# NOTES

## *Hydrogen Bonding in Nitrocellulose*

### INTRODUCTION

The concentration profile of di-*n*-butyl phthalate in a spherical nitrocellulose (NC) small arms propellant grain was described in a recent study.[1] The observed concentration gradient was shown to be caused by hydrogen bonding between unesterified hydroxyl groups in nitrocellulose and the carbonyl groups on the ester.[2] A study was made, therefore, of the hydrogen bonding characteristics of well-characterized nitrocellulose of varying nitrogen content.[3] This investigation only considered the data in terms of their importance to the interaction with di-*n*-butyl phthalate. Further examination of the data has provided new basic information, which is the topic of this paper.

### EXPERIMENTAL

Methods for nitrocellulose separation and its characterization have already been detailed[3] and therefore will only be summarized here.

Nitrocellulose samples obtained from Hercules, Inc., were fractionally precipitated. Data were obtained for number- and weight-average molecular weight calculations by utilizing gel permeation chromatography calibrated with appropriate standards. These number- and weight-average molecular weights for the various nitrocellulose samples, listed in Table I, were calculated by the summation of heights method from chromatographic data.

All of the NC samples were dissolved in MC&B reagent-grade ethyl acetate, and these solutions were cast as films on a salt plate. After film casting, the plates were placed in a vacuum desiccator and subjected to a roughing-pump vacuum for several hours. IR spectra were run for each sample with and without a dry air purge. All spectra were obtained by the use of a Perkin–Elmer IR spectrophotometer model 621.

### DISCUSSION

The $\nu$-OH stretching frequencies were measured for a series of well-characterized nitrocellulose samples under ambient and dry-air purge conditions.[3] Table II lists the results for the various NC samples.

Figure 1 shows the relationship between the various NC samples and the hydroxyl stretching frequency measured under dry-air purge conditions. All the NC samples, with the exception of the 12.3% N sample, fall on the curve. Note that the 12.3% N sample had a considerably higher number- and weight-average molecular weight than did the other four samples, which may account for its failure to conform to the curve. Examination of Figure 1 shows a leveling occurring at a nitrogen content of about 12.5% N, at which point the curve appears to approach a constant value. Miles and Craik,[4] in their studies of the x-ray patterns of NC having a wide range of nitrogen content, noted a critical point at a nitrogen content of 12.8%, where the characteristic pattern of cellulose trinitrate appears. Meyer and Mark reached a similar conclusion.[5] This value appears to be very near the

TABLE I
Molecular Weight Data for Various Nitrogen Content NC Samples

| %N in NC | $M_w$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| 12.10 | 141,500 | 84,500 | 1.67 |
| 12.20 | 154,800 | 92,400 | 1.68 |
| 12.30 | 230,400 | 224,800 | 1.03 |
| 12.60 | 139,600 | 90,450 | 1.54 |
| 13.16 | 128,200 | 76,000 | 1.69 |

Journal of Applied Polymer Science, Vol. 25, 1245–1247 (1980)

0021-8995/80/0025-1245$01.00

TABLE II
$\nu$-OH for Various Nitrogen-Content NC Samples

| %N in NC | $\nu$-OH,[a] $cm^{-1}$ | $\nu$-OH,[b] $cm^{-1}$ |
|---|---|---|
| 12.10 | 3514 | 3525 |
| 12.20 | 3502–3536 | 3544 |
| 12.30 | 3514 | 3538–3540 |
| 12.60 | 3528–3532 | 3558 |
| 13.16 | 3528–3550 | 3560 |

[a] Run in air, expanded spectra (represents five runs).
[b] Run under purge condition, expanded spectra (represents five runs).

12.5% N where the shift of the $\nu$-OH appears to reach a constant value for the range of nitrogen content studied.

