The Stress Cracking of Polyamides by Metal Salts. Part IV. Metal Nitrates

P. DUNN and G. F. SANSOM, *Australian Defence Scientific Service, Defence Standards Laboratories, Department of Supply, Melbourne, Australia*

Synopsis

The stress cracking of polyamide (nylon 6) by a number of metal nitrates in aqueous and nonaqueous solution has been investigated. Copper and zinc nitrates were the most active. Stress cracking parameters were determined and the sorption of the nitrates into nylon 6 film was studied using infrared techniques. Evidence of coordination of some metal nitrates when sorbed into nylon 6 was obtained.

INTRODUCTION

In earlier parts of this work we have described the action[1-3] of metal halides, thiocyanates, and cobaltothiocyanates on polyamide (nylon) materials. In part I it was briefly noted that lithium nitrate in methanolic solution was a weakly active stress cracking agent. In this paper, part IV, the behavior of a number of metal nitrates on nylon 6 is described.

EXPERIMENTAL

Materials

Nylon 6 extruded sheet (Trogamid B, Dyanamit-Nobel A.G., Troisdorf, Germany) and 0.001-in.-thick extruded, blown, unplasticized nylon 6 film as described in our earlier work[1-3] were again employed as standard materials.

Techniques

The stress cracking parameters, time to crack initiation (ΔT) and crack propagation rate (K) as defined in part I[1] were determined using tensile bar specimens. The stressed film technique described in part III[3] was employed to determine critical stress data.

Infrared spectra of nylon 6 films treated with metal nitrates were obtained using a Beckman IR 8 spectrophotometer by means of the techniques described earlier in parts II[2] and III.[3]

RESULTS

Qualitative Determination of Activity

Using simple evaluation trials, saturated aqueous and methanolic solutions of Cu(II), Zn, Co(II), Ni(II), Ca, Mg, and Li nitrates in contact with

TABLE I
Crack Propagation Data of Metal Salt Solutions[a]

	Aqueous saturated solution						Methanolic saturated solution			
	4000 psi		2000 psi		400 psi		4000 psi		2000 psi	
Metal salt	ΔT, min	K, in./min	ΔT, min	K, in./min	ΔT, min	K, in./min	ΔT, min	K, in./min	ΔT, min	K, in./min
Cu(NO$_3$)$_2$	instant	1.2×10^{-2}	instant	0.4×10^{-2}	instant	0.1×10^{-2}	instant	2.0×10^{-4}	40.0	2.2×10^{-4}
Zn(NO$_3$)$_2$	instant	0.1×10^{-3}	instant	0.8×10^{-4}	0.1	$<0.5 \times 10^{-4}$	instant	0.5×10^{-4}	0.1	2.6×10^{-5}
Co(NO$_3$)$_2$	instant	0.8×10^{-4}	instant	$<0.5 \times 10^{-4}$	0.2	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	0.2	$<0.5 \times 10^{-4}$
Ni(NO$_3$)$_2$	instant	0.5×10^{-4}	instant	$<0.5 \times 10^{-4}$	1.0	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	0.2	$<0.5 \times 10^{-4}$
Mg(NO$_3$)$_2$	instant	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	1.0	$<0.5 \times 10^{-4}$	instant	2.5×10^{-4}	0.2	0.6×10^{-4}
Ca(NO$_3$)$_2$	instant	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	1.0	$<0.5 \times 10^{-4}$	instant	1.7×10^{-4}	0.2	0.5×10^{-4}
ZnCl$_2$	instant	1.7×10^{-2}	instant	0.6×10^{-2}	0.1	0.3×10^{-2}	instant	0.5×10^{-1}	instant	0.3×10^{-1}

[a] Conditions: nylon 6 specimens, water content 3.5%, at 21°C.

stressed specimens of nylon 6 were found to be active agents, in that cracking was initiated at tensile stresses of 2000 psi, or less in some cases. Only one salt, lithium nitrate, was found to be inactive in aqueous solution, while all the metal nitrates were active in methanolic solution. In comparative trials, aqueous and methanolic solutions of the corresponding acetates and sulfates were found to be inactive.

Stress Cracking Parameters

The parameters, time to crack initiation (ΔT) and crack propagation rate (K), for various saturated aqueous and methanolic solutions of nitrates are shown in Table I. From these results it appears that only copper(II) nitrate is very active as a stress cracking agent, and this salt has an activity of the same order as that of 80% aqueous zinc chloride solutions previously described.

Critical stress data for the rupture of stressed nylon 6 films by $1M$ solutions of the nitrates tend to confirm these results and are shown in Table II.

