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Antioxidative Efficiency of Substituted *N*-Phenyl *N*-Pyrazolyl-3, *N*-Phenyl *N*-Benzimidazolyl-2 and *N*-Benzthiazolyl-2 *N*-Benzimidazolyl-2 Amines in the Thermooxidation of Polypropylene

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ABSTRACT

The antioxidative efficiency of three different series of nitrogen containing compounds derived from N*-phenyl* N*-(1,5-diphenylpyrazolyl-3),* N*-phenyl* N*-benzimidazolyl-2 and* N*-benzthiazolyl-2* N*-benzimidazolyl-2 amines in the thermal oxidation of polypropylene were compared on the bases of the results of chemiluminescence, dynamic thermogravimetry and differential scanning calorimetry. The effect of substituents on phenyl rings and on the 1-nitrogen of benzimidazol was examined with respect to the antioxidative behaviour of the compounds. Bad dispersion of the additive and its volatility seems to have a large effect, in some cases, on the results of antioxidation tests.*

INTRODUCTION

The antioxidative efficiency of 3-anilino-1,5-diphenyl pyrazols with various substituents X and Y in the phenyl rings in the thermal oxidation of polypropylene, has been studied[1,2] with emphasis on finding the optimum X and Y substitution. It has been observed that the compounds with the substituents $X = CH_3$ and $Y = NO_2$, or $X = H$ and $Y = NO_2$ are the best of Series A. In oxygen at 190°C they result in an induction period for oxidation

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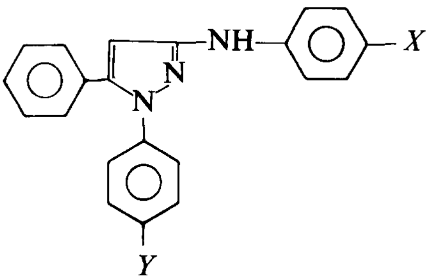
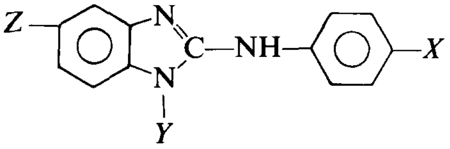


	X	Y
1	H	H
2	CH_3	H
3	CH_3	Br
4	CH_3	NO
5	CH_3	OCH_3
6	Cl	H
7	Cl	OCH_3
8	H	NO
9	H	CH_3
10	H	Br
11	H	OCH_3

Series A

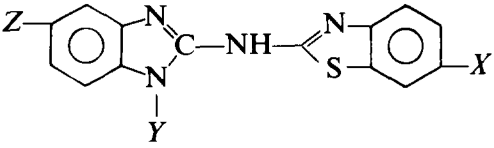
which is about 10 times greater than that for 2,6-ditert.butyl 4-methyl phenol. In addition, the order of antioxidative efficiency determined by chemiluminescence, differential scanning calorimetry and thermogravimetry is in good agreement.

This paper extends the study of the aminic antioxidants to *N*-phenyl *N*-benzimidazolyl-2 amines (Series B) and *N*-benzthiazolyl-2 *N*-benzimidazolyl-2 amines (Series C) where the sequence of efficiency determined by thermogravimetry differs from that determined by differential scanning calorimetry (DSC) or chemiluminescence. Since all the experiments were performed with originally powdered samples and since the additives of Series B and C have melting points mostly above the temperature of the oxidation experiment, this discrepancy gives rise to the question as to which



$Z = H; NO_2$
$Y = H; CH_3; C_6H_5$
$X = H; OCH_3$

Series B



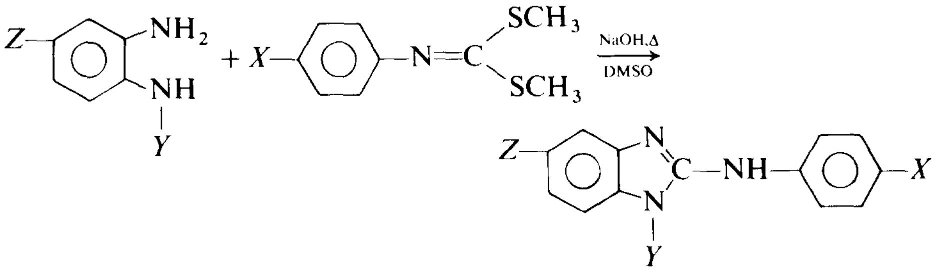
$Z = H; NO_2$
$Y = H; CH_3; C_6H_5$
$Z = H; OCH_3; NO_2$

