

A study on thermal stability of nitrocellulose

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As a fundamental study for spontaneous ignition of nitric esters, thermal degradation process of nitrocellulose (abbreviated as NC, hereafter) and effect of stabilizer were examined.

The results of FTIR analysis of NC and that after having been heated suggested that hydroxyl, hydroperoxide, and carbonyl groups generated, similar to the thermal degradation of usual polymers. And total calorific value of decomposition reaction decreased, according to the results of SC-DSC (Sealed Cell - Differential Scanning Calorimetry). The results also suggested that decomposition temperature became lower, so NC had turned to be a thermally unstable substance.

On the other hand, a little amount of diphenylamine (abbreviated as DPA, hereafter) added as a stabilizer reduced these changes.

1. Introduction

Accidental explosion or fire, which is caused by nitric esters, has been reported repeatedly in many years. Nitric esters are known to have the property of spontaneous ignition. This property is thought to bring down these accidents. But, the mechanism of spontaneous ignition is not fully understood. To establish safety process or review today's method to estimate the stability of explosives, which come in nitric esters, fundamental study on spontaneous ignition is needed.

It is known experimentally that spontaneous ignition is happened more easily after long-term preservation. So, tracing the change of property with time is very important. The concept of this study was that degradation is related with spontaneous ignition. To make clear the phenomena of degradation would lead to the basis

of understanding of spontaneous ignition, and finally to suggestion of establishment of safety process or handling, which has scientific back-born.

In previous studies on degradation of nitric ester, ester hydrolysis was thought to be the main cause. But, the condition or state of sample was not so cautioned, and it is suspended that ester hydrolysis happens even if the nitric ester is dry.

On the other hand, generated gases (NO₂ or NO) are thought to be the cause of degradation. But, reported examples of these products are very few, and the changes of structure or properties are not fully understood.

2. Experimental

2.1 Sample preparation and apparatus

In this study, nitrocellulose (abbreviated as NC, hereafter) (Aldrich; nitrogen weight 12%) was used as typical nitric ester, and diphenylamine (abbreviated as DPA, hereafter) (Aldrich) was used

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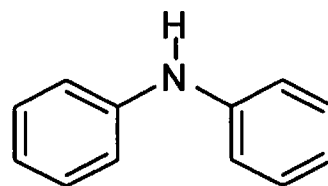


Fig. 1 Structure of DPA

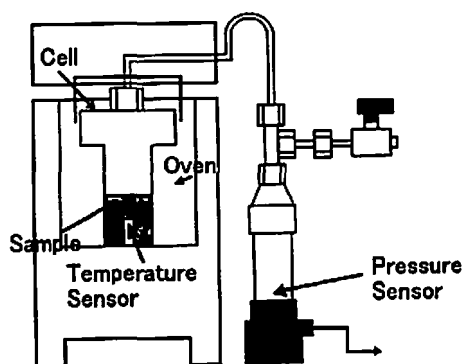


Fig. 2 RADEX apparatus

as typical stabilizer.

NC was dried in vacuum-drier at 303K. Calorific value of NC in this stage was about 3000-3300 J/g. If calorific value was out of this range, the NC was not used.

Heat was applied by RADEX apparatus (Systag Co., Ltd). Holding temperature was set to isothermal. To observe changes of sample, FTIR-8100 (Shimadzu Co., Ltd) and DSC-20 (Mettler Toledo) were used. In FTIR, liquid paraffin was adopted. In SC-DSC, sample mass was about 0.5mg, temperature range was 333-523K, and heating rate was 5K/min. In this study, T_a was used as a barometer of decomposition temperature. T_a means the temperature at which DSC curve arising.

2.2 Heat degradation experiments

NC was heated by RADEX, and the changes of structure or properties were observed by FTIR and SC-DSC. Holding temperature was 393K and 413K, and holding time was 480 min. Amount of NC was 100mg for each run.

2.3 Experiments about stabilizer

NC with DPA was heated by RADEX. After heated, the changes were examined by FTIR and SC-DSC likewise. Holding temperature was 373K, and holding time was 1200 min each. Amount of NC was 100mg, and amount of DPA was 0, 1, 5, 10mg.