A 3560 $cm^{-1}$ $\nu$-OH recorded at this leveling point also happens to be near the lower limit for the cellulose dinitrate free hydroxyl stretching frequency[6] of 3571 $cm^{-1}$. Spurlin in his studies suggested that the chain in lower nitrogen content nitrocellulose is regular enough to offer a high probability that hydroxyl groups in neighboring molecules will form hydrogen bonds.[7] Furthermore, the chain

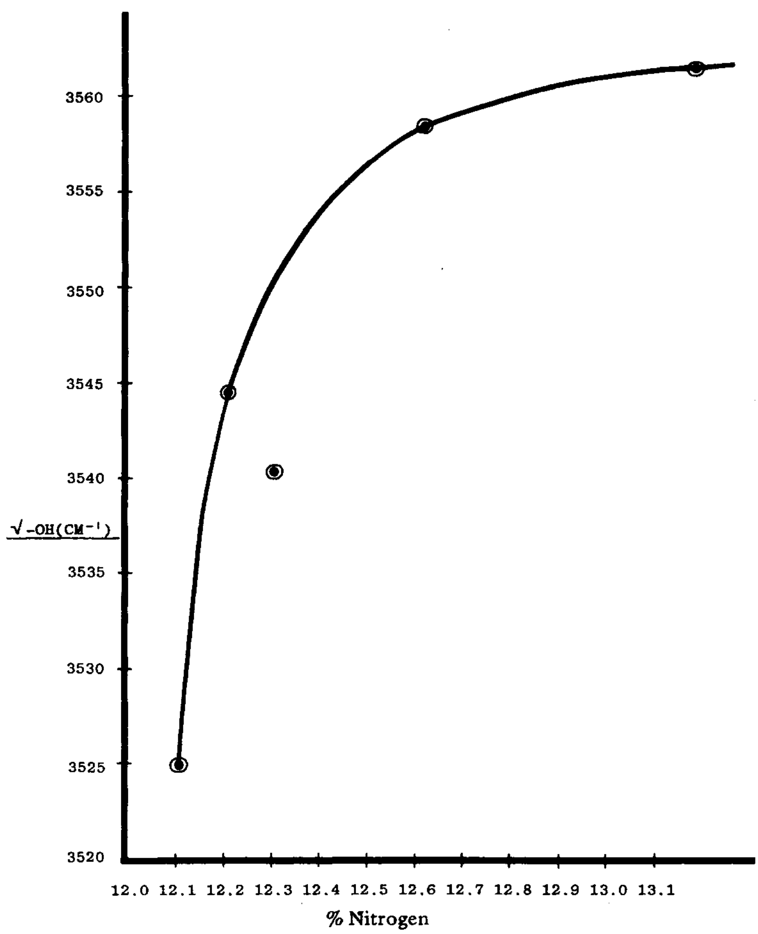


Fig. 1. Hydroxyl stretching frequency relationship for NC samples measured under dry-air purge conditions.

in higher nitrogen content nitrocellulose again possesses a regular enough structure to allow van der Waals forces to exist between nitrate ester groups in neighboring chains.

Thus, it would seem that the observed leveling point at 12.5% N involves going from a hydrogen-bonded structure to one where van der Waals forces become dominant, consistent with the previously cited x-ray diffraction data. At this point, $\nu$-OH appears to reach a constant value involving free or very weak hydroxyl interaction.

## SUMMARY

A series of well-characterized nitrocellulose samples ranging in nitrogen content from 12.1 to 13.16% were examined for changes in hydroxyl stretching frequency. The data indicated a change from a hydrogen-bonded structure to one where van der Waals forces dominate at a nitrogen content of 12.5%.

## References

1. B. W. Brodman, M. P. Devine, R. W. Finch, and M. S. MacClaren, *J. Appl. Polym. Sci.*, **18**, 3739 (1974).

2. B. W. Brodman, M. P. Devine, and M. T. Gurbarg, *J. Appl. Polym. Sci.*, **18**, 943 (1974).

3. B. W. Brodman, M. P. Devine, and M. T. Gurbarg, *J. Macromol. Sci. Chem.*, **8**(4), 837 (1974).

4. F. D. Miles and J. Craik, *J. Phys. Chem.*, **34**, 2607 (1930).

5. K. H. Meyer and H. Mark, *Ber.*, **61**, 593 (1928).

6. V. N. Nikitin, in *Chemistry and Technology of Explosives*, Vol. II, T. Urbanski, Ed., Pergamon, New York, 1965, p. 287.

7. H. M. Spurlin, in *Cellulose and Cellulose Derivatives*, E. Ott and H. M. Spurlin, Eds., Interscience, New York, 1954, p. 1075.

B. W. BRODMAN
M. P. DEVINE

Armaments Division
U.S. Army Armament Research and Development Command
Dover, New Jersey 07801

Received September 5, 1979
Revised October 23, 1979