Series C

process in the oxidised sample we actually measure by the above methods. The role of possible non-homogeneous dispersion and of poor compatibility of an antioxidant with the polymer is also of interest in this respect.

EXPERIMENTAL

All compounds examined as antioxidants of polypropylene were prepared by analogy with the methods previously described.[2–4] The additives of Series B were synthesised according to the general scheme and the compounds of Series C were prepared by a similar route.[4,5]



The additives, at a predetermined concentration, were mechanically mixed with powdered (<0·1 mesh) unstabilised isotactic polypropylene Tatren TH-411 (Slovnaft, Bratislava). The molecular weight of the polymer determined viscometrically was 220 000.

The antioxidative efficiency was determined by the chemiluminescence method (100 mg of powdered sample in glass ampoules in an oxygen atmosphere),[2] by DSC and by thermogravimetric measurements.

Measurements of DSC were made with apparatus DSC-2M (made in the USSR) at a heating rate of 8 K/min. In all cases, the additive, mixed with polypropylene at a concentration of 5×10^{-2} mol/kg, was placed as a powder (5 mg) in gastight aluminium pans.

Thermogravimetric measurements were carried out on a MOM Derivatograph (produced in Hungary). The concentration of additive was 5×10^{-2} mol/kg, the overall sample weight was 50 mg, the programmed heating rate was 10 K/min and the air flow rate was 6 litres/h.

RESULTS AND DISCUSSION

The induction periods of thermooxidation of polypropylene determined by the chemiluminescence method (Table 1) show the order of efficiency within a given series. The antioxidative behaviour of compounds of Series A was

TABLE 1

Induction Periods, τ, of Thermal Oxidation of Polypropylene Determined by the Chemiluminescence Method for Series A, B and C

Series	*Additive*	*Substituents*			*Mp*[a] (°C)	*c*[a] (*mol/kg* × 10^2)	*T*[a] (°C)	τ (*min*)
		X	*Y*	*Z*				
A	1	H	H	H	147	1	190	49
	2	CH_3	H	H	81			72
	3	CH_3	Br	H	121			87
	4	CH_3	NO_2	H	139			144
	5	CH_3	OCH_3	H	104			72
	6	Cl	H	H	96			44
	7	Cl	OCH_3	H	126			26
	8	H	NO_2	H	200			103
	9	H	CH_3	H	134			49
	10	H	Br	H	159			77
	11	H	OCH_3	H	124			58
B	1	H	H	H	179	2	190	28
						2	200	19
	2	OCH_3	H	H	180	2	190	59
						2	200	25
	3	H	H	NO_2	275	2	190	12
						5	190	16
	4	OCH_3	H	NO_2	204	2	190	26
						2	200	20
						5	190	32
	5	H	CH_3	H	191	2	190	43
	6	OCH_3	CH_3	H	153	2	190	94
						2	200	25
						5	190	161
	7	H	C_6H_5	H	163	2	190	15
						2	200	9
	8	OCH_3	C_6H_5	H	81–83	2	190	45
C	1	H	H	H	300	5	160	7
	2	OCH_3	H	H	300			8
	3	NO_2	H	H	300			8
	4	H	H	NO	300			8
	5	OCH_3	H	NO	300			12
	6	NO_2	H	NO	300			7
	7	H	CH_3	H	220			8
	8	OCH_3	CH_3	H	195			30
	9	NO_2	CH_3	H	220			12
	10	H	C_6H_5	H	254			178

[a] *c* is the initial concentration of additive in the polypropylene; *T* is the temperature of the test; *Mp* is the melting point of the additive.

discussed previously[2] with regard to the push–pull effect of substituents.[6] The experiments with Series B show that the melting point of the compounds studied may have an additional physical effect on the antioxidant efficiency, affecting their solubility in the polymer melt and/or their volatility. Comparing the induction periods for non-substituted antioxidants of Series A and B we see that the efficiency of the latter series is several times lower.