TABLE II
Activity of Solutions of Metal Nitrates on Stressed Nylon 6 Films[a]

Metal nitrate in solution[b]	Time to rupture film, sec			
	5100 psi	4900 psi	4700 psi	4500 psi
$Cu(NO_3)_2$	6	31	266	>3600
$Ni(NO_3)_2$	23	97	1380	>366
$Co(NO_3)_2$	50	153	>3600	—
$Zn(NO_3)_2$	125	117	>3600	—
$Mg(NO_3)_2$	191	1000	>3600	—
$Ca(NO_3)_2$	232	1180	>3600	—

[a] Conditions: nylon 6 film, 0.001 in., water content 3.5%, at 21°C. The yield stress of the film as determined by a tensometer was 5310 psi for specimens cut parallel to the direction of extrusion.[3]

[b] Using a 1.0 M aqueous solution.

TABLE III
Infrared Data on Nylon 6 Film Treated with Metal Nitrates

Metal nitrate	Sorption value[a]	Nitrate absorption band		Crack propagation rate
		position, cm^{-1}	shift, cm^{-1}	in./min (at 2000 psi)
Cu(II)	1.308	1290	−80	4.0×10^{-3}
Zn	0.641	1296	−81	8.6×10^{-5}
Co(II)	0.475	1300	−72	1.0×10^{-5}
Ni(II)	0.246	1305	−78	s[b]
Mg	0.137	1332	−18	s[b]
Ca	0.058	1332	−18	s[b]

[a] The measure of sorption is the ratio of the absorbance of the nitrate band at the frequency shown and the C—H band of nylon 6 at 2940 cm^{-1} (D_{NO_3}/D_{CH}), after treatment for 90 min.

[b] Crack initiation occurred but crack propagation was extremely slow, that is, less than 1.0×10^{-6} in./min.

The activity of the metal nitrates is in the order

$$Cu(II) > Zn > Co(II) > Ni(II) > Mg > Ca > Li$$

and, with the exception of the nitrates of Mg, Ca, and Li, all were more active in aqueous solution than in methanolic solution.

The correlation between stress cracking activity and the rate of absorption of the active salts, which was previously demonstrated for metal thiocyanates,[3] is also shown by the metal nitrates. Data showing this correlation are given in Table III.

Effects of Sorption of Nitrates on Infrared Spectra

Nylon 6 films were treated with metal nitrates by immersing the films in aqueous saturated solutions of the salts for various periods of time. As described for the metal thiocyanates,[3] the sorption of the nitrate was followed by measuring the optical density of both the nitrate infrared absorp-
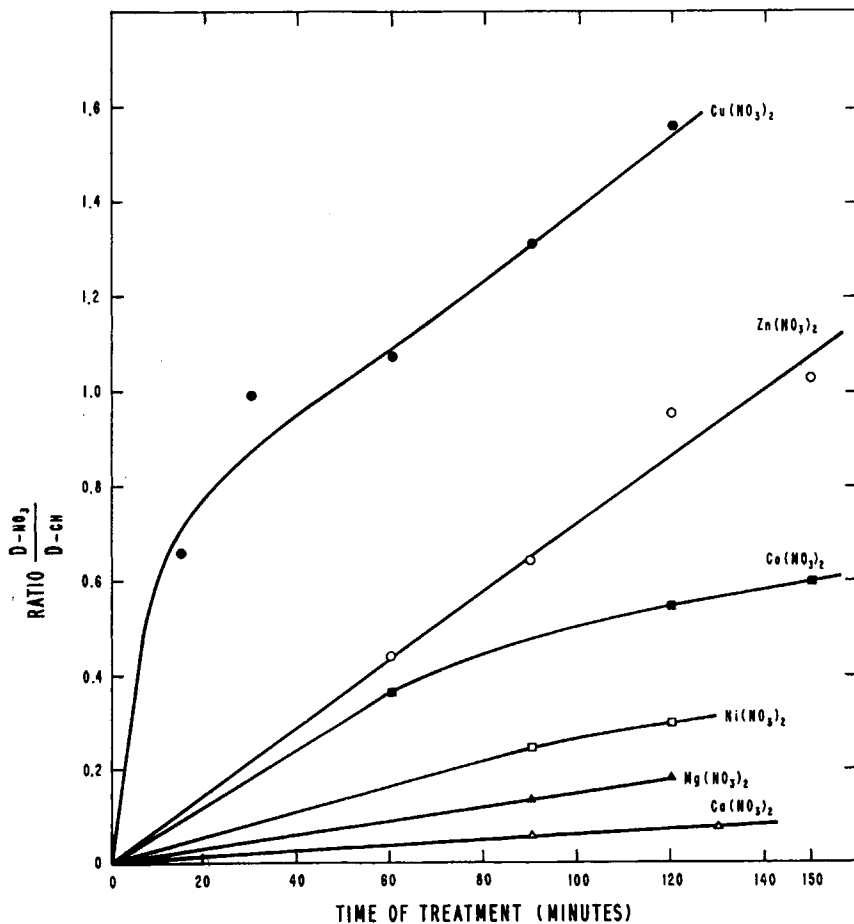

Fig. 1. Sorption of metal nitrates by nylon 6 film.

tion band and the nylon 6 C—H absorption band at 2940 cm^{-1}. Curves showing the sorption of the various nitrates into nylon 6 film are shown in Figure 1.

