

2,3,6,7-Naphthalenetetracarboxylic Dianhydride (NTCDA) as a Monomer for Polyimide[†]

MORI Hiroaki^{*1} NAKAO Hiroaki^{*2}

Abstract:

JFE Chemical has developed the thermal transformation of aromatic carboxylates to industrially produce 2,3,6,7-naphthalenetetracarboxylic acid (NTC) and NTCDA. The metal ion-catalyzed transformation was investigated on the influence of the anion moiety. The probable mechanism of the reaction is the formation of the metal salt of the carboxylic acid as an intermediate of the transformation. Further, the catalytic activity of the zinc compounds is examined in detail on the transformation of disodium naphthalenedicarboxylate. By optimizing ZnI₂-catalyzed transformation NTC yield improved to about 25%, that is almost equal to that by the cadmium catalyst with high toxicity. Based on this result, a new process for NTCDA is developed. Polyimides derived from NTCDA are synthesized. Those polyimide films showed high modulus of elasticity, low thermal expansion coefficient and electrical reliability. They satisfy the required properties of printed circuits with high performance.

1. Introduction

JFE Steel Group found that 2,3,6,7-naphthalenetetracarboxylic Dianhydride (NTCDA) is formed by applying transcarboxylation (hereafter, the “Henkel Reaction”) to a naphthalene carboxylic acid sodium salt such as naphthoic acid^{1,2)}. The authors have investigated and developed an industrial process of manufacturing NTCDA by applying the Henkel Reaction using a zinc compound instead of highly toxic cadmium compound, and also have studied the reaction mechanism. This paper describes the results of the study.

With the spread of higher performance digital electric appliances in recent years, polyimides, which have

the highest heat resistance among organic polymers, have become indispensable as a board material owing to their favorable thermal, mechanical, and electrical properties. Recently, however, board materials are being changed to the next-generation type and the raw materials are also being improved. Polyimide is manufactured from the raw materials of a dianhydride and a diamine. There are several types of dianhydride that can be used as raw material for polyimide, so polyimide manufacturers want to use one that has high performance. The developed NTCDA, which has a rigid polycyclic aromatic structure, is expected to be a high-performance reforming material. By evaluating and comparing the properties of a polyimide resin derived from NTCDA with those of a general-purpose polyimide, the reforming functions of the developed polyimide resin required to attain high performance were identified. The details of the study are described below.

2. Development of the NTCDA Manufacturing Process

2.1 Method of Synthesizing NTCDA and Analyzing the Reaction Product

According to the Henkel Reaction, an alkaline salt of aromatic carboxylic acid is subjected to thermal treatment at temperatures between 400°C and 500°C under a CO₂ atmosphere in the presence of a cadmium compound, in which the carboxyl group undergoes intermolecular rearrangement, thereby forming a more thermally stable aromatic carboxylic acid.

The synthesis of NTCDA utilizing the Henkel Reaction was carried out in the following steps. An alkaline salt of carboxylic acid, a zinc or cadmium compound

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^{*1} Staff Manager,
Fine Chemical Dept.,
JFE Chemical



^{*2} Fine Chemical Dept.,
JFE Chemical

as the catalyst, and NaI as the co-catalyst, were dried at a specified temperature and put into an autoclave. By substituting the atmosphere in the reactor with carbon dioxide gas, thermal treatment was applied to the mixture at a specified temperature for a specified period. After completing the reaction, the reactant was analyzed by high performance liquid chromatography to evaluate the product composition and yield. The yield of NTCDA was defined as the percentage of NTCDA formed to the theoretical quantity of NTCDA obtained from the starting material:

$$Y = nP_{\text{NTC}} / P_{\text{NCAs}} \times 100$$

where Y is the yield of NTCDA (%), P_{NTC} is the quantity of NTCDA formed (mol), P_{NCAs} is the quantity of naphthalenecarboxylate used as the starting material (mol), and n is the number of carboxyl groups in naphthalene carboxylic acid as raw material.

