# Effects of metal chelates on the oxidation of polyolefins at high temperatures

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The oxidation of carboxy-terminated polybutadiene (CTPB) and polypropylene (PP) has been investigated at temperatures above 150°C. Studies have also been made of the effects on the oxidation of these polymers of a number of transition metal chelates, namely, the bis(3,5-diisopropyl salicylato) (DIPS) derivatives of Co(II), Ni(II) and Cu(II), bis(3,5-diisopropyl salicylato) hydroxyaquo Cr(III), the bis(*N*-n-butyl salicylaldimino) (NBS) compounds of Cu(II) and Ni(II), and bis(stilbene dithiolato)nickel (II) (NiSDT). At the temperatures concerned, the antioxidant activity of some of the chelates, in particular the DIPS compounds, was limited by their thermal stability. NiSDT was found to be a uniquely effective antioxidant at temperatures up to ~290°C. Mechanisms have been proposed to account for the dual role, as both catalysts and inhibitors of thermal oxidation, of the DIPS and NBS chelates.

## INTRODUCTION

Although the oxidation of polyolefins at relatively low temperatures has been extensively studied, relatively few investigations have been made of the reactions of these polymers with oxygen at temperatures higher than ~150°C.

When carboxy-terminated polybutadiene (CTPB) is exposed to air at 250°C, a tough black skin is formed on the surface and this completely protects the interior of the polymer against oxidation[1]. This skin owes its strength to the crosslinks formed during oxidation. It has also been shown that, at this temperature, anaerobic crosslinking and cyclization reactions occur in the bulk of the polymer[1].

When stereoregular polypropylene (PP) is heated in air at temperatures below the melting point, the oxidative degradation which takes place is largely confined to the amorphous parts of the sample, since the crystalline regions are impermeable to oxygen[2]. Studies of the oxidation of PP, below 140°C, have shown that the rate is also determined by sample thickness, and that, when this is less than 0.1 mm, the rate is no longer diffusion-controlled[3–5]. In the melt phase, it might therefore be expected that the film thickness, temperature and extent of conversion are the sole factors which determine the rate of oxidation of PP.

This paper reports the results of studies of the high temperature oxidation of CTPB and PP, and of the influence of NiSDT and a number of Schiff base and DIPS chelates on the oxidation of these polymers.

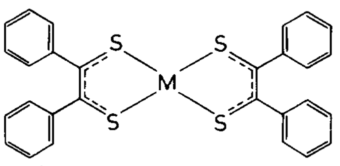
## EXPERIMENTAL

### *Materials*

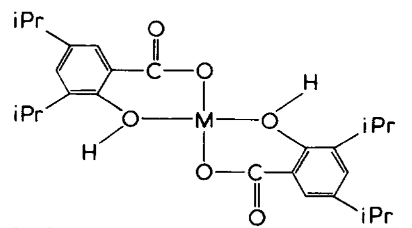
Carboxy-terminated polybutadiene (HC 434) was supplied by the Thiokol Corporation. The polymer, a thick viscous liquid of $\bar{M}_w$ 3960, contained 1.5 %w/w phenyl-β-naphthylamine as an antioxidant; 1,2 and *cis*-1,4 and *trans*-1,4 structures were present in the proportions 18, 24 and 56% respectively. The polymer was not cured prior to studies of its reactions. Polypropylene HF20 was supplied by ICI Ltd; it was isotactic, contained no added stabilizers and had a value for $\bar{M}_w$ of ~400 000.

The metal chelates were kindly provided by the Ministry of Defence, Explosives Research and Development Establishment, where they had been prepared according to previously described methods[6–10]. The structures of the compounds used are shown in *Figure 1*.

