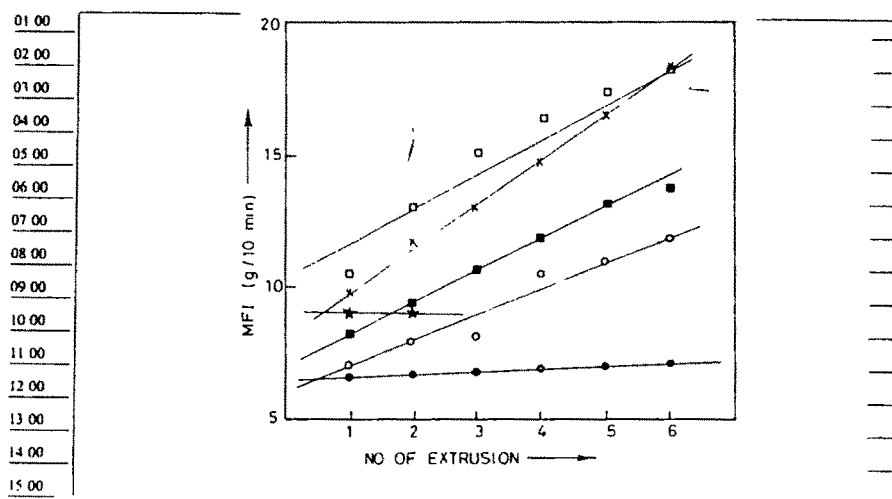


Fig. 3. Melt flow index plotted against number of extrusion; (○) BHT, (●) Ultrinox, (□) iPP, (☆) AO₁, (×) AO₂, (■) AO₃.

Tab. 1. Processing stability of iPP; multiple extrusion at a melt temperature of 210 °C and a screw speed of 25 r.p.m.; iPP with 0.1 wt.-% of calcium stearate and 0.025 wt.-% of stabilizer.

Additives	Melt flow index MFI 230/2.16 g/10 min)					
	Extrusion cycles					
	1	2	3	4	5	6
— ^a	10.21	13.72	15.04	16.35	17.46	18.57
BHT	7.06	7.85	8.01	10.14	11.01	11.82
Ultrinox	6.45	6.65	6.69	6.92	6.92	7.38
AO ₁	9.01	9.34	— ^b	— ^b	— ^b	— ^b
AO ₂	10.01	11.75	13.06	14.91	16.67	18.93
AO ₃	8.43	9.32	10.62	11.91	13.63	14.35

^a iPP without stabilizer.

^b ■

01.00 18.57. This shows that without any antioxidants, the degradation of iPP is very
02.00 fast, this probably because of the formation of free radicals.

03.00 However, with commercially available antioxidants like BHT, the MFI
04.00 values do not increase rapidly. The MFI values are quite stable up to the 6th
05.00 extrusion, after that it increases very fast. With Ultrinox the MFI values
06.00 remain constant which means that the melt viscosity as well as the molecular
07.00 weight of the polymer remain intact; thus Ultrinox is an effective antioxidant.

08.00 From Tab. 1 and Fig. 3 it has been observed that AO_1 is not a suitable
09.00 antioxidant for iPP because of its high melting point (273°C). The extrusion
10.00 of iPP was carried out at 210°C , at this temperature the antioxidant AO_1
11.00 could not intrude into the polymer matrix of iPP and thus could not show any
12.00 effect.

13.00 The MFI values of AO_2 indicate that the degradation of iPP in presence of
14.00 AO_2 is equal to isotactic polypropylene without any antioxidant. So it is not
15.00 a suitable antioxidant for iPP, too.

16.00 With synthesized antioxidant AO_3 , the MFI values are quite comparable
17.00 with that of iPP with BHT. The MFI values are quite stable up to the 3rd
18.00 extrusion. So it is an effective antioxidant.

19.00 In case of antioxidants AO_2 and AO_3 the melting points are 186°C and
20.00 80°C , respectively, and since the extrusion of iPP was carried out at 210°C ,
21.00 at this temperature AO_2 and AO_3 could intrude into the polymer matrix.

22.00 On comparing the structures of antioxidants AO_2 and AO_3 , it is observed
23.00 that when the hydroxy group at the 4'-position is replaced by a pentyloxy
24.00 group, resulting antioxidant is not effective, however, when this hydroxy group
25.00 is replaced by a decyloxy group, the activity is enhanced.

26.00 The molecular weights of antioxidants AO_2 and AO_3 are 438 and 508,
27.00 respectively. Tochacek and Sedlar¹¹ reported that in case of series of phenolic
28.00 antioxidants, the maximum performance was observed for the molecular
29.00 weight of 500–550. This is in good accord with that observed for the stabiliza-
30.00 tion efficiency of antioxidant AO_3 .

31.00 More than the molecular weight, probably, the influence of the individual
32.00 chemical structure is responsible for the maxima of performance. Each struc-
33.00 ture is characterized by its physical properties and its behaviour in polymer.
34.00 The presence of performance maxima reported by different authors^{11–13} of
35.00 different molecular weights support this idea.

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39.00 Ltd. for the award of a Junior Research Fellowship.



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