Spectra of nylon 6 films treated with copper(II) nitrate and zinc nitrate showed the development of a new absorbance band (Fig. 2) at 1590 cm^{-1},
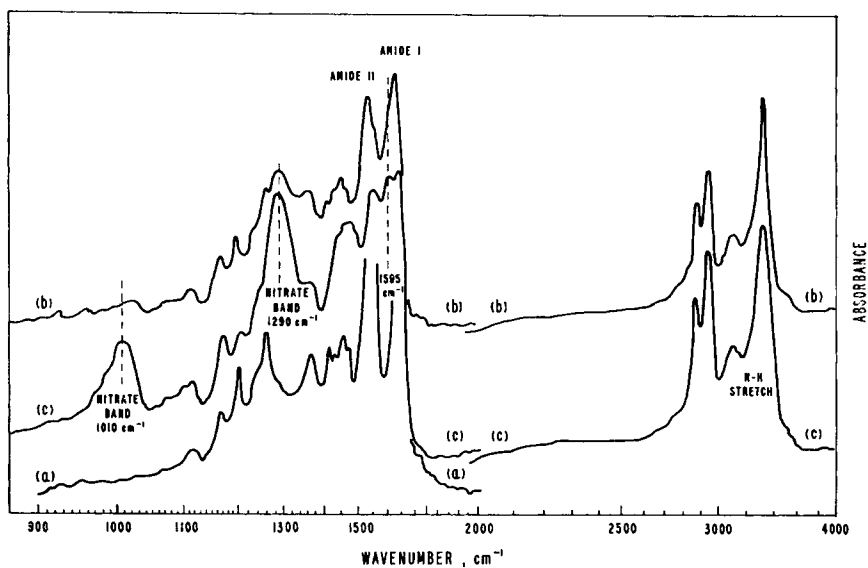

Fig. 2. Spectral changes in nylon 6 films treated with metal nitrates: (a) untreated; (b) treated with Zn(NO$_3$)$_2$ for 90 min; (c) treated with Cu(NO$_3$)$_2$ for 90 min.
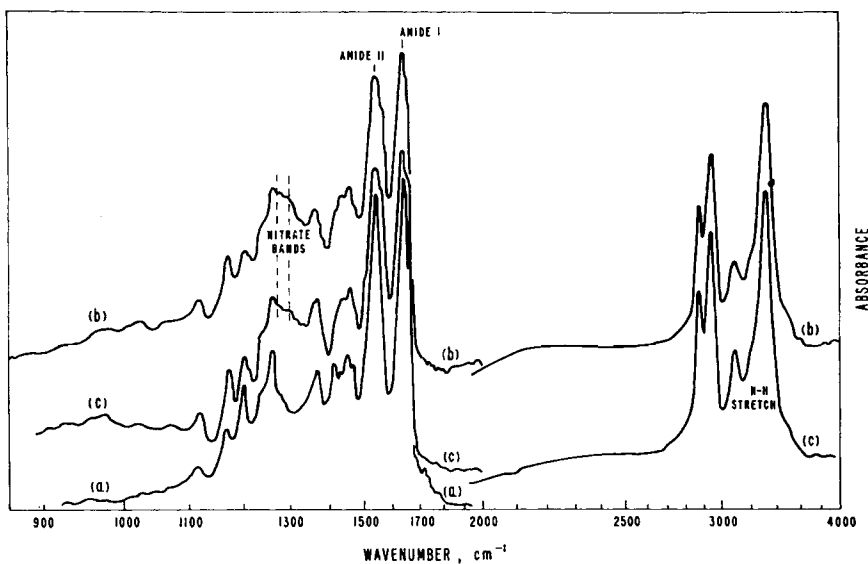

Fig. 3. Spectral changes in nylon 6 films treated with metal nitrates: (a) untreated; (b) treated with Co(NO$_3$)$_2$ for 60 min; (c) treated with Ni(NO$_3$)$_2$ for 90 min.