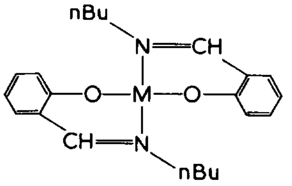
All the metal chelates were introduced into the polymers at a concentration of 1%w/w. The additives were incorpora-



Bis (stilbene dithiolato) metal (M)
(SDT)



Bis (3,5-diisopropyl salicylato) metal (M)
(DIPS)



Bis (*N*-n-butyl salicylaldimino) metal (M)
(NBS)

*Figure 1* Structures of the metal chelates

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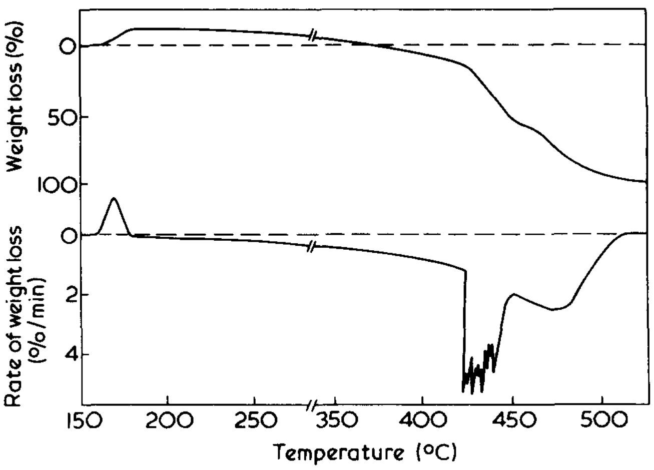


*Figure 2* T.g. and d.t.g. curves for CTPB heated in air at 3°C/min. Sample size, 8 mg

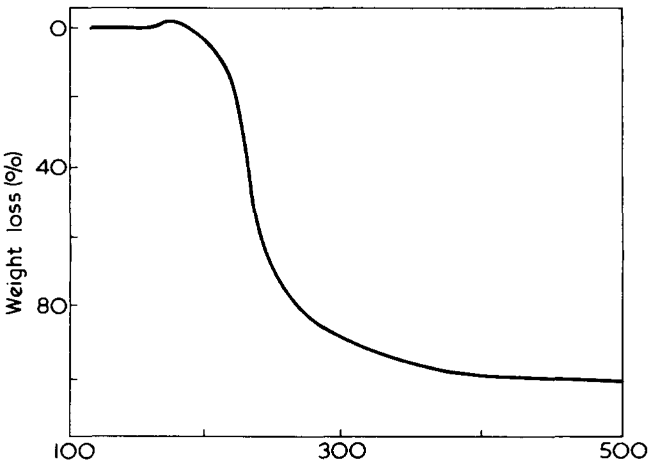


*Figure 3* T.g. curve for PP heated in air at 3°C/min. Sample size, 8 mg

ted into CTPB by dissolving them in a solution of the polymer in dichloromethane; the solvent was then evaporated off under vacuum at 45°C using a rotary film evaporator. Incorporation into PP was carried out by mixing the constituents, under nitrogen at 170°C, in a Brabender Plastograph. The resulting mixture was then placed between two sheets of aluminium foil and pressed into films at 185°C on a hand-operated press. A brass spacing sheet with a hole in the middle was used to ensure a uniform film thickness of 0.1 mm. The edge of the film, which had been in contact with the brass and exposed to air, was trimmed off and discarded.

### *Apparatus*

Thermal degradation experiments were carried out using a Mettler 'Thermoanalyser 2' thermobalance, which enabled the weight change, rate of weight change and temperature to be simultaneously recorded while the sample was heated at a constant rate. Throughout this work, standardized conditions of gas flow rate (60 $cm^3$/min), sample size (8 ± 1 mg) and heating rate (3°C/min) were used except where otherwise stated. A flat Pt/10% Rh crucible, of diameter 16 mm, was used in all the thermogravimetric (t.g.) runs. Samples of CTPB were smeared evenly over the surface of the crucible; whereas PP samples were cut from the polymer film.

Supplementary visual information about the oxidation of the polymers was obtained by hot-stage microscopy, which facilitated the interpretation of the t.g. curves and provided information which was otherwise unobtainable. Samples were heated at a constant rate in a Stanton Redcroft hot-stage and viewed through an Olympus X-TR stereo microscope. The specimens were illuminated by a quartz–halogen lamp and a fibre–optic light guide which gave a suitable source of cold light.