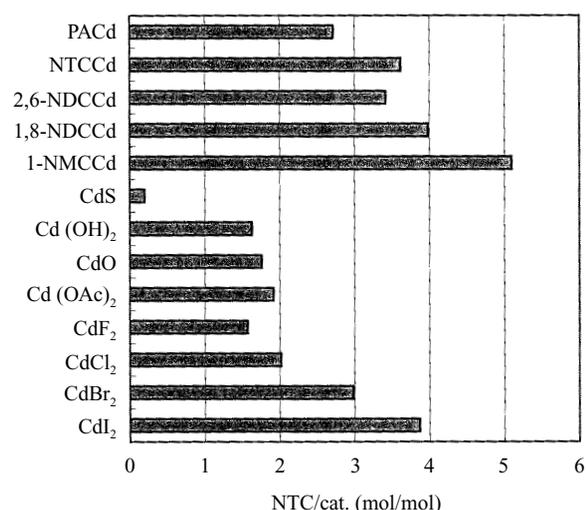
2.2 Reaction Results and Discussion

2.2.1 Henkel Rearrangement Reaction using a cadmium compound as the catalyst

As described above, the industrial manufacturing process of the Henkel Reaction requires using a zinc compound as the catalyst having low toxicity and light environmental load. The activity of a zinc compound catalyst is, however, significantly low compared with that of cadmium compound, so a zinc compound catalyst cannot be used in the industrial manufacturing process without improvement. Therefore, assuming that a zinc catalyst is used for the Henkel Reaction, the authors conducted a detailed study of the Henkel Reaction with the cadmium catalyst, and speculated on the mechanism of the reaction.

It is known that the difference in anion moiety of cadmium catalyst affects the yield. The catalytic activities of cadmium compounds were studied for various aromatic carboxylates. According to these studies, the catalytic activity of the anion increases in the order of: $\text{I}^- > \text{Cl}^- > \text{F}^- > \text{CO}_3^{2-} \sim \text{O}^{2-} > \sim\text{benzene carboxylates} \gg \text{Cd metal}^3$. The catalytic activity in synthesizing NTC dianhydride was also investigated.

Figure 1 shows the relation between the anion moiety of various cadmium compounds and the catalytic activity in the Henkel Reaction of disodium 1,8-naphthalate (1,8-NDCNa₂). Among inorganic cadmium salts, the activity decreased in the order of: halides $>$ AcO⁻ $>$ O²⁻ $>$ OH⁻. The activity of sulfide was the lowest. Regarding the halides, the order of activity was: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, showing the same result as the order of activity reported for the Henkel Reaction of many aromatic carboxylates³. Among the surveyed cad-



The reactions were carried out at 430°C for 3 h in the presence of 75 wt% of NaI and 5 wt% of the catalyst on disodium 1,8-naphthalate. The initial pressure of CO₂ was 3 MPa.

PACd: Phthalic acid cadmium salt

NTCCd: 2,3,6,7-Naphthalenetetracarboxylic acid cadmium salt

NDCCd: Naphthalenedicarboxylic acid cadmium salt

1-NMCCd: 1-Naphthalic acid cadmium salt

Fig. 1 Catalytic activity of various cadmium compounds on the Henkel Reaction of disodium 1,8-naphthalate

mium compounds, NTCDA using an aromatic cadmium carboxylate as the catalyst gave a yield of about 30%, showing catalytic activity equivalent to or higher than that of halides. The findings suggest that the selection of anion moiety is a key for the catalyst selection also for the case of zinc compounds.

2.2.2 The roles of catalysts

For considering the mechanism of transcarboxylation in the presence of cadmium compound, the following investigation was carried out.

First, without cadmium compound, no transcarboxylation occurred even when a co-catalyst such as NaI existed. The phenomenon is presumably caused by some kind of interaction between naphthalenecarboxylate as the substrate and the cadmium compound. To verify the mechanism, the Henkel Reaction of 1,8-naphthalate (1,8-NDCNa₂) using CdCl₂ as the catalyst and KI as the co-catalyst was investigated. The reaction product was extracted in hot water to isolate the solid, and the formed NaCl was identified in the solid. The result showed the occurrence of double decomposition from 1,8-NDCNa₂ and CdCl₂, suggesting that the cadmium 1,8-naphthalate (1,8-NDCCd) is formed during the reaction process, which then becomes an intermediate of the transcarboxylation. In fact, cadmium salt of NTC (NTCCd₂) was formed using cadmium naphthalenecarboxylate as the starting material. The presence of NaI significantly contributed to the reaction. That is, without Na, the cadmium salt of NTC (NTCCd₂) is thermally

unstable and so most of the formed NTCCd_2 is immediately decomposed. In the presence of NaI , however, a metal interchange occurs between the formed NTCCd_2 and NaI , and NTC presumably becomes a Na salt (NTCNa_4) which is thermally stable.

