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## Synthesis and properties of rubber-steel cord adhesion promoter nickel borate acylate<sup>①</sup>

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**[Abstract]** The synthesis of nickel borate acylate (NBA), a kind of rubber-steel cord adhesion promoter (AP), through nickel carbonate, borate and mixed carboxylic acid was studied. Nickel carbonate could be prepared by the reaction of nickel sulfate with sodium carbonate in aqueous solution. After strong stirring for 2 h, the mixed nickel carboxylate could be synthesized by the reaction of nickel carbonate with isooctanoic acid and acetic acid. The mole ratio of these chemicals was 1: 1: 1. NBA was synthesized by reaction of mixed nickel carboxylate with tributyl borate under strong stirring at 200~ 250 °C for 6 h. By detecting and comparing with 680C product from Manobond Company of England, the NBA synthesized through isooctanoic acid and tributyl borate is very similar with 680C in IR data, 300% fixed extension strength, tensile strength, hardness and cure curve. However, tensile failure extensibility and hot air aging of NBA are a little lower than those of 680C. The experimental results show that NBA can be used as rubber-steel cord AP.

**[Key words]** nickel borate acylate; adhesion promoter; nickel carbonate; borate

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### 1 INTRODUCTION

Adhesion promoters (APs) are usually added in the processing and manufacturing of rubber composite materials such as steel wire radial ply tyres, conveyor belts, and reinforced hoses in order to make the combination of metallic materials with rubber stronger, improve the quality of rubber products and prolong their service life<sup>[1, 2]</sup>. The popular APs mainly include cobalt salts of organic carboxylic acids (i. e. cobalt naphthenate, cobalt stearate) and cobalt borate acylate (CBA, i. e. 680C product of Manobond Co., England)<sup>[3~ 12]</sup>, and also nickel salts<sup>[3, 6, 12]</sup>. The metal nickel is far cheaper than the metal cobalt, while production cost of nickel salts is lower than that of cobalt salts. However, the property of cobalt salts as APs is better than that of nickel salts. So cobalt salts are more popularly used<sup>[4, 5, 7~ 12]</sup>. China is very rich in natural resources of nickel which provides ample raw materials for preparing of nickel-containing compounds. As nickel and cobalt have similar chemical properties, so we replaced cobalt by nickel and synthesized a compound, nickel borate acylate (NBA), which was similar with structure of CBA. The experimental results show that the NBA synthesized with nickel carbonate, isooctanoic acid and tributyl borate would be used as rubber-steel wire APs.

### 2 EXPERIMENTAL

#### 2.1 Main instruments and reagents

The main reagents were nickel sulfate, sodium carbonate, acetic acid and tributyl borate, and all were chemical purity; isooctanoic acid was a laboratory reagent.

The main instruments used in experiment were motor stirrer, organic synthesizer, vacuum pump, 10ZG gas chromatography, Perkin-Elmer 983 IR spectrum instruments.

#### 2.2 Experimental procedure

Nickel carbonate was synthesized by the reaction of nickel sulfate and sodium carbonate. Add 0.2 mol nickel carbonate, some isooctanoic acid, acetic acid and solvent into 250 mL three-neck glass flask. After stirring and refluxing for a period of time, the reaction system was changed into distilling apparatus to remove all solvent and water produced in the reaction, then get intermediate product intermediate mixed nickel carboxylate. Afterwards the distilling apparatus should be changed into the former reaction system again, and add some tributyl borate into the flask, stir and reflux for a fixed time, then remove by-product *n*-butyl acetate by reduced pressure distillation, and pour out at once, then get solid product NBA.

### 3 RESULTS AND DISCUSSION

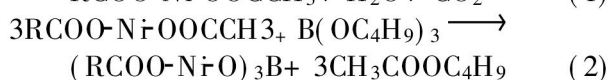
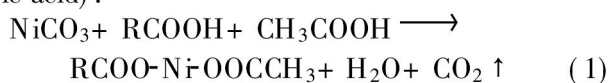
#### 3.1 Synthesis route

Because there was no research report for synthesis of NBA, we designed and performed the experi-