This may be due to the different electron densities on carbon 3 of the pyrazol ring and on carbon 2 of the benzimidazol ring[7] which influence the basicity of the nitrogen of the aminic group. These effects are related to radical forming processes from the parent amine (electron or H atom transfer).

A simple comparison of the particular effect of each substituent, X, Y or X, Z pairs separately and in mutual interaction can be seen from the values of the constants m, n, o and p of the empirical equation:

$$\tau_{ij} = mc_i + nc_j + o\sqrt{c_i c_j} + pc_o \qquad (1)$$

Constants m and n express the contributions of group i and j to the overall induction period, τ_{ij}, the constant o denotes synergistic or antagonistic effects of the two groups in one molecule while p is a contribution of the non-substituted derivative. c_i, c_j and c_o are the concentrations of the respective groups in mol/kg. Constants of the empirical equation (1) calculated from inhibition periods of chemiluminescence are given in Table 2. From values of the constant o of series A, it may be seen that only for $i = X = CH_3$ and $j = Y = NO_2$ does synergism exist between substituents while in all other cases examined antagonism prevails. On the other hand, for analogous

TABLE 2
The Values of the Coefficients m, n, o and p of Eqn (1) of Substituent Pairs X, Y and X, Z for Series A and B

Series	*Substituents*			*Coefficients*[a]			
	X	*Y*	*Z*	*m*	*n*	*o*	*p*
A	CH_3	Br	H	2300	2800	−1300	4900
	CH_3	NO_2	H	2300	5400	1800	4900
	CH_3	OCH_3	H	2300	900	−900	4900
	Cl	OCH_3	H	−500	900	−2800	4900
B	OCH_3	CH_3	H	1150	750	1000	1400
	OCH_3	C_6H_5	H	1550	−650	−50	1400
	OCH_3	H	NO_2	1550	−800	−850	1400

[a] m, n, o and p are in min kg/mol.

substituents in compounds B3 and B4 in Series B, a relatively low efficiency was observed. The synergistic effect was not observed except for $i = X = OCH_3$ and $j = Y = CH_3$.

The compounds substituted with NO_2 groups were below their melting temperatures during chemiluminescence measurements so the results could not be satisfactorily compared with others.

The order of efficiency in Series B determined by the chemiluminescence method at 190°C is

$$6 > 2 \geq 8 \geq 5 > 1 \geq 4 \geq 7 \geq 3$$

while at 200°C the difference in τ values is considerably lower (Table 1). With increasing temperature, the efficiency of the more effective compound B6 significantly decreases while that of B4 changes only slightly. The relatively high temperature coefficient of the values of τ which may be noted from experiments carried out at 190 and 200°C for additives B6 or B2 of Series B (Table 1) may be an indication of the more homogeneous initial dispersion of the additives B6 and B2 in the polymer as compared with additive B4, which has the higher melting point.

Increasing concentration of additives B3 and B4 leads to rather small increases of induction period (Table 1) at 190°C while additive B6, which is presumably more homogeneously dispersed in the polymer, shows a quite distinct increase of induction period.

Another indication of a qualitative difference in oxidising systems of initially powdered stabilised polypropylenes may be seen from maximum values of chemiluminescence intensity (I_{max}). For compounds below their melting point (B3 and B4) I_{max} is comparable with that of pure polypropylene. Additives measured above their melting point show a maximum chemiluminescence intensity approximately twice as great (Fig. 1). The effect of melting point of the compounds investigated on the determination of their antioxidant efficiency is particularly obvious in Series C. The first six additives of this series in polypropylene which have melting points above 300°C have an induction period of thermal oxidation practically the same as for pure polypropylene, the oxidation experiments being conducted at 160°C.

For Series B, the non-isothermal DSC method carried out up to 550 K in closed pans gave approximately the same rating as the chemiluminescence method (Table 3). According to the temperature at which oxidation starts, samples B-2 and B-6 were again the best, while sample B-3 was the worst, being even worse than 4-methyl, 2,6-ditert. butyl phenol.