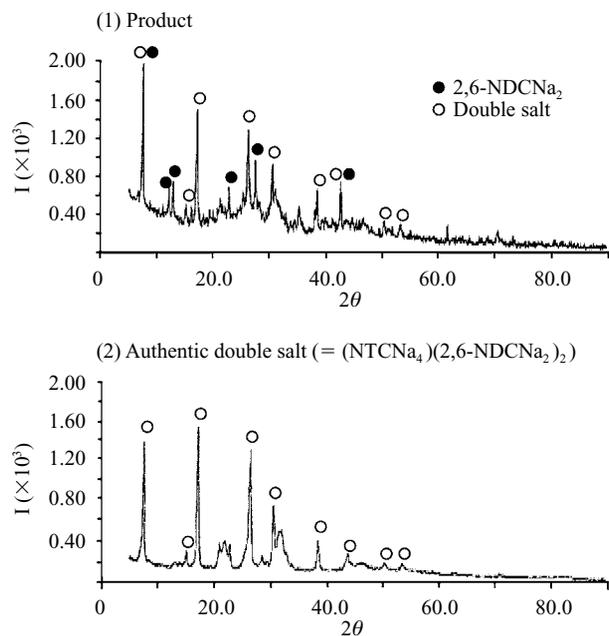


Fig.2 XRD of the typical Henkel Reaction product (1) and double salt consisted of 2,3,6,7-NTC and 2,6-NDCNa (2)

Various reaction conditions were investigated to improve the NTC yield, and the highest yield was as low as 30% for all the tested conditions. To identify the cause of the limit of 30% yield, X-ray diffraction of the reaction product was analyzed (Fig. 2). The analysis showed a different diffraction pattern for the reaction product from that of NTCNa_4 and of NDCNa_2 . From the X-ray diffraction pattern, it is confirmed that the crystal structure of the reaction product matches that of the double salt of $\text{NTCNa}_4/\text{NDCNa}_2 = 1/2$ (molecular ratio) which can be synthesized by mixing aqueous solution of NTCNa_4 and aqueous solution of NDCNa_2 (Fig. 2). The finding suggests that the reaction proceeds while forming a double salt (TD_2) from the formed NTCNa_4 and NDCNa_2 , and that ultimately the reaction reaches an equilibrium state when the reaction product becomes only the double salt (TD_2). Thus, the speculated reaction mechanism is shown in Fig. 3. According to the mechanism, the raw material 2,6-NDCNa₄ necessary to form one molecule of NTCNa_4 is theoretically four molecules.

2.2.3 Henkel Rearrangement Reaction using a zinc compound as the catalyst

Based on the investigation of the Henkel Reaction with cadmium catalyst, the Henkel Reaction using 2,6-NDCNa₂ as the starting material was studied to use the zinc compound as a substitute catalyst. With ZnO

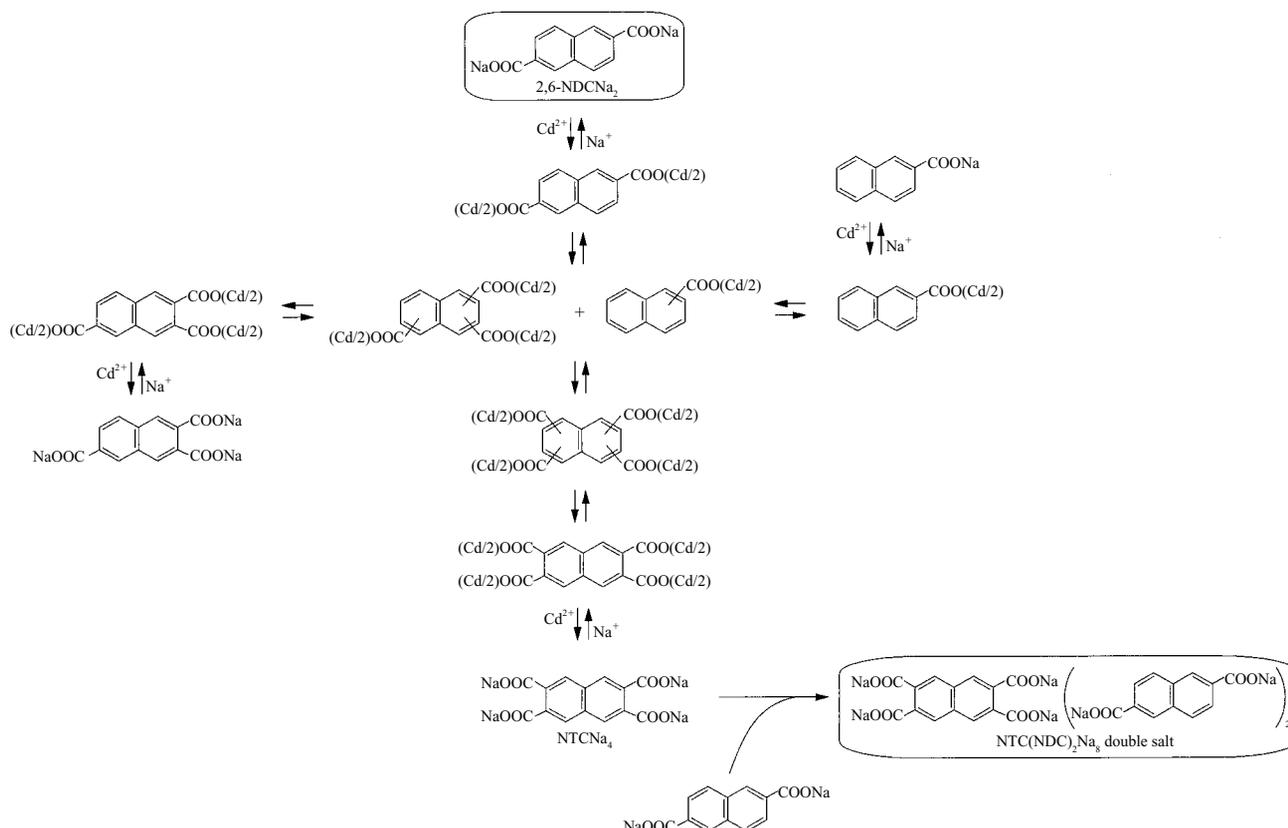
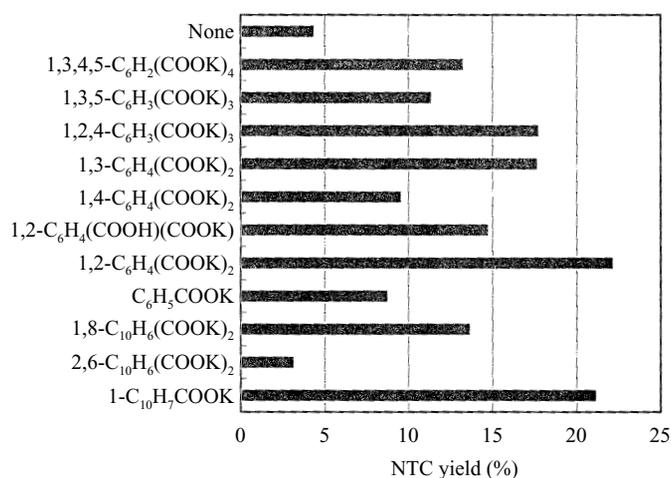


