

Investigations on Polyvinyl Nitrate as a High Energetic Material

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Untersuchungen an Polyvinylnitrat, einer energiereichen Verbindung

Polyvinylnitrat (PVN) ist einer der weniger bekannten polymeren Explosivstoffe. PVN wurde dargestellt durch kontrollierte Zugabe von kalter Salpetersäure zu einer vorgekühlten Suspension von Polyvinylalkohol in Essigsäureanhydrid und nachfolgender Aufarbeitung des Reaktionsproduktes. Der Stickstoffgehalt verschiedener PVN-Proben lag zwischen 11,76% und 15,71% bei einem Molekulargewicht um 100000. Verschiedene Eigenschaften des PVN sind untersucht und korreliert worden mit dem Nitrierungsgrad. Scanning Electron-Mikrographien von PVN-Fasern zeigen eine poröse Oberfläche. Die Werte des Abel-Tests bei 82°C weisen auf eine leidlich gute Stabilität des faserigen PVN, die abnimmt mit der Zunahme des Stickstoffgehalts. Eine Zugabe von geringen Mengen (0,25 Gew. %) an DPA, 2NDPA, Centralit I und Resorcin zu PVN (mit 15,71% N) verbessert seine Wärmestabilität. Mit ansteigendem N-Gehalt nimmt die Zündtemperatur von PVN ab und die Schlagempfindlichkeit zu. PVN mit 15,71% N ist ebenso schlagempfindlich wie Tetryl. Bei einem N-Gehalt des PVN zwischen 11,76% und 15,71% nimmt seine Verbrennungswärme ab und 3744 cal/g auf 3023 cal/g und die Explosionswärme zu von 456 cal/g auf 987 cal/g aufgrund der Zunahme der Sauerstoffbilanz.

Etudes sur le polyvinylnitrate, composé énergétique

Le polyvinylnitrate (PVN) est l'un des quelques explosifs polymères connus. Le PVN a été préparé par addition contrôlée d'acide nitrique froid pour former une suspension prérefroidie d'alcool polyvinylique dans de l'anhydride acétique et traitement subséquent du produit de réaction. La teneur en azote de différents échantillons de PVN était située entre 11,76% et 15,71% pour un poids moléculaire de l'ordre de 100000. On a étudié différentes propriétés du PVN et on les a mises en corrélation avec le degré de nitration. Des microscopies électroniques à balayage de fibres PVN révèlent une surface poreuse. Les valeurs du test d'Abel à 82°C indiquent que le PVN fibreux possède une stabilité relativement bonne, qui diminue lorsque la teneur en azote augmente. Une addition de faibles quantités (0,25% en poids) de DPA, 2NDPA, Centralit I et résorcinol au PVN (avec 15,71% de N) améliore sa stabilité thermique. Lorsque la teneur en N augmente, la température d'amorçage du PVN diminue et la sensibilité au choc augmente. Le PVN à 15,71% de N est aussi sensible au choc que le tétryl. Pour une teneur en N du PVN située entre 11,76% et 15,71%, sa chaleur de combustion diminue de 3744 cal/g à 3023 cal/g et sa chaleur d'explosion augmente de 456 cal/g à 987 cal/g en raison de l'augmentation du bilan d'oxygène.

Summary

Polyvinyl nitrate (PVN) is one of the few known polymeric explosives. PVN was prepared by controlled addition of cooled nitric acid to a pre-cooled suspension of polyvinyl alcohol in acetic anhydride and subsequent processing of the reaction product. Nitrogen content of different PVN samples was in the range 11.76% to 15.71%, and the molecular weight about 100000. Several properties of PVN have been investigated and correlated with its degree of nitration. Scanning electron micrographs of PVN fibres show a porous surface. Abel heat test values at 82°C indicate that fibrous PVN has a fairly good degree of stability, which decreases with increase in its % N. Addition of small amounts (0.25% by wt.) of DPA, 2NDPA, carbamite and resorcinol into PVN (15.71% N) improves its heat stability. With increasing % N, ignition temperature of PVN decreases and impact sensitivity increases. PVN (15.71% N) is as sensitive to impact as tetryl. With increasing % N from 11.76% to 15.71%, heat of combustion decreases from 3744 cal/g to 3023 cal/g, and heat of explosion increases from 456 cal/g to 987 cal/g, due to increase in oxygen balance.