3. Results and discussion

3.1 Thermal degradation of NC

After heat had been applied, color of NC changed.

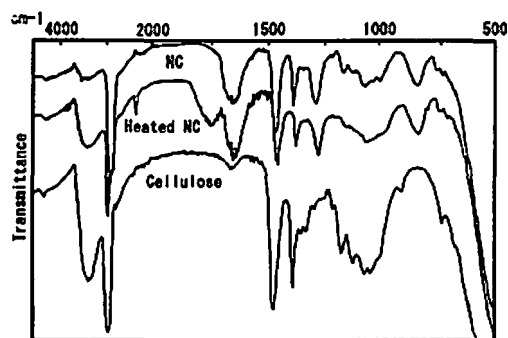


Fig. 3 FTIR spectra of NC, heated NC, and cellulose

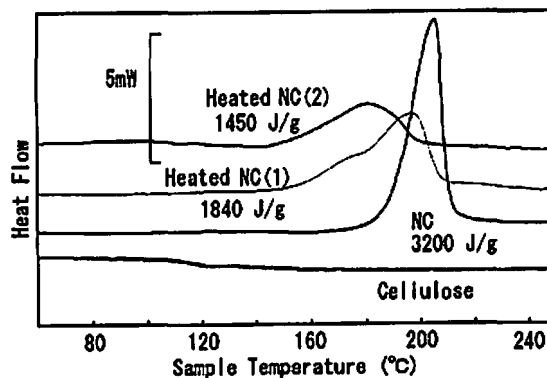


Fig. 4 SC-DSC curves of NC and heated NC

At first NC was white powder. After being hold at 393K for 480min, color of the NC became yellow. And after being hold at 413K for 480min, color of it became brown. Color was changed uniformly, not partially.

In the FTIR spectra (Fig.3), the newly peaks that were not seen in original NC were found. These peaks were corresponding to existence of hydroxyl or hydroperoxide groups ($3800-2500\text{cm}^{-1}$), and carbonyl groups (1750cm^{-1}), so these groups were generated by heat degradation. The both NC, which was heated at 393K or 413K, showed almost the same chart. These peaks are also generated when polymers, such as plastics or rubbers, are deteriorated. Degradation of NC might undergo likewise.

By applying of heat, heat of decomposition of NC measured by SC-DSC was decreased (Fig.4). T_a was also lowered, and this means NC became thermally unstable. In Fig.4, the sample "heated NC (1)" means what had been heated at 393K, and "heated NC (2)" means what had been done at 413K.

Cellulose was examined by SC-DSC as well. Cellulose did not have exothermic property in this

Table 1 Results of experiments of stabilizer

Amount of DPA	Color	Newly IR-Peak	T _g [°C]	Q _{DSC} [J g ⁻¹]
0 mg	Light yellow	○	130	1800
1 mg	Fern green	×	165	3000
5 mg	Green	×	140	2700
10 mg	Deep green	×	140	2900