Fig.3 Proposed mechanism of the Henkel Reaction of naphthalenecarboxylic acid sodium salt

and ZnCl_2 as the zinc compound, no NTC formation was observed. With ZnCl_2 as the zinc compound, the yield was 0.5% at the highest.

As described above, in view of the fact that the activity of zinc catalyst in the Henkel Reaction using sodium naphthalene carboxylate as the raw material was low, and that there are many examples of starting materials of potassium aromatic carboxylate, such as the rearrangement of dipotassium 1,8-naphthalate (1,8-NDCK₂) to 2,6-NDCK₂ and of dipotassium phthalate to dipotassium terephthalate⁴⁻⁷), the authors conducted the reaction described below. Speculating that the coexistence of potassium carboxylate in the raw material forms a zinc naphthalenecarboxylate, and that NTC can be synthesized in the presence of zinc catalyst, the reactions upon adding various potassium carboxylates to 2,6-NDCNa₂ were tested. The results are shown in **Fig. 4**. The effect of the coexistence of potassium salt is significant. In particular, when dipotassium phthalate coexisted with potassium 1-naphthoate, the NTC yield achieved a value as high as 25%, which is equivalent to the reaction yield in the presence of cadmium catalyst.

The reason why the Henkel Reaction with zinc catalyst is enhanced by the addition of a potassium carboxylate is thought to be as follows. If the reaction mechanism assumed for the case of cadmium catalyst is applied to the case of zinc catalyst, the alkaline metal of carboxylic acid is substituted by zinc, and the zinc carboxylate thus formed should contribute to the actual rearrangement. If, however, only the sodium carboxylate exists, zinc carboxylate should not be formed. Since the coexistence of potassium salt drastically enhances the rearrangement reaction, the potassium salt presumably



The reactions were carried out at 450°C for 3 h in the presence of equimolar potassium salt, 75 wt% of NaI and 5 wt% of the catalyst on 2,6-NDCNa₂. The initial pressure of CO₂ was 3 MPa.

Fig. 4 Influence of various carboxylic acid potassium salts added on ZnI_2 -catalyzed Henkel Reaction of disodium 2,6-Naphthalenedicarboxylate

assists the ready formation of zinc carboxylate through the double decomposition with the zinc compound.

As described above, an industrial method of manufacturing NTC by applying a zinc compound as the catalyst to the raw material containing both sodium carboxylate and potassium salt has been developed.