1. Introduction

Polyvinyl nitrate or PVN, $(C_2H_3NO_3)_n$, is the nitric ester of polyvinyl alcohol. It is one of the few known polymeric

explosives, and bears a formal resemblance to the better known cellulose nitrate. Preparation methods and several properties of PVN have been reported in literature⁽¹⁻¹⁰⁾. Being a nitrated polymer, PVN is expected to exhibit variations in explosive and other properties depending on its degree of nitration (% N). The propensity of PVN towards explosive decomposition is attributable to the presence of the weak N-O bond (bond energy 53 kcal/mol) in large number throughout the chains. This paper presents the results of our studies on PVN, especially the effect of nitrogen content and some additives on its energetics and stability.

2. Experimental

2.1 Materials

Polyvinyl alcohol (PVA), designated Gohsenol NM-11, manufactured by M/S Nippon (Japan), was used as received. Its degree of polymerization was 1100 (approx), and degree of hydrolysis 99-100%.

Three grades of nitric acid were used, viz.

(a) 98-99% HNO_3 , (b) $70.7 \pm 1\%$ HNO_3 , (c) $63.7 \pm 1\%$ HNO_3 .

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Table 1. Reaction Conditions for Preparation of PVN Samples having Different Nitrogen Content

Reagents	Conditions during addition of reagents		Conditions after addition of reagents		Overall reaction time [h]	Nitrogen in PVN [%]*
	Temperature [°C]	Time [h]	Temperature [°C]	Time [h]		
PVA + 98-99% HNO ₃	-10 to -5	2	-5 to 10 10 to 20	2 3	7	15.71
PVA + 70.7 ± 1% HNO ₃	-10 to -5	2	-5 to 15 15 to 20	2 2	6	14.95
PVA + 98-99% HNO ₃	-10 to -5	2	-5 to 8 8 to 19	2 1	5	13.34
PVA + 63.7 ± 1% HNO ₃	-10 to -5	2	-5 to 15 15 to 20	2 2	6	11.76

* determined by C,H,N Analyzer

The following compounds, in CP grade, were used as additives in gelatinized PVN for some tests:

carbon black, lead stearate, lead salicylate, diphenylamine (DPA), 2-nitrodiphenylamine (2NDPA), diethylphenylurea (carbamide), resorcinol.

2.2 Preparation of PVN

Several batches of PVN were prepared by nitration of PVA powder by slowly adding an excess of cooled nitric acid to a pre-cooled suspension of PVA in acetic anhydride at -10°C. The procedure given in a Patent⁽³⁾ was followed for preparation of PVN with a high nitrogen content. By altering the nitric acid concentration and reaction temperature-time schedule, as indicated in Table 1, it was possible to prepare batches of PVN containing 15.71%, 14.95%, and 11.76% nitrogen.

3. Results and Discussion

3.1 Nitrogen Content

PVN has a theoretically maximum nitrogen content of 15.73%. The samples of PVN employed for this study showed, on elemental analysis in a C,H,N Analyzer, the following nitrogen content:

15.71%, 14.95%, 13.34% and 11.76% N.

3.2 Physical Properties

The PVN samples were, generally, white and fibrous in appearance. The mol.wt. of typical PVN samples was found, by GPC technique using polystyrene as a standard, in the order of 100000. The softening temperature for PVN (11.76% to 15.71% N) ranged from 39°C to 50°C. PVN samples were found to be soluble in polar organic solvents like acetone, solubility increasing with % N.

When fibrous PVN was worked up with acetone at room temperature, it underwent gelatinization and formed a

homogeneous mass on removal of excess solvent. Viscosity of 0.5% solution of PVN (15.71% N) in acetone, determined in an Ostwald type viscometer, was 0.433 cp at 27°C; viscosity increased with the decrease in temperature or % N.

3.3 Infrared Spectra

IR spectrum of PVN containing 15.71% N, taken in a Perkin-Elmer double beam spectrophotometer, is shown in Fig. 1. Strong absorption peaks obtained at 690 cm⁻¹ and 750 cm⁻¹ (for -NO₂), 1275 cm⁻¹ and 1675 cm⁻¹ (for -ONO₂), and 1430 cm⁻¹ (for -CH₂), were assigned as per literature^(10,11,12). Notably, -OH absorption is absent.