## RESULTS AND DISCUSSION

### *Oxidation of polybutadiene*

When CTPB is heated, no weight change is observed until the phenyl-β-naphthylamine antioxidant is used up and the polymer then rapidly gains weight as the concentration of peroxides increases until a maximum value is obtained (*Figure 2*). A surface film is formed which protects the interior of the polymer from oxidation until a temperature is reached where the rate of formation of anaerobic breakdown products exceeds their rate of diffusion out of the polymer[11]. After the surface film is ruptured, the underlying polymer rapidly reacts to form volatile products. Hot stage microscopy revealed that the former surface film ultimately remains as a char which is burnt off at higher temperatures (>450°C).

### *Oxidation of polypropylene*

When PP is heated in air, a very small gain in weight is observed after the sample has melted; this is due mainly to an increase in the concentration of hydroperoxides. Loss of weight follows the uptake of oxygen and the polymer is oxidized to leave only a small amount (~6%) of char (*Figure 3*). At higher temperatures this char is burnt off completely as can be seen clearly from the d.t.g. curves in *Figure 4* Changes in sample size resulted in large variations in the shape of the d.t.g. curves (*Figure 4*); this is probably attributable partly to diffusion control of the oxidation and partly to the melting behaviour of the polymer. Thus, when the effects of the metal chelates were compared, care was taken to ensure that equal weights of polymer were taken.

Unlike CTPB, which is oxidized to a protective surface film as a result of the addition of free radicals to C=C bonds, PP does not form a skin and the effect of oxidation is to cause chain scission and hence lower the melt viscosity. Hot-stage

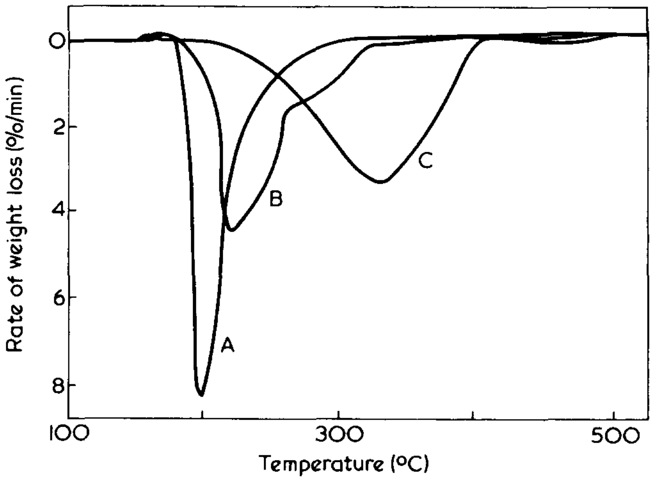


*Figure 4* The effect of sample size on the d.t.g. curve for PP heated in air at 3°C/min. Sample size: A, 0.7 mg; B, 9.6 mg; C, 101.0 mg

*Table 1* Effects of metal chelates on the oxidation of CTPB

| Metal chelate | Temperature of maximum rate of weight increase (°C)<br>Heating rate, 1°C/min | <br>Heating rate 5°C/min |
|---|---|---|
| None | 158 | 183 |
| NiSDT | 180 | 207 |
| CuNBS | 201 | 238 |
| CoDIPS | 166 | – |
| NiDIPS | 163 | 188 |
| NiNBS | 173 | 188 |
| CrDIPS | 161 | – |
| CuDIPS | – | 241 |

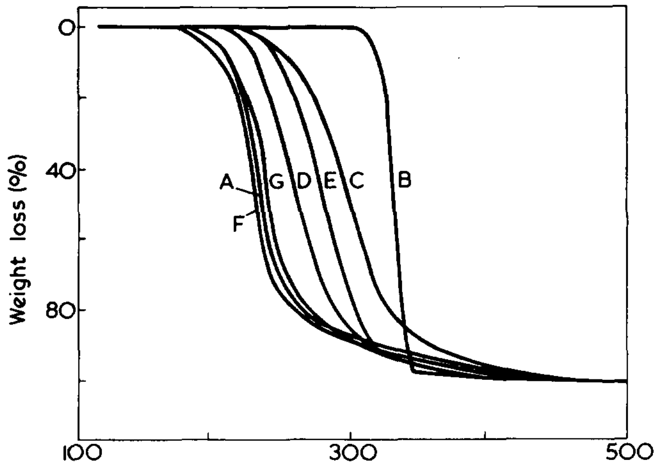


*Figure 5* The t.g. curves for PP heated in air at 3°C/min in the absence and presence of 1%w/w metal chelates. Sample size, 8 mg. A, No additive; B, NiSDT; C, CuNBS; D, CoDIPS; E, NiDIPS; F, NiNBS; G, CrDIPS