2.2.4 Investigation of purification method to obtain high-purity NTC

The Henkel Reaction described in section 2.2.2 reaches an equilibrium state when a double salt (TD₂) structured by $\text{NTCNa}_2/\text{NDCNa}_2$ with a molecular ratio of 1/2 is formed. Accordingly, NTCNa_4 in the carboxylic composition is only about 40 mass%, and the balance of 55 to 60 mass% is 2,6-NDCNa₂. It is necessary to improve the purity of this low-grade composition NTC to 99% or more. In the conventional purification method, carboxylic acid is converted to an ester, which is then treated by recrystallization to achieve the desired purity, and further by hydrolysis to regenerate the carboxylic acid⁸). To avoid this complicated procedure, the authors have developed a simple method to raise the purity of NTC in the free acid state. Since there is no appropriate solvent to dissolve 2,6-NDC, the method of extracting NTC selectively using a solvent that dissolves NTC well was adopted. Appropriate solvents for the purpose were surveyed, and CH_3OH was found to be an effective one. By dispersing a mixture of carboxylic acid containing 30% of NTC into CH_3OH , the NTC is selectively extracted into CH_3OH , and NTC of 98% purity is obtained from the extract at a yield of 95% (vs. the mixture of acids). That is, the objective is attained by a simple procedure consisting of dissolving in CH_3OH and recovering the filtrate by filtration.

Figure 5 shows the NTC manufacturing process. The established process is to attain the target NTCDA at 99.9% or higher purity by the Henkel Rearrangement Reaction of the mixture composed of 2,6-NDCNa₂, 2,6-NDCK₂, and ZnI_2 , followed by CH_3OH extraction.

As described above, adding to the optimization of reaction conditions using ZnO , an industrially applicable method has also been developed in the purification stage.

2.2.5 Manufacture in 50 l autoclave

To verify the results of the above-described small-scale test, and to supply the product to customers for sample evaluation, a 50 l autoclave was installed at the Kasaoka Plant of JEF Chemical. Since the reaction temperature is preferably controlled within $\pm 10^\circ\text{C}$ of the optimum temperature, an external heater was used for local heating. Trays to which the raw material composition was charged, as shown in **Fig. 6**, were stacked in the autoclave to minimize the temperature gradient. The

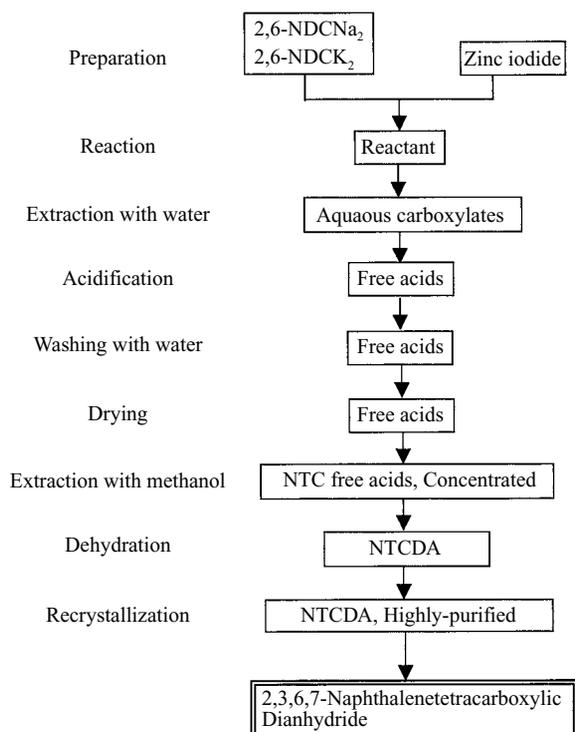


Fig.5 Schematic diagram of NTCDA production

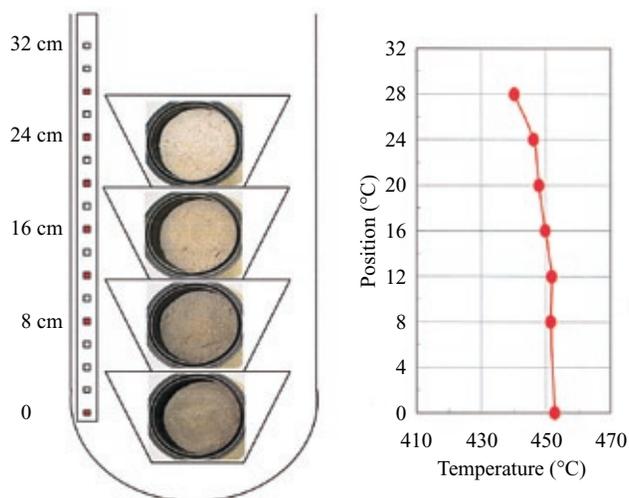


Fig.6 NTC Production using 50 l autoclave (1) product appearance, (2) temperature distribution

reaction of the small-scale test was well reproduced in the autoclave, and the production of NTCDA at 1 kg/d has started. The products are being supplied to customers, and also used for evaluating the properties of polyimide as described below.