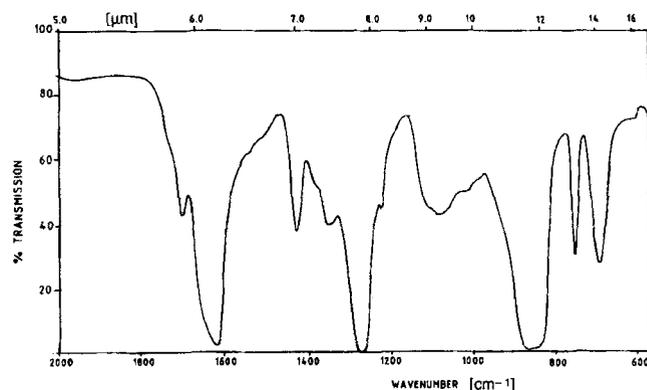


Figure 1. Infrared spectrum of PVN (15.71% N).

3.4 Scanning Electron Microscopy (SEM)

The morphology of PVN samples (fibrous and gelatinized) was determined using a JSM, T-200 scanning electron microscope. Typical micrographs are shown in Fig. 2. It is observed that the surface of fibrous PVN is porous. However, on treatment with acetone (solvent), the fibrous and porous nature of PVN is lost (due to gelatinization).

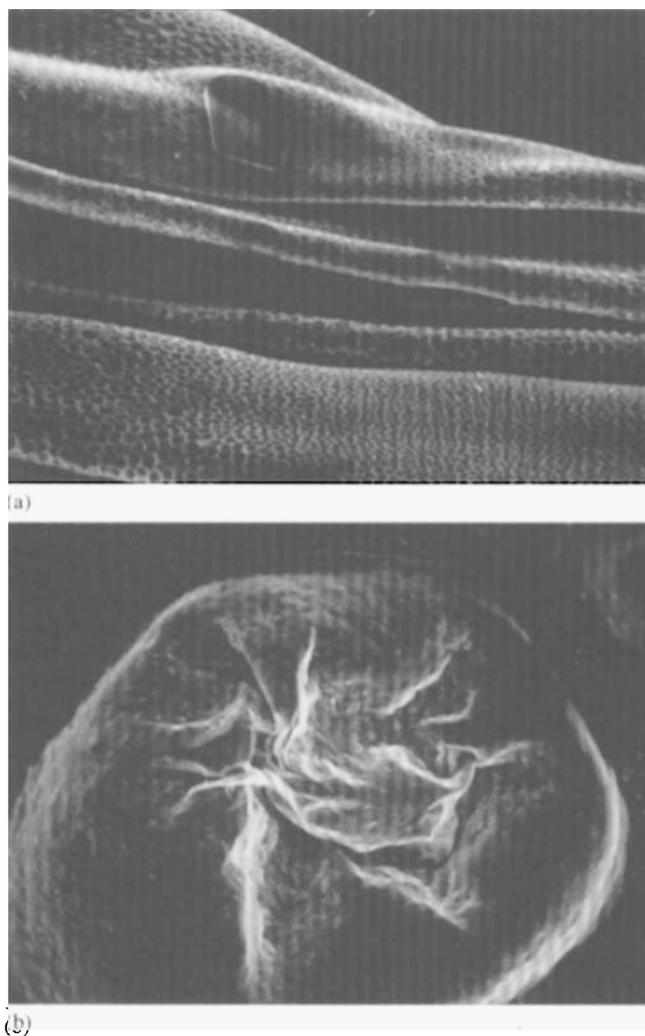


Figure 2. Scanning electron micrographs of PVN (16.71% N), X 350.
(a) Fibrous (b) Gelatinized

3.5 X-Ray Diffraction

X-ray diffraction study of two PVN samples (15.71% and 11.76% N) was carried out on a Philips PW 1730/10 diffractometer mounted on a Philips PW 1050/70 (40 kV, 20 mA) generator. Copper $\text{CuK}\alpha$ radiation ($\lambda = 1.5414 \text{ \AA}$) was used in all experiments.

From the diffractograms, the percent crystallinity was calculated by using the standard formula⁽¹³⁾ and found to be 47.62% for PVN (15.71% N) and 41.78% for PVN (11.76% N), compared to 40.38% for PVA.

3.6 Stability Tests

Nitrate esters are inherently unstable due to the presence of a relatively weak N-O bond and tend to decompose at elevated temperatures. Nitrogen oxides and moisture formed during this decomposition, catalyse further decomposition of the nitrate ester.

Abel heat test and Vacuum stability test were employed for evaluating the relative thermal stability of PVN and the

effect of additives, viz., DPA, 2NDPA, carbamite and resorcinol thereon.

