Synthesis and properties of nickel borate acylate as a new rubber-steel cord adhesion promoter

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Abstract: The synthetic method of nickel borate acylate (NBA), a kind of rubber-steel cord adhesion promoter (AP), through nickel carbonate, borate and mixed carboxylic acid was studied. The preparation of nickel carbonate could be performed through reaction of nickel sulfate with sodium carbonate in aqueous solution, in which fractional conversion of nickel was more than 99.9%. The mixed nickel carboxylate was prepared by the reaction of nickel carbonate with isooctanoic acid and acetic acid, under strong stirring for 2 h, the mole ratio of these chemicals were 1:1:1.1 respectively, and water should be removed completely by adding of inert organic solvent after reaction was finished so as to avoid hydrolysis of tributyl borate in the second reaction. NBA was synthesized by reaction of mixed nickel carboxylate with tributyl borate under strong stirring at 200-250 °C for 6 h. By detection and comparison with 680C product from Manobend Company of England, the NBA synthesized through isooctanoic acid and tributyl borate was very similar to product 680C in IR data, 300% fixed extension strength, tensile strength, hardness and cure curve, and was slightly lower than those of product 680C in tensile failure extensibility and hot air aging. The experimental results show that the prepared NBA can be used as rubber-steel cord AP.

Key words: nickel borate acylate; adhesion promoter; nickel carbonate; borate

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, to improve the quality of rubber products and to prolong their service life[1,2]. The popular APs include mainly cobalt salts of organic carboxylic acids (e.g. cobalt naphthenate, cobalt stearate) and cobalt borate acylate (CBA, e.g. 680C product of Manobond Co., England)[3-12], and also nickel salts[3,6,12]. By comparison, the metal nickel is far cheaper than the metal cobalt, and 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 widely used[4,5,7-12]. China is very rich in natural resources of nickel, which provides ample raw materials for preparation of nickel-containing compounds. As is known to all that nickel and cobalt are in the same period and cluster, and are similar in chemical properties. So we replaced cobalt by nickel and synthesized a compound, nickel borate acylate (NBA), which had the similar structure of CBA. The experimental results show that the NBA synthesized with nickel carbonate, isooctanoic acid and tributyl borate can be used as rubber-steel wire APs.

1 Experimental

1.1 Main instruments and reagents

1.1.1 Main reagents

Nickel sulfate, sodium carbonate, acetic acid and tributyl borate, are all chemical purity;
Isooctanoic acid is a laboratory reagent.

1.1.2 Main instruments

Motor stirrer, organic synthesizer, vacuum pump, 10ZG gas chromatography, Perkin-Elmer-983 IR spectrum instruments.

1.1.3 Experimental procedure

Nickel carbonate was synthesized through nickel sulfate and sodium carbonate. 0.2 mol of nickel carbonate, some of isooctanoic acid, acetic acid and solvent were added into 250 mL a three-neck glass flask equipped with a condenser and a thermometer. The reaction mixture was stirred for a period of time at refluxing temperature. After the reaction apparatus was changed into distilling apparatus to remove all solvent and water produced in the reaction, finally intermediate product mixed with nickel carboxylate was obtained. Afterwards the distilling apparatus should be changed into the former reaction apparatus, and add some of 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.

2 Results and discussion

2.1 Synthesis route

Because there was no research report for synthesis of NBA, so we referred to the synthesis method\(^\text{(4)}\) of cobalt borate acylate to design and perform the experiment. The authors prepared Ni(OH)\(_2\) through reaction of nickel sulfate solution with sodium hydroxide solution, then mixed Ni(OH)\(_2\) with acetic acid and isooctanoic acid. This acid-base neutralization reaction should be performed easily. However, many experiment results showed that Ni(OH)\(_2\) was difficult to react with aliphatic acids, and parts of Ni(OH)\(_2\) did not react from beginning to end even being heated for a long time. This indicates that Ni(OH)\(_2\) prepared by this method is not reactive enough because the solubility of Ni(OH)\(_2\) (8 × 10\(^{-19}\)) is too small, which makes it difficult 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):

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\begin{align*}
\text{NiCO}_3 + \text{RCOOH} + \text{CH}_3\text{COOH} & \rightarrow \text{RCOO}^-\text{Ni}--\text{OOCCH}_3 + \text{H}_2\text{O} + \text{CO}_2 \uparrow \quad (1) \\
3\text{RCOO}^-\text{Ni}--\text{OOCCH}_3 + \text{B(OCH}_3\text{)}_3 & \rightarrow \quad (2)
\end{align*}
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2.2 Preparation of nickel carbonate and its reactivity

Preparation of nickel carbonate can be performed through 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 was controlled from 8.5 to 9.0 at the end of reaction and the precipitation produced were treated successively by filtration, washing and drying, we got reactive nickel carbonate, a light green particle in appearance and with 48.9% (mass fraction) of nickel (49.5% in calculation). Fractional conversion of nickel in the reaction was more than 99.9%.

Nickel carbonate is not so easy to react, as in the simple neutralization reaction, with monocarboxylic aliphatic acid because it is a weak acid. By experiments on mixture ratio, charging method, 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, filtration, washing and drying to the constant weight, which can react with isooctanoic acid at room temperature and give out lots of carbon dioxide.

2.3 Preparation of mixed nickel carboxylate

Mixed nickel carboxylate can be prepared according to reaction (1). It was 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. We paid attention to the effect of reaction time on