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# A STUDY OF THE PERFORMANCE OF SOME FIRST ROW TRANSITION METAL COMPLEXES OF 2-(p.TOLYL)PYRIDINE AND 4-AMINOQUINALDINE AS COLOURING MATERIALS FOR POLYSTYRENE

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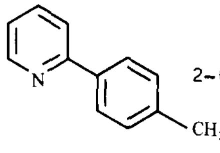
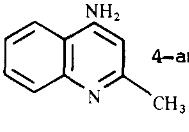
ABSTRACT
The chloro complexes of 2-(p.tolyl)pyridine and 4-aminoquinaldine with cobalt (II), nickel (II) and copper (II) have been prepared. The 4-aminoquinaldine complexes have polymeric octahedral structures. The cobalt and copper complexes of 2-(p.tolyl)pyridine have tetrahedral and tetragonal structures while the nickel complex has a polymeric octahedral structure. The initial decomposition temperatures of the complexes have been studied by thermogravimetry. The performance of the complexes as colouring materials for polystyrene has been investigated; weather resistance, light fastness, migration resistance and heat stability have been considered.

## INTRODUCTION

Investigations of transition metal complexes as colourants and stabilizers for polystyrene have been reported (1-3). The promising results have encouraged further studies using the chloro complexes of cobalt, nickel and copper with 2-(p.tolyl)pyridine and 4-aminoquinaldine.


2-(p.tolyl)pyridine


4-aminoquinaldine

The co-ordination chemistry of the complexes has been documented (4,5). The nickel complex of 2-(p.tolyl)pyridine and the complexes of 4-aminoquinaldine have polymeric octahedral structures. The cobalt and copper complexes of 2-(p.tolyl)pyridine have tetrahedral and tetragonal structures respectively. Information about the stereochemistry of the complexes was obtained from spectral and magnetic studies. Results from study of these compounds as colourants for polystyrene are reported.

## EXPERIMENTAL

Preparation of the complexes. The metal halide (1g) was dissolved in warm ethanol (50ml); 2-(p.tolyl)pyridine (5ml) was added and the warm solution was stirred. On cooling, the compound precipitated. It was filtered off, washed with a solution of 2-(p.tolyl)pyridine in ethanol and dried at 60°C. The 4-aminoquinaldine complexes were prepared in ethanolic solution using 4-aminoquinaldine and the hydrated metal halides (4).
The initial temperature of decomposition (Table 1) for each compound was obtained on a Stanton Redcroft STA 781 thermobalance working at a heating rate of 10°/min in static air.
Preparation of polystyrene samples. The pigmented polymer samples were produced from pigment (0.3g; 1%), zinc stearate (0.3g;1%) and polystyrene (30g). The polymer was added to a Brabender Plasticorder at 187°C and milled until fused. The other ingredients were then dispersed individually into the fused polymer and milled for 30 min. The samples were then compression-moulded at 150°C.
Testing procedures. The weather resistance of the polystyrene samples was studied by exposing them for six months (beginning of November 1988 to end of April 1989) on the roof at Napier Polytechnic, Edinburgh. Two sets of samples were used, supported by a wooden board; one set faced south at 45° and the other was horizontal.
The lightfastness of both coloured and uncoloured samples of polystyrene was examined by exposing half of each of the samples to a xenon lamp for 320 hours. While xenon hour equivalents of daylight exposure must be viewed qualitatively rather than absolutely, it has been

shown by the Research Association for the Paper and Board Printing and Packaging Industries (Leatherhead, Surrey) (6) that 10 hours in xenotest equipment is equivalent to four days exposure facing south during summer months and would not be far from the annual mean figure. The lightfastness of coloured samples was assessed using a 1-8 blue wool scale standard (7). The migration resistance of the polystyrene samples was measured using a compression set. It involved sandwiching the coloured polymer samples between two pieces of white pigmented polystyrene. The sandwich was left in the compression set at room temperature for 14 days.
The effects of acid and alkali on coloured and uncoloured polystyrene samples were studied by immersing the samples in distilled water, dilute acid ($H_2SO_4$, 2mol/$dm^3$) and dilute alkali (NaOH, 2mol/$dm^3$) and measuring changes after 28 days using a reflection densitometer.
The dispersibility of the colour in the polystyrene was observed during the addition of the transition metal compounds to the polymer in a Brabender and by qualitative visual examination of the pressed samples.
The heat stability was examined by taking six samples of each coloured polystyrene and six of uncoloured polystyrene on melinex sheet and placing in an air oven at 170ºC. Every five minutes up to 30min, samples of each coloured polystyrene and of the uncoloured polymer were removed and compared with a control.
The transparency of the transition metal compounds was examined using an Eel Opacimeter.

## RESULTS AND DISCUSSION

The colours and initial temperatures of decomposition of the transition metal compounds are listed in Table 1. Their performance as colourants for polystyrene is given in Table 2. The densitometer readings for samples exposed to dilute acid or dil. alkali are given in Table 3.

| Compound | Colour | Decomposition Temperature (K) |
|---|---|---|
| $Co(C_{12}H_{11}N)_2Cl_2$ | Blue | 415 |
| $Ni(C_{12}H_{11}N)_2Cl_2$ | Green | 418 |
| $Cu(C_{12}H_{11}N)_2Cl_2$ | Blue | 421 |
| *$Co(C_{10}H_{10}N_2)_2Cl_2$ᵃ | Turquoise | 487 |
| *$Ni(C_{10}H_{10}N_2)_2Cl_2$ᵃ | Green | 433 |
| *$Cu(C_{10}H_{10}N_2)_2Cl_2$ᵃ | Green | 448 |

TABLE 1. Stoichiometry, colour and initial decomposition temperature of compounds.
* reference 4;
a anhydrous compounds obtained by heating the hydrated compounds on a thermobalance at a fixed temperature to constant weight.