3.6.1 Abel Heat Test⁽¹⁴⁾

This test was carried out on PVN samples, without and with additives (in 0.25%, 0.5%, 0.75% and 1% concentrations by wt), at $65 \pm 1^\circ\text{C}$ ($150 \pm 2^\circ\text{F}$) and/or $82 \pm 1^\circ\text{C}$ ($180 \pm 2^\circ\text{F}$). Results are presented in Table 2.

Table 2. Abel Heat Test Values of PVN Samples without and with Additives

Sample Composition			Abel heat test values, [min]	
PVN type	Additive	Conc. of Additive [%]	Test temperature $65 \pm 1^\circ\text{C}$	Test temperature $82 \pm 1^\circ\text{C}$
PVN (11.76% N), fibrous	none	0.00	> 75	60
PVN (13.34% N), fibrous	none	0.00	38	15
PVN (14.95% N), fibrous	none	0.00	> 60	20
PVN (15.71% N), fibrous	none	0.00	> 65	10
PVN (15.71% N), gelatinized	none	0.00	> 85	06
	DPA	0.25	> 90	50
		0.50	-	67
		0.75	-	67
		1.00	> 90	> 70
	2NDPA	0.25	> 90	20
		0.50	-	90
		0.75	-	> 90
		1.00	> 90	35
	Carbamite	0.25	> 90	45
		0.50	-	> 40
		0.75	-	35
Resorcinol	1.00	> 90	20	
	0.25	> 90	50	
	0.50	-	> 60	
	0.75	-	40	
	1.00	> 90	45	

- From the results at $82 \pm 1^\circ\text{C}$, we conclude that
- Fibrous PVN appears to be fairly stable. However, with increasing % N, stability decreases.
 - PVN (15.71% N) in gelatinized form is less stable than in fibrous form.
 - DPA, 2NDPA, carbamite and resorcinol are effective as stabilizers even in 0.25% concentration in PVN. However, effectiveness is not linearly related to concentration.
 - On overall appraisal, DPA is superior to 2NDPA, carbamite and resorcinol in concentrations up to 1%.

3.6.2 Vacuum Stability Test⁽¹⁴⁾

This test was carried out on PVN (15.71% N) samples, without and with additives (in 0.25% and 1% concentrations by weight). Results are given in Table 3.

Vacuum stability results lead to the following conclusions –

- Fibrous PVN (15.71% N) is slightly more stable than gelatinized PVN (15.71% N).
- DPA, 2NDPA and carbamite at 0.25% concentration in gelatinized PVN have a marginally negative effect. However, when used in 1% concentration, DPA,

Table 3. Vacuum Stability Test Results of PVN (15.71% N) without and with Additives

Sample Composition		Volume of gas evolved (at 100°C, 40 h)	
PVN type	Additive	Conc. of additive [%]	[ml/g]
PVN (15.71% N), fibrous	none	0.00	6.74
PVN (15.71% N), gelatinized	none	0.00	7.98
		DPA	0.25
	DPA	1.00	7.00
		2NDPA	0.25
	2NDPA	1.00	6.25
		Carbamite	0.25
	Carbamite		1.00
		Resorcinol	0.25
	Resorcinol		1.00

2NDPA and carbamite have a favourable effect, 2NDPA being the most effective. Interestingly, resorcinol shows the opposite trend.

3.7 Ignition Delay and Activation Energy

Ignition delays of fibrous PVN samples, differing in % N, were determined in a special apparatus employing Wood's metal bath⁽¹⁴⁾. The ignition delays were noted at bath temperatures varying from 468 K to 538 K (195°C to 265°C) at intervals of 5 K. The results are presented in Table 4.

The ignition temperatures, corresponding to 5-s ignition delay, for PVN samples containing 15.71%, 14.95%, and 13.34% N are 513 K, 523 K and 533 K, respectively. Thus, ignitibility of PVN increases with increasing % N.

Activation energy of PVN samples was calculated using Semenov equation, viz.:

$$D = C \cdot e^{-E/RT}$$

where D is ignition delay, E is activation energy, R is universal gas constant, T is absolute temperature, and C is a constant (depends on the composition of material).

Plotting log D against 1/T, a straight line was obtained. From the slope of the curve, the following values of activation energy of PVN samples were obtained:

PVN (15.71% N)	16.076 kcal/mol
PVN (14.95% N)	13.299 kcal/mol
PVN (13.34% N)	16.017 kcal/mol

Thus, the activation energy of PVN varies with its nitrogen content. This variation may be due to difference in the crystallinity of PVN polymer chains (fibres) caused during the progressive nitration of PVA.