3. Properties and Uses of NTC Polyimide

The required properties of polyimide film as a next-generation electronic board material are the following⁹⁾.

- (1) High elasticity to allow the formation of thin film
- (2) Small coefficient of linear thermal expansion and

Table 1 Dianhydrides used for polyimide films

Formula	Chemical name	Abbreviation
	Pyromellitic dianhydride	PMDA
	Bisphthalic dianhydride	BPDA
	2,3,6,7-Naphthalenetetracarboxylic dianhydride	NTCDA

small coefficient of humidity expansion, with small dispersion in each of them

- (3) Solder reflow heat resistance on IC bonding and mounting
- (4) High insulation reliability under high temperature and high humidity conditions

The main material used for electronic boards at present is polyimide with pyromellitic dianhydride (PMDA) and Bisphthalic dianhydride (BPDA) used as the dianhydride. This type of polyimide film, however, does not fully satisfy the above-described properties required for the next-generation electronic board material. In contrast, the NTCDA that is being developed by JFE Chemical has a rigid polycyclic aromatic structure, and is expected to serve as a reforming material to attain high performance. This section describes the results of measuring the properties of polyimide film which uses NTCDA as the carboxylic dianhydride, comparing the measured properties with those of polyimide films using PMDA and BPDA, respectively, and investigating the contribution of NTCDA to the reforming for attaining higher performance.

The structural formulae and abbreviations of individual dianhydrides used for fabricating the respective polyimide films are listed in **Table 1**. As for the diamine component, 4,4'-Oxydianiline (4,4'-ODA) was used.

3.1 Synthesis and Evaluation of NTC Polyimide

3.1.1 Procedure for synthesizing polyamic acid

A 500-ml separable flask equipped with a nitrogen gas inflow pipe, a calcium chloride pipe, a thermometer, a sample entrance slot, and agitation blades, was prepared. Dehydrated N,N'-dimethylacetamide (50 ppm or lower water content) at a 15 mass% of solid part concentration was put into the flask, and 0.07 mol of diamine which was preliminarily treated by alcoholic refining was also put into the flask to dissolve the solid matter

at normal temperature. Then, a dianhydride was slowly added to the mixture by an amount of equivalent mole to that of the diamine while checking the temperature, and the mixture was allowed to react in the nitrogen gas stream atmosphere under agitation for 3 h, to produce polyamic acid. The obtained polyamic acid was subjected to thermal treatment at 80°C to a specific intrinsic viscosity.

3.1.2 Procedure for preparing polyimide film

The surface of a horizontally-placed glass plate was coated uniformly with the polyamic acid solution obtained by the method described in section 3.1.1. Held in the horizontal position, the glass plate with coating was heated successively from 60°C to 150°C in a vacuum dryer to distil away the solvent. After the solvent had been distilled away, the film was subjected to thermal treatment in the as-attached state onto the glass plate in a constant temperature bath to imidize the film material at successively: (1) 150°C for 30 min, (2) 200°C for 60 min, and (3) 300°C for 10 min. The thermally treated film was separated from the glass plate, which was then fixed to a frame made of stainless steel. Then, the film was subjected to thermal treatment in a constant temperature bath at 300°C for 60 min to complete the imidization and to increase the film strength.

3.1.3 Method for measuring the properties of polyimide film

(1) Thermogravimetric Analysis

(a) 5% weight loss temperature (T1)

The measurement was done by TGA-50 (Shimadzu Corp.) under the condition of 30–1 000°C, $\Delta 10^\circ\text{C}/\text{min}$, N_2 atmosphere.

(b) Glass transition point (T2)

The measurement was done by DSC-50 (Shimadzu Corp.) under the condition of 30–500°C, $\Delta 20^\circ\text{C}/\text{min}$, N_2 atmosphere.

(c) Coefficient of linear thermal expansion (CTE)

The measurement was done by TMA-50 (Shimadzu Corp.) under the condition of 50–200°C, $\Delta 10^\circ\text{C}/\text{min}$, N_2 atmosphere.

(2) Tensile Properties

The measurement was done in accordance with JIS C 2318.

(3) Water Resisting Properties

(a) Hygroscopic content

Room temperature, 50% RH, 24 h storage

(b) Water content

Room temperature, immersion in water, 24 h storage

(4) Electrical Properties

The measurement was done in accordance with JIS C 6471.

3.2 Experimental Results and Discussion

3.2.1 Thermal and mechanical properties

Tables 2 and 3 show the results of the thermogravimetric analysis and tensile test, respectively.

These tables reveal that, compared with general-purpose polyimide films using PMDA and BPDA, the polyimide film which uses NTCDA has a high temperature of thermogravimetric change and of glass transition, and large modulus of elasticity with small coefficient of linear thermal expansion (CTE).