On the other hand, from dynamic TG traces of individual samples of series B (Fig. 2), we see that B4 is best. Also, all samples of polypropylene with additives show a higher thermal stability compared with pure

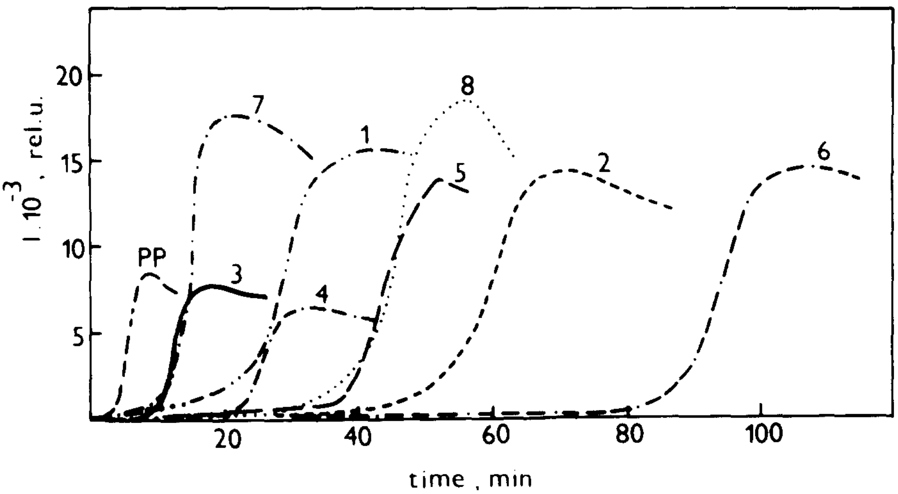


Fig. 1. Chemiluminescence intensity as a function of time for oxidation of polypropylene at 190°C in oxygen (Series B) (additives 1–8); initial concentration of additive 2×10^{-2} mol/kg.

polypropylene. In order to obtain a quantitative description of the TG curves, the equation

$$\ln\left(\frac{-\ln\{f[1-(1-w)]^m\}}{T^2}\right) = -\frac{E}{RT} + \ln\frac{AR}{\beta E}$$

was used, which was derived by Coats & Redfern[8] for non-isothermal thermogravimetry (w is the actual weight of sample, E and A are the

TABLE 3
Parameters Determined from DSC Measurements for Oxidation of Polypropylene in Series B

Sample	$T_{in}(K)^a$	$T_{max}(K)^a$
polypropylene	459	476
polypropylene + 4-methyl 2,6-ditert. butyl phenol	510	516
1	527	533
2	545	550
3	474	495
4	519	528
5	533	537
6	545	549
7	520	527
8	526	531

[a] T_{in} = temperature of the beginning of oxidation, T_{max} = temperature of the maximum of oxidation exotherm.

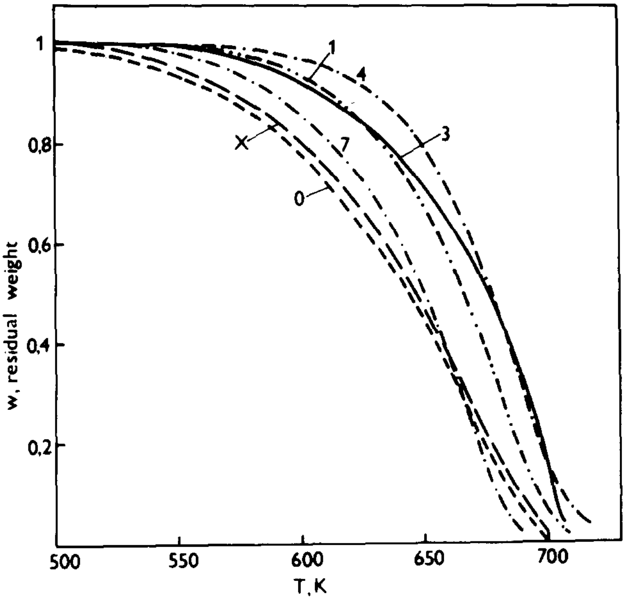


Fig. 2. Non-isothermal thermogravimetry studies of Series B; samples were heated in air at a rate of heating of 10 K/min. The initial amount of samples was 50 mg and the initial concentration of additive 5×10^{-2} mol/kg. O, pure polypropylene; X, 4-methyl, 2,6-di tert. butyl phenol.