3.8 Impact Sensitivity

Impact sensitivity measurements on samples of PVN and "doped" PVN were carried out using a standard "Fallhammer apparatus"⁽¹⁴⁾. 20 mg of the sample was placed on the anvil and 2-kg weight was dropped onto it from an arbitrary height. Successive trials were carried out at intervals of 5 cm and continued until sufficient data were collected. From the data obtained, the percentage of explosion for each height was calculated.

A graph was plotted between the median height of fall and percentage of explosion for gelatinized and ungelatinized PVN samples, without and with additives (1% wt/wt). The median heights of fall for 50% explosion are shown in Table 5.

After repeating the experiments with RDX and Tetryl, the Figure of Insensitivity (F of I) of the test samples was calculated⁽¹⁴⁾, taking RDX as the reference standard (F of I = 80). The F of I values are also presented in Table 5.

Results show that:

- (a) With increasing % N in fibrous PVN samples, the median height of fall for 50% explosion decreases, that is, impact sensitivity increases.

Table 4. Ignition Delays of Fibrous PVN Samples having Different Nitrogen Content

Temperature [K]	1/T × 10 ⁻⁴ [K]	PVN (15.71% N)		PVN (14.95% N)		PVN (13.34% N)	
		Ignition delay, D [s]	log D [s]	Ignition delay, D [s]	log D [s]	Ignition delay, D [s]	log D [s]
468	21.4	23.5	1.37	-	-	-	-
473	21.1	19.0	1.28	-	-	34.0	1.53
478	20.9	15.5	1.19	14.0	1.15	27.0	1.43
483	20.7	13.0	1.11	13.8	1.14	26.0	1.41
488	20.5	12.5	1.10	13.0	1.11	17.0	1.23
493	20.3	9.0	0.95	12.0	1.08	12.0	1.08
498	20.1	7.5	0.88	9.0	0.95	11.0	1.04
503	19.9	6.0	0.78	8.0	0.90	10.0	1.00
508	19.7	5.5	0.74	6.5	0.81	9.0	0.95
513	19.5	5.0	0.69	6.0	0.78	8.5	0.93
518	19.3	4.6	0.66	5.5	0.74	8.0	0.90
523	19.1	-	-	5.0	0.69	7.0	0.84
528	18.9	-	-	4.5	0.65	6.5	0.81
533	18.8	-	-	-	-	5.0	0.69
538	18.6	-	-	-	-	4.5	0.65

Table 5. Results of Impact Sensitivity Test on PVN without and with Additives

Sample Composition		Median height of fall for 50% explosion [cm]	F of I (RDX=80)
PVN type	Additive		
PVN (11.76% N), fibrous	none	90.0	141.2
PVN (13.34% N), fibrous	none	85.0	133.3
PVN (14.95% N), fibrous	none	82.5	129.4
PVN (15.71% N), fibrous	none	81.0	127.1
PVN (15.71% N), gelatinized	none	82.0	128.6
	Carbon black 1%	62.0	97.2
	Lead stearate 1%	55.0	86.3
	Lead salicylate 1%	46.0	72.2
* Tetryl	none	81.5	127.8
** RDX	none	51.0	80.0

* included for comparison

** Reference standard

(b) Fibrous and gelatinized samples of PVN (15.71% N) as well as the well known "intermediary" high explosive Tetryl are equally sensitive to impact loads (F of I range 127-129).

(c) Carbon black, lead stearate and lead salicylate are very effective as "sensitizer" additives in small (1%) dosage.

3.9 Calorific and Calorimetric Values

Heat of combustion (calorific value) of PVN was determined in a Gallenkamp adiabatic bomb calorimeter, using oxygen at 25 atm pressure. Similarly, heat of explosion (calorimetric value) was determined using nitrogen at 25 atm pressure. The following results were obtained:

Specimen	Heat of combustion [cal/g]	Heat of explosion [cal/g]
PVN (11.76% N), fibrous	3744	456
PVN (15.71% N), fibrous	3023	987
PVN (15.71% N), gelatinized	3065	864

The heat of combustion values for PVN (15.71% N), whether gelatinized or ungelatinized (fibrous), are almost equal. However, the heat of combustion of PVN (11.76% N), is appreciably higher than that of PVN (15.71% N), probably due to the presence of a larger number of hydrogen atoms in the chain of the former and consequent availability of extra heat when burnt in oxygen.