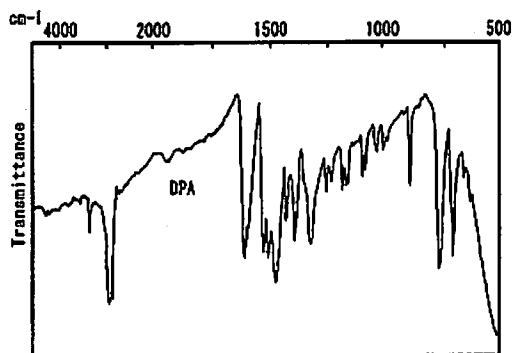


Fig. 5 FTIR spectrum of DPA

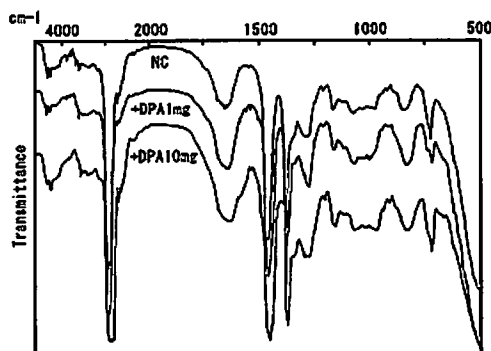


Fig. 6 FTIR spectra of NC, NC with DPA

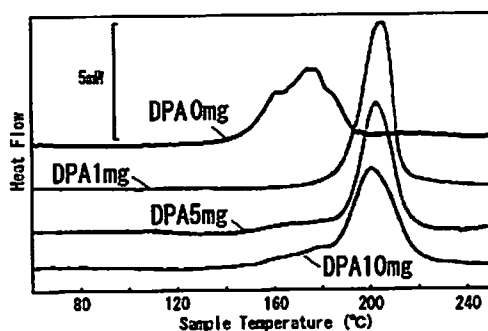


Fig. 7 SC-DSC curves of NC with DPA

range, so nitric ester is the key of exothermal property. From these results, it could be said that nitric ester group would be lessened by heat.

3.2 Effect of DPA on NC degradation

The results were shown in Table 1. The color, IR-Peak, T_g, and Q_{DSC} were listed.

After NC with DPA was heated, the color of it had been changed dramatically. White powder changed to green or deep-green one.

About the FTIR spectra, the newly peak was not found when NC was heated with DPA (Fig.5, 6). Peak of it would be seen as the addition of that of NC and DPA. But, peak of DPA is so many that newly peak might be hid among them.

By adding DPA to NC, the decomposition of NC by heat was prevented (Fig.7). Q_{DSC} of heated NC with DPA were almost the same as NC without heating. To NC 100mg, only 1mg of DPA was effective in this condition. But, much amount of DPA turned to affect the DSC curve. It suggested that DPA might react with NC (or generated gasses). Total calorific value seemed to be decreased when 5mg of DPA was added, but it would be the error of measurement of sample mass. The way of adopting of base line might be the cause.

3.3 Degradation mechanism of NC

The results of FTIR suggested that degradation of NC was similar to that of other polymers. Therefore, in considering degradation mechanism, commonly known reactions were adopted, like "hydrogen drawing-out", and "auto-oxidation". Experimentally observed groups were to be generated and taken into account chiefly.

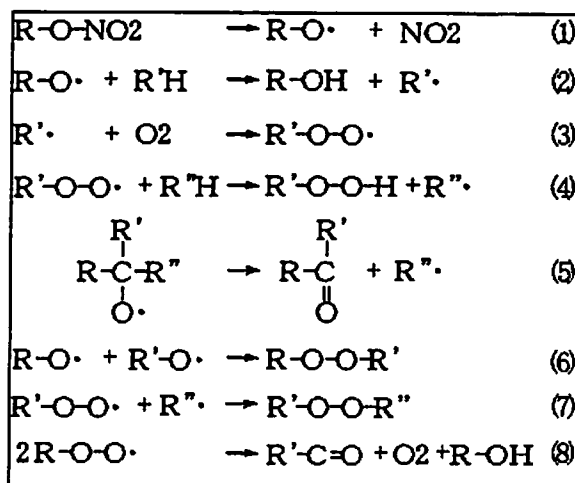


Fig. 8 Presumption of NC degradation

This mechanism would not conflict with the mechanism which had been suggested by Kimura et al. Radical reaction is very complicated and there might be many other ways, but this scheme would be the simple and essential one for making products.

In this study, the effect of NO₂ was not studied. But, as some researchers had suggested, NO₂ would play the important role. Not only O₂ but also NO₂ might be a main cause of sustaining auto-oxidation. Further investigation about the effect of these gasses is needed.

4. Conclusions

In this study, degradation of NC and effect of DPA were examined. When NC was deteriorated by heat, new groups, which correspond to hydroxyl, hydroperoxide, carbonyl groups were generated in NC. After degradation, heat of decomposition of NC by SCDSC was decreased, and decomposition temperature was lowered. When dried-NC without DPA is being preserved, thermally unstable substance, such as hydroperoxide, would have been

generated. But, small amount of stabilizer was proved to be efficient.

Further investigation on the presumptive mechanism would lead to suggestion of safety process, which has scientific back-born.

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