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ment according to the synthesis method of cobalt borate acylate<sup>[4]</sup>.  $\text{Ni}(\text{OH})_2$  was prepared through the reaction of nickelous sulfate solution with sodium hydroxide solution, then mixed with acetic acid and isooctanoic acid. This acid-base neutralization reaction should be performed easily. However, many experiment results show that  $\text{Ni}(\text{OH})_2$  was difficult to react with aliphatic acids, and some of  $\text{Ni}(\text{OH})_2$  did not react even by heating for a long time. This indicated that  $\text{Ni}(\text{OH})_2$  prepared by this method is not reactive enough in that maybe solubility product of  $\text{Ni}(\text{OH})_2$  ( $8 \times 10^{-19}$ ) too small to react with higher fatty acids which are not strong in acidity. So we used basic nickel carbonate or nickel carbonate, prepared under a given condition in our laboratory, as source of nickel, and found that they were active enough to react with mixed carboxylic acids. Therefore, synthesis routes for NBA were determined as follows, nickel carbonate as initiative compound (RCOOH represents isooctanoic acid):



### 3.2 Preparation of nickel carbonate and its reactivity

Nickel carbonate can be prepared by the reaction of nickel sulfate with sodium carbonate in aqueous solution. Attention should be paid to two problems: first, fractional conversion of nickel should be high; second, reactivity of nickel carbonate should be good. Our experiment results indicated that when pH value of reaction system is controlled from 8.5 to 9.0 at the end of reaction, collect the precipitation, wash and dry it, then we can get the reactive nickel carbonate, a light green particle in appearance with 48.9% (mass fraction) of nickel (49.5% in calculation). Fractional conversion of nickel in the reaction was more than 99.9%.

The reaction of nickelous carbonate with monocarboxylic aliphatic acid is not so easy as the common neutralization, because the acid is too weak. By experiments on mixture ratio, the methods of adding

reactant and drying temperature of nickel carbonate, it is found that nickel carbonate can be prepared with good reaction activity through stirring at 60 °C for 0.5 h in reaction system, filtrating, washing and drying to the constant mass, which can react with isooctanoic acid at room temperature and give out lots of carbon dioxide.

### 3.3 Preparation of mixed nickel carboxylate

Mixed nickel carboxylate can be prepared according to reaction (1). It is a solid-liquid phase reaction, so the reaction should be carried out under strong stirring at reflux temperature in order to quicken the reaction speed. From reaction (1) the mole ratio of nickel carbonate, isooctanoic acid and acetic acid was 1:1:1, which, in fact, should be 1:1:1.1 as a result of experiments. The effect of reaction time on preparation of mixed nickel carboxylate was investigated, as shown in Table 1.

Table 1 shows that acid amount in distillate decreases gradually with increasing reaction time, and nickel carbonate has consumed almost completely after reacting for 1.5 h. The reaction time should be selected 2 h in order to make nickel carbonate to be consumed fully. From experiments No. 4 and No. 5 in Table 1 the amount of real consumed acid was more than theoretical amount 0.4 mol, it might be because of the volatilization of acetic acid.

In order to make the next borate acylation reaction take place smoothly, it should be guaranteed that there is no water in the reaction system when reaction (1) finished. Otherwise, tributyl borate will be hydrolyzed by the existing water. So it is necessary to add an inert organic solvent (IOS), benzene, in the reaction system to remove water by distillation (see Table 2).

Table 2 indicates that the amount of distilled water increases with addition of IOS, because IOS carries water over which is included in mixed nickelous carboxylate.

### 3.4 Preparation of NBA

NBA was prepared according to reaction (2). In order to make the reactant molecules contact completely, the reaction should be carried out at higher

**Table 1** Effect of reaction time on preparation of mixed nickel carboxylate

No.	Reflux time / h	Amount of acid in distillate / mol	Real consumed acid / mol	Mole ratio of nickel to real consumed acid
1	0.5	0.064	0.356	1: 1.78
2	1.0	0.045	0.375	1: 1.88
3	1.5	0.023	0.390	1: 1.99
4	2.0	0.010	0.410	1: 2.05
5	2.5	0.008	0.412	1: 2.06

**Table 2** Effect of inert organic solvent (IOS) on removal of water (g)

No.	Without addition of IOS		Addition of IOS		
	1	2	3	4	5
Amount of removed water/g	2.61	3.15	3.62	3.61	3.65

temperature and be stirred strongly. In fact the mixed materials in reaction flask is still heavy bodied at 200~ 250 °C. The reflux should be performed for a period of time in order to make it react completely, and butyl acetate be distilled completely. The effect of reaction time on this reaction is listed in Table 3.