microscopy showed that at 160°C the polymer film melted without losing its shape. At 180°C, where the rate of oxidation is considerable, molten polymer was seen to flow away from the exposed top and sides of the sample. On attainment of a temperature of 210°C the oxidizing polymer melt was spread evenly over the whole of the crucible.

Discolouration was observed when samples were heated above 225°C. This was uneven and the discoloured patches ultimately remained as a char.

### *Effects of metal chelates*

Comparisons have been made of the effects of the additives on the oxidation of CTPB by heating samples of the additive-containing polymer in air at a constant rate, and measuring the temperature at which the weight gain due to peroxide formation takes place. All the metal chelates except CrDIPS functioned, to varying extents, as antioxidants in CTPB (*Table 1*), raising the temperature at which the maximum rate of weight gain occurred. This deferment to higher temperatures of the weight gain was however the only change observed in the t.g. curves of metal chelate-containing CTPB samples; the subsequent stages were completely unaffected.

The temperature at which the onset of weight loss occurs when PP is heated in air has been used to compare the effects of additives, as the temperature at which the maximum rate of increase in weight takes place cannot be accurately defined with very small weight gains. Again, the metal chelates functioned as antioxidants (*Figure 5* and *Table 2*), although both CrDIPS and NiNBS showed no measurable effects. NiSDT proved, however, to be an exceptionally good inhibitor for PP (although it was only mediocre in CTPB) and it stabilized the polymer up to a temperature of ~290°C. With the exception of the latter compound, the order of activity of the chelates in the two polymers is similar, viz:

$$\mathrm{CuDIPS} \hat{=} \mathrm{CuNBS} > \mathrm{CoDIPS} \hat{=} \mathrm{NiDIPS} > \mathrm{NiNBS} \hat{=} \mathrm{CrDIPS} \hat{=} 0.$$

When antioxidants are used at high temperatures, decomposition and volatilization of the additive may be important in determining the oxidative stability of the inhibited polyolefins. In order to assess the thermal stabilities of the metal chelates, their t.g. curves were obtained in air using a heating rate of 3°C/min. The results (*Figure 6* and *Table 3*) show clearly that the DIPS chelates are much less stable than the NBS chelates and that NiSDT starts to decompose only at the relatively high temperature of 282°C.

Although all the chelates lost weight in more than one stage (this can easily be seen from the differential thermogravimetric curves), it is the first stage of the decomposition which determines the effectiveness of the compounds as high temperature antioxidants. Thus, with PP, it can be shown that, on attainment of the temperature at which the polymer starts to lose weight, a substantial amount of NiSDT, CoDIPS and NiDIPS has already decomposed (*Table 4*).

*Table 2* Effects of metal chelates on the oxidation of PP. Heating rate, 3°C/min

| Metal chelate | Temperature of onset of weight loss (°C) |
|---|---|
| None | 184 |
| NiSDT | 289 |
| CuNBS | 213 |
| CoDIPS | 201 |
| NiDIPS | 213 |
| NiNBS | 175 |
| CrDIPS | 180 |