$C_{12}H_{11}N_2$ = 2-(p.tolyl)pyridine
$C_{10}H_{10}N_2$ = 4-aminoquinaldine

TABLE 2. Performance properties. E=excellent, G=good, FG=fairly good, F=fair, P=poor.
light resistance; blue wool scale 1-8 where 8 is the dye of highest lightfastness
* visual assessment, densitometer readings are shown in Table 3.

| Properties | Weather Resistance | Light Resistance | Migration Resistance | Acid Resistance* | Alkali Resistance* | Heat Stability | Dispersibility | Opacity % |
|---|---|---|---|---|---|---|---|---|
| Compounds | | | | | | | | |
| $Co(C_{12}H_{11}N)_2Cl_2$ | F | 3 | E | G | G | E | G | 57.2 |
| $Ni(C_{12}H_{11}N)_2Cl_2$ | G | 5/6 | E | E | G | E | P | 64.3 |
| $Cu(C_{12}H_{11}N)_2Cl_2$ | FG | 4 | E | G | G | E | G | 59.6 |
| $Co(C_{10}H_{10}N_2)_2Cl_2 2H_2O$ | F | 4 | E | E | E | E | G | 83.0 |
| $Ni(C_{10}H_{10}N_2)_2Cl_2 1.5H_2O$ | FG | 4/5 | E | E | E | E | G | 82.6 |
| $Cu(C_{10}H_{10}N_2)_2Cl_2 2.5H_2O$ | E | 8 | E | E | E | E | E | 100 |

| Compound | Initial | Acid | Alkali | Water |
|---|---|---|---|---|
| | | ← After 28 Days → | | |
| $Co(C_{12}H_{11}N)_2Cl_2$ | 0.90 | 1.18 | 1.03 | 0.98 |
| $Ni(C_{12}H_{11}N)_2Cl_2$ | 0.80 | 0.88 | 0.97 | 0.91 |
| $Cu(C_{12}H_{11}N)_2Cl_2$ | 0.86 | 0.71 | 0.74 | 0.69 |
| $Co(C_{10}H_{10}N_2)_2Cl_2 2H_2O$ | 1.25 | 1.22 | 1.09 | 1.18 |
| $Ni(C_{10}H_{10}N_2)_2Cl_2 1.5H_2O$ | 1.06 | 1.04 | 1.11 | 1.12 |
| $Cu(C_{10}H_{10}N_2)_2Cl_2 2.5H_2O$ | 2.20 | 2.06 | 2.00 | 1.90 |

TABLE 3. Acid and alkali resistance tests. Densitometer readings.

Of the compounds tested, only $Cu(C_{10}H_{10}N_2)_2Cl_2.2.5H_2O$ had excellent weathering properties and showed no change after six months. The compound $Ni(C_{12}H_{11}N)_2Cl_2$ was rated good although slight darkening occurred after 30 days. The compounds $Ni(C_{10}H_{10}N_2)_2Cl_2.1.5H_2O$ and $Cu(C_{12}H_{11}N)_2Cl_2$ were classed as fairly good for weathering resistance but showed significant darkening after 30 days. The compounds $Co(C_{10}H_{10}N_2)_2Cl_2.2H_2O$ and $Co(C_{12}H_{11}N)_2Cl_2$ darkened badly over the period of the test and were rated as only fair; the change commenced after approximately 30 days. These observations were in line with the ratings for lightfastness on the blue wool scale.

All the compounds, when present in polystyrene, had excellent resistance to migration at room temperature. When the sandwiched polystyrene was separated, no indication of colour was observed on the white polystyrene.

The compounds showed excellent resistance to water, acid and alkali when immersed for 28 days at room temperature, with the exceptions of $Cu(C_{12}H_{11}N)_2Cl_2$ which faded slightly in acid and alkali, $Co(C_{12}H_{11}N)_2Cl_2$ which darkened slightly in acid and alkali, and $Ni(C_{12}H_{11}N)_2Cl_2$ which darkened slightly in alkali. The samples all showed excellent heat stability.

The compounds dispersed well into polystyrene and were qualitatively rated good to excellent. The only exception was $Ni(C_{12}H_{11}N)_2Cl_2$ which was difficult to disperse and was classed poor.

The opacities of the samples were determined using an Eel opacimeter. The complexes of 2-(p.tolyl)pyridine gave low readings; the complexes of 4-aminoquinaldine were significantly more opaque, particularly the copper complex.

## CONCLUSIONS

The complexes of 4-aminoquinaldine showed better performance as colourants for polystyrene than the complexes of 2-(p.tolyl)pyridine. In particular, the copper complex of 4-aminoquinaldine produced excellent in all the tests. The tests on the cobalt, copper and nickel complexes of 2-(p.tolyl)pyridine indicated that the compounds were unlikely to be useful as colourants for polystyrene.

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