activation energy and pre-exponential factor, T is temperature in K and β is the rate of heating in K/min). The factor m depends upon the kind of reaction investigated. It was shown[9] that, for higher initial weights of polymer, 2 is a reasonable value. For $m = 1$, the above equation and Coats–Redfern dependence for the reaction order $n = 1$ become identical.

The factor f is a correction factor which makes it possible to shift the values of E and A to the optimum value of the correlation coefficient in the long narrow valley of the plots of E and $\ln A$ parameters.[10] Thermogravimetric curves were evaluated in the interval $w = 1 - 0{\cdot}7$. The optimum values of E and $\ln A$ for a rate of heating of 10 K/min, an initial amount of additive of 5×10^{-2} mol/kg, 50 mg sample and an air atmosphere are summarised in Table 4. In parallel with increasing efficiency of antioxidant, the values of apparent activation energy and pre-exponential factor also increase. Decreasing values of E thus determine the sequence of efficiency, which, for Series B, is as follows:

$$B4 > B1 \geq B8 > B7 > B6 \geq B2 > B5 > B3$$
$$> \text{4-methyl 2,6-di tert.butyl phenol} > \text{pure polypropylene.}$$

Non-isothermal thermogravimetry, which is capable of reflecting the gradual improvement of the homogeneity of the system due to increasing

TABLE 4
Values of Apparent Activation Energy E and $\ln A$ Determined from Non-isothermal Thermogravimetry for 5×10^{-2} mol/kg Additive in Series B and C

Series	*Number of substituent*	*E (kJ/mol)*	*ln A (A is in min)*
	1	220	37·9
	2	181	30·2
	3	161	26·4
B	4	228	38·4
	5	174	29·9
	6	182	30·9
	7	194	34·3
	8	214	37·2
	pure polypropylene	130	22·1
	polypropylene + 4-methyl 2,6-ditert.butyl phenol	142	24·5
	1	112	17·2
	2	106	15·9
	3	103	15·5
	4	116	17·8
	6	114	16·7
	7	122	19·7
	8	127	19·9
	9	94	12·8
	10	129	20·0

temperature, gives the best rating for $i = X = OCH_3$ and $j = Z = NO_2$ as in Series A while the combination of OCH_3 and CH_3 (sample 6) is somewhere in the middle part of the scale. It should be remembered that a higher apparent activation energy corresponds to a shift of the TG curve to higher temperatures including the temperature of initial weight loss. The suppression, by inhibitor, of the radical chain oxidation reaction which may develop to its full extent only after complete consumption of inhibitor may have two features. The first is concerned with the effect of additive as an inhibitor for the whole volume of sample from the very beginning of the oxidation reaction. The observed TG curves are then steeper than in the second case when the inhibiting effect is negligible at temperatures below 200°C and becomes obvious only at higher temperatures after better homogenisation of the system. The additives of Series C give a quite different picture of non-isothermal TG plots (Fig. 3); the values of apparent activation energies are below the values for pure polypropylene (Table 4).