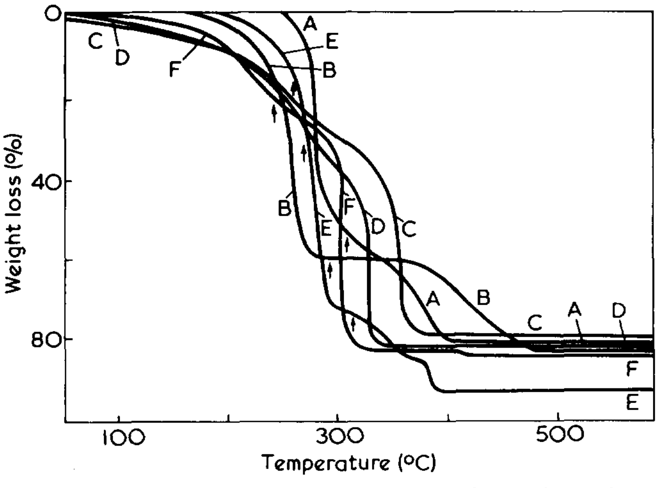


*Figure 6* The t.g. curves for metal chelates heated on their own in air at 3°C/min. Sample size, 8 mg. A, NiSDT; B, CuNBS; C, CoDIPS; D, NiDIPS; E, NiNBS; F, CrDIPS. † denotes end of first stage of weight loss

*Table 3* Thermal stability in air of the metal chelates. Heating rate, 3°C/min

| | | First stage of weight loss | | Residue | | |
|---|---|---|---|---|---|---|
| Metal chelate | No. of stages in t.g. curve | % | Temperature for 50%wt loss (°C) | % | Colour | Remarks |
| NiSDT | 4 | 54.9 | 282 | 18.5 | Grey | Previously reported decomposition temperature, 292°C[12] |
| CuNBS | 2 | 60.4 | 255 | 16.9 | Grey | – |
| CoDIPS | 3 | 20.2 | 213 | 20.6 | Black | Slowly lost weight at room temperature |
| NiDIPS | 2 | 31.4 | 241 | 17.6 | Grey–black | Started losing weight at ~80°C |
| NiNBS | 3 | 75.6 | 276 | 7.3 | Green–black | – |
| CrDIPS | 3 or 4 | 18.7 | 207 | 16.1 | Green | Slowly lost weight at room temperature |

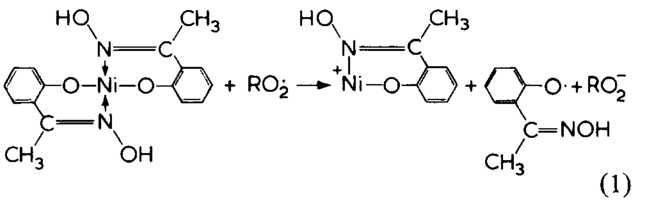
*Table 4* Extents to which the decomposition of the metal chelates affects the oxidation of PP

| Metal chelate | Temperature at which polymer starts to lose weight (°C) | Weight lost from metal chelate at temperature at which polymer starts to lose weight<br>Weight lost in first stage of decomposition of metal chelate |
|---|---|---|
| NiSDT | 289 | 0.81* |
| CrNBS | 213 | 0.10 |
| CoDIPS | 201 | 0.41 |
| NiDIPS | 213 | 0.39 |
| NiNBS | 164 | 0.01 |
| CrDIPS | 180 | 0.23 |

* Error is large as the rate of decomposition is high

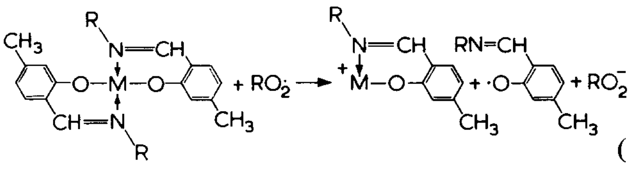
Other workers have reported that the principal effects of various Schiff base, oxime and DIPS chelates on the low-temperature thermal[13,14] and photochemical[15] oxidation of hydrocarbons and polyolefins are to give rise to an induction period and to cause the subsequent rate of oxidation to be increased. In this study, only antioxidant behaviour has been observed for the metal chelates. The reason for this is that the oxidation reaction immediately following the weight gain is diffusion-controlled, so that the pro-oxidant effects of the metal chelates are not apparent.