**Table 3** Effect of reaction time on nickel content in product

Reaction time/h	2.0	2.5	3.0	4.0	5.0	6.0	6.5	7.5
w (Ni) / %	17.0	19.2	21.1	21.8	22.4	23.4	23.5	23.5

Table 3 shows that nicked content in the product does not increase any more after reacting for 6h, which means that the reaction is completed. The nickel content in product is lower than theoretical value (26.4%), because the by-product *n*-butyl acetate was not distilled completely and a small amount of it was included in heavy-bodied material, solid was formed immediately when pouring product out from the reaction flask at high temperature. This solid is NBA, which is of marked fruit perfume due to a small amount of ester in it.

To verify that this reaction underwent according to reaction (2), boiling point of the distillate which was obtained by reduced pressure distillation was detected. It has the same boiling point as that of *n*-butyl acetate. The distillate was also analyzed together with commercial *n*-butyl acetate of chemically pure standard by gas chromatography. It was found that retention time of both detection and analysis are identical. So the by-product in this reaction is *n*-butyl acetate.

### 3.5 Properties and IR analysis of NBA

The physical and chemical properties of NBA are listed in Table 4.

The product appearances agree well with that published in the literature[3]. Boron content in the product is a little lower than the calculated value (1.63%) because there is a small amount of *n*-butyl acetate in it.

The IR data of both products NBA and CBA are very similar, and characteristic peak values for bond B-O ( $1297\text{ cm}^{-1}$  and  $1299\text{ cm}^{-1}$  respectively) and group  $\text{COO}^-$  ( $1418\text{ cm}^{-1}$ ,  $1571\text{ cm}^{-1}$  and  $1416\text{ cm}^{-1}$ ,  $1567\text{ cm}^{-1}$  respectively) are almost the same, and characteristic peak positions of alkyl groups are identical and characteristic peak for bond B-O of tributyl borate has disappeared.

### 3.6 Applied properties of NBA

Applied properties of NBA (product NC-201) detected by a radial-ply tyre workshop of rubber factory are listed in Table 5.

From Table 5 we find that by comparison of NC-201 with 680 C both are closed in cure curve, hardness and 300% fixed extension strength, excepting tensile failure extensibility and hot air aging adhesion property.

According to Ref.[5] nickel caprylate was used as adhesion promoter for natural rubber-brass plating steel wire cord. It was found that hot air aging adhesion strength would increase 13% when the amount of nickel caprylate increased 33%. The hot air aging adhesion property of NBA synthesized by the authors is 25.3% more than that of nickel caprylate, indicating that this product has better applied properties than that of nickel caprylate which does not contain any boron. The reason for this is that boric acid group in NBA is amphiprotic, and can absorb acidic or alkaline materials in gross rubber, and reduce effectively corrosion of corrosive molecular residue or water on metal. So NBA has good ability of anticorrosion, and shows a property of increasing adhesion property after aging.

**Table 4** Physical and chemical properties of nickel borate acylate

Appearance	w (Ni) / %	w (B) / %	Solvent (gasoline)	Heat distortion point / °C	Pour point / °C	Relative density
Deep green, brittle, solid	2.35	1.53	Dissolve	110	145	1.20

**Table 5** Applied properties comparison of nickel borate acylate NC-201 with cobalt borate acylate 680 C

Adhesion promotor	300% fixed extension strength/ MPa	Tensile strength/ MPa	Tensile failure extensibility/ %	Shore hardness	Hot air aging/ N	Cure curve / min
680 C	13.6	21.2	445	70	311	7.8 18.6
NC-201	14.0	20.0	404	71	301	7.3 18.8

## 4 CONCLUSIONS

1) The new synthetic route of NBA was put forward which possesses such characteristics as easy controlling of reaction conditions, simple reaction operation, good active nickel carbonate and smooth reaction of saponification and borate acylation.

2) Water should be removed completely in synthesis of mixed carboxylate. The borate acylation should be carried out at higher than 200 °C and *n*-butyl acetate should be removed as complete as possible. The IR data of synthesized NBA and CBA (680 °C) are very similar.

3) The applied properties shows that adhesion property of NBA product is better than that of nickel caprylate and a little lower than that of 680 °C. However, the other physical and chemical properties of this NBA are almost closed to that of product 680 °C. So the synthesized NBA can be used as rubber-steel cord AP.

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