The heat of explosion of fibrous PVN (15.71% N), is higher than that of gelatinized PVN (15.71% N). The heat of explosion of PVN (11.76% N) is, however, much less than that of PVN (15.71% N). This is due to the presence of a much larger number of -ONO₂ groups and, therefore, higher oxygen balance in the latter, which allows more complete combustion and greater heat release when burnt in an inert atmosphere or limited oxygen supply.

These values of heat of combustion and heat of explosion of PVN are in good agreement with literature^(6,9).

Using the above data on heat of combustion and empirical equations for combustion reaction, the heat of formation

(ΔH_f) of PVN was calculated, at 25°C, after applying the necessary corrections, and was found to be as follows:

PVN (11.76% N), fibrous	- 751.25 kcal/kg
PVN (15.71% N), fibrous	- 241.25 kcal/kg
PVN (15.71% N), gelatinized	- 205.12 kcal/kg

4. Conclusion

Results of our investigations on polyvinyl nitrate confirm that it is a high energetic material, with its properties showing a strong dependence on % N. The main conclusions are:

- PVN fibres have a porous surface topography.
- Degree of crystallinity in fibrous PVN increases with increasing % N.
- With increasing % N in fibrous PVN, its Abel heat test value (thermal stability) at 82°C decreases. Addition of DPA, 2NDPA, carbamite and resorcinol, in 0.25% concentration, improves the heat stability of PVN. However, there is no linear relation between the additive concentration and stabilizing effect.
- Vacuum stability of PVN is improved by addition of DPA, 2NDPA and carbamite in 1% concentration.
- With % N in PVN increasing from 13.34% to 15.71%, the ignition temperature decreases from 533 K to 513 K. However, activation energy is minimum (13.3 kcal/mol) for PVN with 14.95% N.
- With increasing % N in fibrous PVN, its impact sensitivity increases. PVN (15.71% N) is as sensitive as Tetryl, an "intermediary" high explosive. Addition of 1% carbon black, lead stearate, or lead salicylate increases the impact sensitivity of PVN.
- With increasing % N in fibrous PVN from 11.76% N to 15.71%, heat of combustion decreases from 3744 cal/g to 3023 cal/g, while heat of explosion increases from 456 cal/g to 987 cal/g, due to increase in the oxygen balance.

The results of our investigations on some other properties of PVN, such as burn rate, thermal decomposition kinetics, performance evaluation, etc. would be reported separately.

5. References

- G. Frank and H. Kruger, Ger. Pat. 537303 (1929); *Chem. Abstr.* 26, 1125 (1932).
- S.M. Kaye (Ed.), "Encyclopedia of Explosives and Related Items", U.S. ARRADCOM, New Jersey 1978, vol. 8, pp. 356-358.
- R.A. Streker and F.D. Vederame, U.S. Pat. 3, 965, 081; *Chem. Abstr.* 85, 162921 (1976).
- T. Urbanski, "Chemistry and Technology of Explosives", Pergamon Press, New York 1965, vol. 2, p. 173 and, 1984, vol. 4, pp. 413-419.
- R.D. James, "Propellants and Explosives", Noyes Data Corporation 1974, pp. 183-184.
- W. Diepold, *Explosivstoffe* 18,2 (1970).
- Chem. Abstr.* 97, 111996b (1982).
- R. Meyer, "Explosives", 3rd Ed., VCH Verlagsgesellschaft, Weinheim 1987, p. 274.

- (9) "Properties of Explosives of Military Interest", AMCP 107-177, 5001 Eisenhower AVC., Alexandria, VA 22333 Jan 1971.
- (10) S. Krimm and C.Y. Liang, *J. Appl. Phys.*, 29 (10), 1409 (1958).
- (11) Koji Nakanishi, "Infrared Absorption Spectroscopy-Practical", Holden-Day, Inc., San Francisco and Nankods, Tokyo, 1962, pp. 28-50.
- (12) L.J. Bellamy, "The Infrared Spectra of Complex Molecules", Chapman and Hall, London 1975, vol. 1, pp. 331-345.
- (13) H.P. Klug and L.E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials", John Wiley and Sons, Inc., New York 1954, pp. 621-630.
- (14) "Services Textbook of Explosives", HMSO Publication, U.K., 1972.

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