It has been suggested by Ranaweera and Scott[16] that the antioxidant effect of nickel oxime chelates is due to the ability of these compounds to reduce alkylperoxy radicals with the simultaneous formation of stabilized phenoxy radicals:



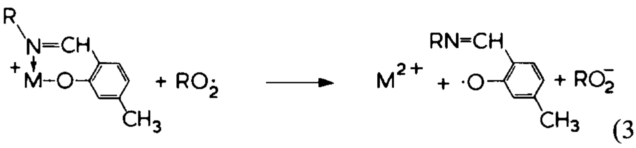
(1)

The behaviour of Schiff base chelates as oxidation inhibitors can be explained by a mechanism similar to reaction (1):



(2)

Furthermore, if reaction (2) does occur, then the further reaction:

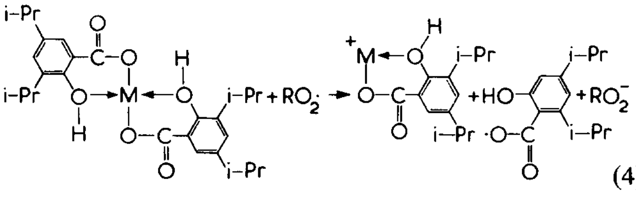


(3)

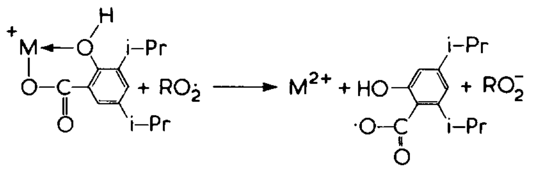
may take place.

One consequence of the reactions (1) and (2) would be the formation of free metal ions in the system. Thus, as soon as the metal chelate is broken down by alkylperoxy radical attack, the metal ions catalyse oxidation by induced decomposition of hydroperoxides. This mechanism explains the dual behaviour of Schiff base chelates as both inhibitors and catalysts, as well as the fact that ZnNBS shows no activity as a catalyst[14]. It accounts too for the observation that ZnNBS acts as a synergist with dilauryl-3,3'-thiodipropionate[14] (a known hydroperoxide decomposer). It is of interest, in this connection, that acetophenone oxime chelates, which have a somewhat similar structure to Schiff base chelates, strongly catalyse decomposition of the hydroperoxides[17].

A mechanism analogous to reactions (2) and (3) will also explain the behaviour of the DIPS chelates:



(4)



(5)

Although reactions (1)–(5) will account for the dual role of Schiff base, oxime and DIPS chelates as both inhibitors and promoters of oxidation, the species responsible for reduction of alkylperoxy radicals may be, not the metal chelate ($ML_2$) or the intermediate ($^+$ML), but the dissociated ligand itself ($L^-$). Thus the observed behaviour of the metal chelates can be equally well explained in terms of reactions (6)–(8):

$$ML_2 \rightleftharpoons {}^{+}ML + L^{-} \qquad (6)$$

$${}^{+}ML \rightleftharpoons M^{2+} + L^{-} \qquad (7)$$

$$L^{-} + RO_2\cdot \rightarrow L\cdot + RO_2^{-} \qquad (8)$$

instead of by reactions (1)–(5).

The latter mechanism, which also explains the experimental observations of Uri[13,14], is supported by numerous studies of the facile oxidation of phenolic anions to phenoxy radicals[18,19]. It can be seen that reactions (1)–(5) have the same net effect as reactions (6) and (8) or reactions (7) and (8). It is thus difficult to say with any certainty which mechanism is responsible for the observed effects of metal chelates on the oxidation of the polymers studied. However, the ease of dissociation would clearly be an important factor in determining the effectiveness of the additives as antioxidants, if inhibition occurs by reactions (6)–(8).

The contrast between the action of NiSDT in PP and in CTPB is of some interest. Since NiSDT is known to be an extremely powerful hydroperoxide decomposer[10,20], it is suggested that the reduced activity of NiSDT in CTPB is due to the fact that in the oxidized polymer a large proportion of the peroxidic oxygen is present in structures other than hydroperoxide groupings. Nevertheless, it is remarkable that NiSDT can stabilize polyolefins against oxidation at temperatures up to ~290°C.

## ACKNOWLEDGEMENTS

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