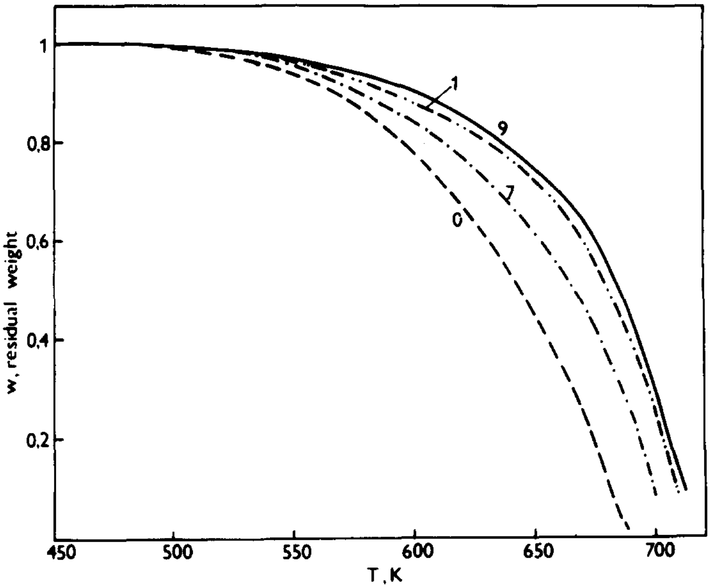


Fig. 3. Non-isothermal thermogravimetry studies of Series C (samples 1, 7, 9) in air. Rate of heating, 10 K/min; initial amount of sample, 50 mg; initial concentration of additive, 5×10^{-2} mol/kg. O is pure polypropylene.

Since all curves are shifted to the right on the temperature axis when compared with pure polypropylene, the additives are indeed functioning as antioxidants. The initial weight loss temperature is, however, comparable with that of pure polymer. As a consequence, the observed TG curves are less steep, which explains the lower values of apparent activation energy when compared with pure polypropylene. A similar conclusion also follows from chemiluminescence measurements with the additives of Series C where the beginning of the oxidation is comparable with that of pure polypropylene.

The higher melting point of an antioxidant corresponds obviously to its lower volatilisation from the polymer. The processes which are responsible for light emission (chemiluminescence experiments) and the release of heat (DSC experiments) are apparently located at the polymer surface or in its close proximity. Provided that additives are sufficiently volatile, they suppress the oxidation reaction on the surface of the polymer melt from the very beginning of oxidation; if not, the surface oxidation occurs but it cannot propagate throughout the volume of the sample and weight loss measurements may thus give different ratings than the chemiluminescence or DSC measurements. The interplay of the gradual homogenisation of the system and the different processes monitored by the respective methods seems thus to be of importance when comparing the results of different antioxidants tests.

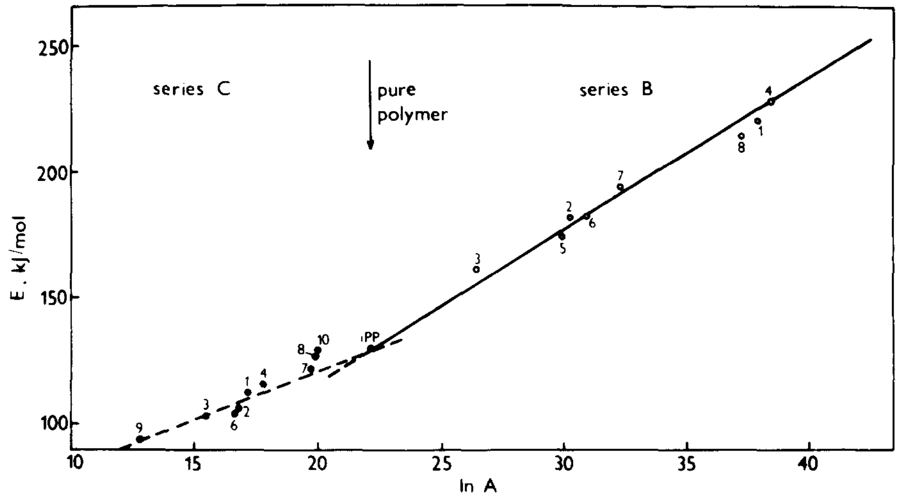


Fig. 4. Compensation of E and $\ln A$ from dynamic thermogravimetry of antioxidants in polypropylene (Series B and C).

The compensation between values E and $\ln A$ determined from non-isothermal thermogravimetry experiments for Series B and C (Fig. 4) indicates the difference in the behaviour of the two groups of additives; the greater the efficiency within groups B or A, the higher the value of activation energy for a given concentration of additive. The opposite seems to be true for additives of Series C where the lowest value of apparent activation energy indicates the best additive with the most pronounced effect in the high temperature region.

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