Regarding the molecular structure, NTCDA has a rigid structure compared with that of PMDA and BPDA. Accordingly, using the same kind of diamine, NTCDA has an increased number of geometric plane structures, thereby forming a molecular chain order structure. As a result, the heat resistance such as glass transition point and modulus of elasticity of the polyimide film are thought to increase due to strong intermolecular interaction. Polyimide having this type of rod-like structure is known to be likely to induce in-plane orientation and to have low CTE⁹⁾.

Next, the degree of influence of NTCDA was investigated by measuring the changes of CTE and modulus of elasticity for various resins of polyimide structured by PMDA and 4,4'-ODA, when NTCDA was denatured in increments of 25% (Fig. 7). The investigation revealed that CTE decreased and modulus of elasticity increased with the increase of the degree of denaturation of NTCDA, suggesting that the increases of both the rigidity and the in-plane orientation of the polyimide structure are expressed as the properties mentioned above. This finding proves that NTCDA is a material which provides high heat resistance, small expansion coefficient,

Table 2 Thermogravimetric analysis and coefficient of linear thermal expansion of polyimide films

Polyimide	T1 ^{a)} (°C)	T2 ^{b)} (°C)	CTE ^{c)} (ppm/°C)
PMDA/ODA	576	400<	24.6
BPDA/ODA	530	300	28.5
NTCDA/ODA	592	400<	17.0

^{a)} Temperature at which 5% weight loss was measured

^{b)} Glass transition point

^{c)} Coefficient of linear thermal expansion

Table 3 Tensile properties of polyimide films

Polyimide	Tenacity (MPa)	Elongation (%)	Modulus of elasticity (GPa)
PMDA/ODA	98.8	14.1	4.0
BPDA/ODA	100.5	16.4	3.9
NTCDA/ODA	84.6	8.5	6.0

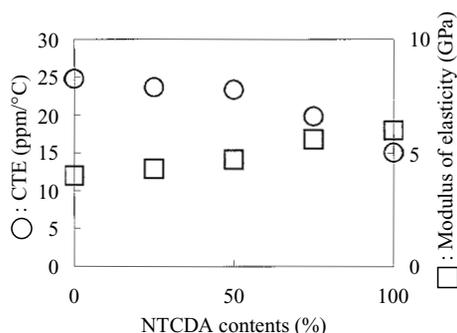


Fig. 7 The relation of NTCDA content, CTE, and modulus of elasticity

and large modulus of elasticity.

3.2.2 Water absorption

One of the drawbacks of polyimide film is its large water absorption, which is caused by the large polarity of the carbonyl group in the imide ring¹⁰. To attain appropriate mechanical properties and electrical reliability under humid environments, the water absorption must be reduced. **Table 4** shows the result of a water-absorption test and the surface energy of various polyimide films. The water absorption of NTCDA was smaller than that of PMDA and BPDA. This is presumably because the imide group concentration and polar groups such as ether bonding of the polyimide structure of NTCDA decrease compared with those of PMDA and BPDA. As a result, decreased surface energy makes NTCDA less susceptible to the effects of water¹⁰. In other words, water absorption, which is a drawback of polyimide, is improved by using NTCDA as the raw material.

3.2.3 Electrical properties

Table 5 shows the measured values of dielectric breakdown voltage, volume resistivity, and dielectric

Table 4 Hygroscopic and water content, surface energy of polyimide films

Polyimide	Hygroscopic content (%/50%RH)	Water content (%)	Surface energy (mJ/m ²)
PMDA/ODA	1.3	2.7	66.9
BPDA/ODA	0.9	1.3	31.1
NTCDA/ODA	0.7	1.2	29.1

Table 5 Electrical properties of polyimide films

Polyimide	Dielectric breakdown voltage (kV/mm)	Volume resistivity ($\times 10^{16} \Omega\text{cm}$)	Dielectric constant (1 kHz)
PMDA/ODA	173.0	3.1	3.2
BPDA/ODA	172.0	3.0	3.2
NTCDA/ODA	110.0	5.0	3.1

constant.

The polyimide film using NTCDA gives all these properties equivalent to those of polyimide films using PMDA and BPDA, and the polyimide film was proved to be of practical use without problem.

3.2.4 Preservation stability as raw material

Depending on the preserving environment, dianhydride reacts with moisture in air causing a partially ring-opening reaction in some cases, and so its properties deteriorate⁹. Thus, the quantity of dianhydride in the charged raw material is insufficient compared with the quantity of diamine, which leads to insufficient reaction and so the deteriorated dianhydride cannot be used as the raw material of polyimide synthesis. In particular, PMDA has very high reactivity but has poor preservation stability, thus the storage of PMDA requires sufficient de-humidifying measures. **Figure 8** shows the hygroscopicity confirmed for three kinds of dianhydride after being left standing at room temperature and in a saturated humidity for several days. If all the absorbed water is assumed to be consumed in the carboxylic acid ring-opening reaction, the preservation stability and the reactivity of NTCDA are the same level as those of BPDA. That is, NTCDA has appropriate preservation stability and reactivity as a raw material.