TABLE IV
Infrared Data on Nylon 6 Films Treated with Metal Nitrates

Nylon 6 film treatment[a]	Amide I band		Amide II band		Amide II overtone		New band
	Position, cm^{-1}	Shift, cm^{-1}	Position, cm^{-1}	Shift, cm^{-1}	Position, cm^{-1}	Shift, cm^{-1}	Position, cm^{-1}
Untreated nylon 6	1637	Nil	1537	nil	3080	nil	—
Copper(II) nitrate	1630	−7	1560	+23	3120	+40	1595
Zinc nitrate	1630	−7	1555	+18	3110	+30	1610
Cobalt(II) nitrate	1635	−2	1550	+13	3100	+20	1595[b]
Nickel(II) nitrate	1635	−2	1545	+8	3100	+20	1595[b]
Magnesium nitrate	1640	+3	1535	−2	3085	+5	—
Calcium nitrate	1640	+3	1540	+3	3085	+5	—

a Treated with saturated solutions at room temperature.
b Approximate position of shoulder.

which we have previously shown[2] is characteristic of certain agents designated as Type I metal salts. Other active metal salts which do not produce this characteristic absorption band have been designated as Type II. With the other Type I nitrates, this is less noticeable but is shown for nickel(II) nitrate and cobalt(II) nitrate in Figure 3. Characteristic shifts of the amide I, amide II, and amide II overtone bands were also noted and are tabulated in Table IV.

Also noted was a marked shift of the nitrate absorbance band, as shown in Table III, to a position consistent with the NO_2—O→M coordinated form. This occurred in nylon films treated with the Type I nitrates of Cu(II), Zn, Co(II), and Ni(II).

With the Type II nitrates of Mg, Ca, and Li, this effect was not noted and only minor shifts of the nitrate band occurred.

DISCUSSION

The infrared spectra of solid metal nitrates and of metal nitrates in tributyl phosphate (TBP) solution have been compared with the spectra of the same nitrates in aqueous solution by Katzin,[4] who concluded that in the nonaqueous solvent the nitrate ions are coordinated by the cation and that a similar interaction exists in the crystalline state for many metal nitrates.

We have found that the nitrate infrared absorption bands due to sorbed nitrates of Type I metal cations in polyamide (nylon 6) films correspond to the bands shown by such coordinated nitrates in nonaqueous solution and in the crystalline state. This is shown in Table V by the data for $Cu(NO_3)_2$ comparing reported infrared bands by Katzin,[4] Miller and Wilkins,[5] and Mathieu and Lounsbury[6] with our own spectral data. In each case the reported main band is italicized.

In the crystalline state, $Cu(NO_3)_2$ is reported[5] to be uncoordinated and to have its major band at 1378 cm^{-1}. In tributyl phosphate solution it is coordinated and has its major band shifted to 1285 cm^{-1}. Thus it would appear that copper nitrate is also coordinated when sorbed into nylon 6 film because the major nitrate band occurs at 1290 cm^{-1}. There is no evidence that copper nitrate exists in coordinated form in saturated aqueous solution.[6]

TABLE V
Infrared Absorption Bands of Copper Nitrate

Nitrate form	Nitrate absorption band
$Cu(NO_3)_2 \cdot 3H_2O$, crystalline[4]	836 cm^{-1}, *1378 cm^{-1}*, 1587 cm^{-1}, 1790 cm^{-1}
$Cu(NO_3)_2$, in TBP solution[4]	*1285 cm^{-1}*, 1495 cm^{-1}, 1543 cm^{-1}
$Cu(NO_3)_2$, saturated aqueous solution[6]	719 cm^{-1}, 1024 cm^{-1}, 1048 cm^{-1}, 1315 cm^{-1}, 1405 cm^{-1}, 1480 cm^{-1}
$Cu(NO_3)_2$, sorbed in nylon 6	746 cm^{-1}, 807 cm^{-1} 1010 cm^{-1}, *1290 cm^{-1}*

Similarly, the observed shifts of the major nitrate bands on zinc nitrate, cobalt(II) nitrate and nickel(II) nitrate (Table III) indicate that when sorbed into nylon 6 these nitrates are also present in the coordinated form.

It thus appears that nitrates of Type I metal cations, when sorbed into nylon 6 films, become coordinated by the cation despite their noncoordinated state in the aqueous solution from which they are sorbed. However, nitrates of the Type II cations remain uncoordinated on sorption into the nylon. This result is not unexpected in light of the previously proposed structures of complexes formed by Type I and Type II metal salts with polyamides[2] and is strong confirmation that coordination of the cation is usual with Type I cations, but not with Type II cations, in their interaction with polyamides.

References

1. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13,** 1641 (1969).
2. P. Dunn, and G. F. Sansom, *J. Appl. Polym. Sci.*, **13,** 1657 (1969).
3. P. Dunn, and G. F. Sansom, *J. Appl. Polym. Sci.*, **13,** 1673 (1969).
4. L. I. Katzin, *J. Inorg. Nucl. Chem.*, **24,** 245 (1962).
5. F. A. Miller, and C. H. Wilkins, *Anal. Chem.*, **24,** 1253 (1952).
6. J. P. Mathieu, and M. Lounsbury, *Dis. Faraday Soc.*, **9,** 196 (1950).