3.2.5 Preservation stability as precursor

Polyamic acid as a precursor of polyimide has a drawback of poor preservation stability caused by

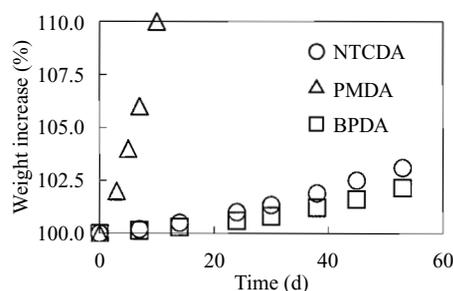


Fig.8 Hygroscopicity of tetracarboxylic dianhydrides

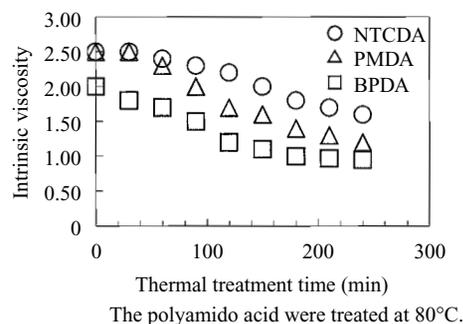


Fig.9 The temperature dependence of intrinsic viscosity

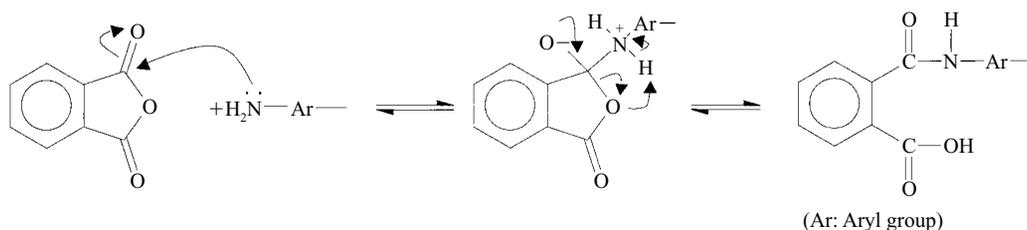


Fig.10 The reaction mechanism of dianhydrides and diamin

hydrolysis resistance, and the market requires higher preservation stability⁹⁾. **Figure 9** shows the measurements of hydrolysis resistance of various polyamic acids after thermal treatment at 80°C¹⁰⁾. Generally, thermal treatment of polyamic acid as the precursor of polyimide enhances the hydrolysis reaction, thereby decreasing the intrinsic viscosity and stabilizing the intrinsic viscosity at a certain level. This occurs because the amic acid forming reaction is an equilibrium reaction, as shown in **Fig. 10**. The polyamic acid using NTCDA shows a slow decrease in the intrinsic viscosity and has high hydrolysis resistance compared with those of polyamic acids using PMDA and BPDA. Hence, NTCDA has the potential to solve the issue of preservation stability.

3.3 High Performance Reforming of NTCDA

The properties required of polyimide for next-generation electronic boards were described earlier in this paper. The polyimide using NTCDA has sufficient heat resistance, small coefficient of linear thermal expansion, and large modulus of elasticity, and also has excellent hygroscopic resistance. Furthermore, this type of polyimide provides high stability in the raw material stage and also in the polyamic acid stage as the precursor of resin. As a result, NTCDA offers good potential as a high performance reforming material that satisfies the properties required of next-generation electronic board materials.

4. Conclusions

This paper described the manufacturing process and expected applications of NTCDA.

(1) By detailed investigation of the Henkel Reaction, the processes of formation of cadmium carboxylate

as an intermediate, and of stabilization of the product in the form of a double salt of 2,3,6,7-naphthalene tetracarboxylate and 2,6-naphthalene dicarboxylate were proposed.

- (2) Through the Henkel Reaction of a raw material of sodium carboxylate and potassium salt coexisting with a catalyst of zinc compound, a NTCDA yield of 25% was achieved, and a manufacturing process without using toxic cadmium was established.
- (3) A sample-work manufacturing system using a 50 l autoclave is now ready, and samples in lot sizes ranging from 100 g to several kilograms are being made available to customers.
- (4) Polyimide using NTCDA has good potential for next-generation electronic boards, having the required material properties such as high heat resistance and small coefficient of linear thermal expansion.

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