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STEREOREGULAR POLYVINYL NITRATE

R. A. STRECKER

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

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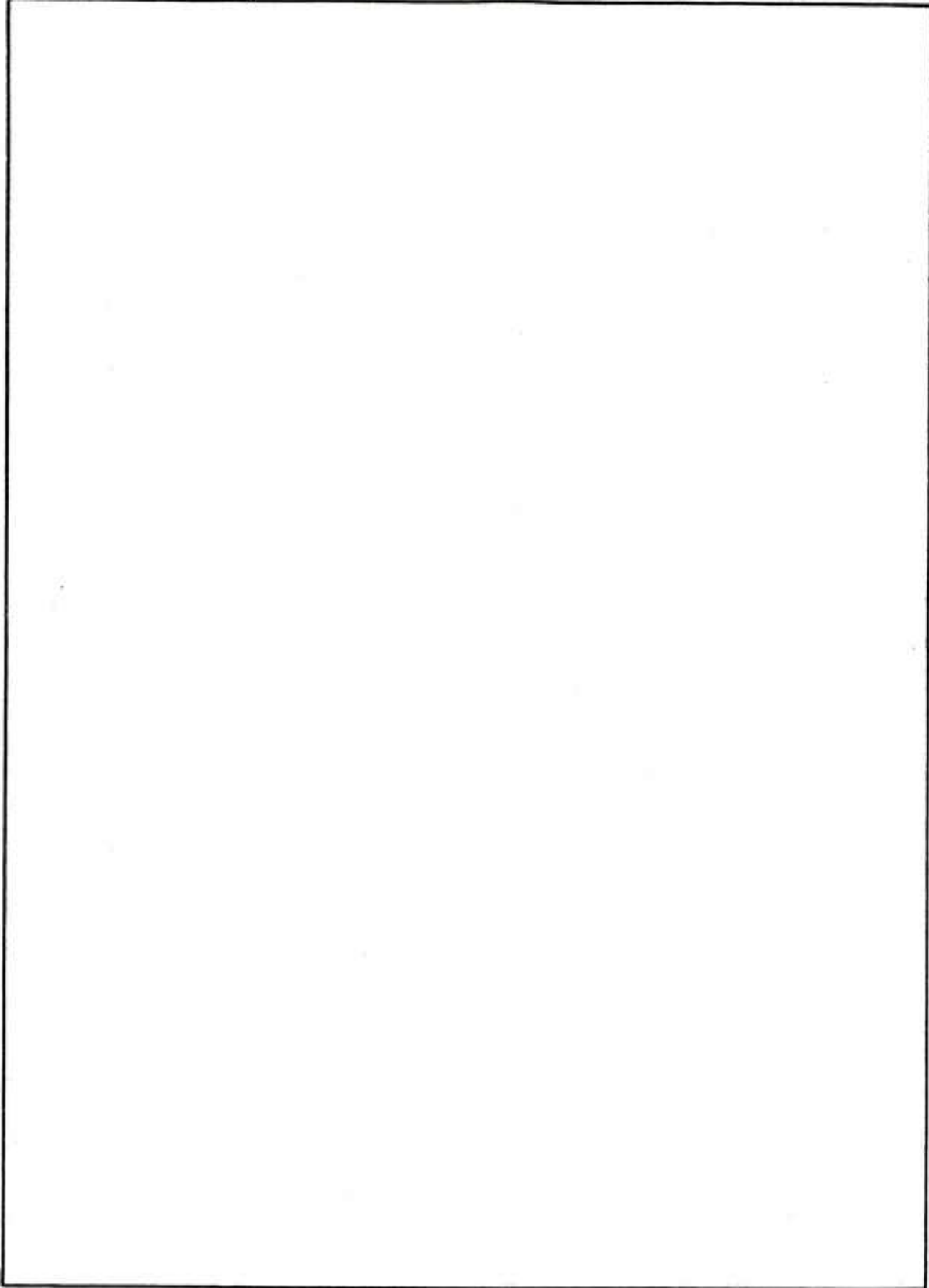
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Isotactic polyvinyl nitrate (PVN) was prepared to investigate the effect of stereoregularity on the physical properties of PVN. The isotactic PVN had a higher softening point and was more difficult to stabilize than regular PVN.		

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INTRODUCTION

Polyvinyl nitrate (PVN) has been investigated as a potential propellant material for the past 50 years. Early work involved the development of various methods of nitration and stabilization (refs 1 through 5). The theoretical nitrogen level for PVN is 15.7%. A variety of nitrating agents has been used, and nitrogen levels in the range of 14-15% are easily attainable. A fully nitrated PVN has been prepared (ref 6). Obtaining stable PVN for use in propellants has been and continues to be a problem. Several methods for stabilizing PVN have been studied, and the results indicate that PVN with thermal stabilities comparable to nitrocellulose can be prepared (refs 2, 7, 8). It was also found that as the molecular weight of PVN increases, it becomes more difficult to stabilize (ref 2).

The most significant problem associated with the use of PVN in military propellants is its low softening temperature which is in the range of 40°C to 65°C (refs 3, 6, 7, 8, 9). When PVN is combined with other ingredients such as nitrocellulose and stabilizers, the softening temperature of the mixtures decreases as the percentage of PVN is increased (refs 3 and 10). This necessitates keeping the amount of PVN at a low level in any given propellant composition.

The use of PVN in propellants has been reported to yield propellants that are cooler burning and have increased propulsive force (refs 11, 12). These advantages are presently limited by the decrease in softening temperature with increasing amounts of PVN in a propellant composition. In order to overcome the problem, a study was made to determine possible ways of raising the softening temperature of PVN.

A search of the literature indicated that increasing the molecular weight would not have much effect on raising the softening temperature (ref 6). Another approach was to investigate the possibility of introducing stereoregularity into the PVN molecule in order to enhance the potential for crystallinity. It is known that increasing the crystallinity of a polymer can raise its melting point. Stereoregular PVN has been prepared (ref 13). This report describes the effect of stereoregularity on the softening point and stabilization of PVN.

EXPERIMENTAL

Stereoregular polyvinyl alcohol (PVA) is not available commercially. Therefore, isotactic PVA was prepared in the laboratory through the polymerization of vinyloxytrimethylsilane using low temperature and a cationic catalyst (refs 14 through 17). Table 1

gives the conditions of polymerization and the properties of the isotactic PVA obtained.

Table 1. Polymerization conditions and properties of isotactic PVA.

Solvent	Toluene
Catalyst	EtAlCl ₂
Temperature	-78°C
Time	3 hr
\overline{MW}_w	44,000
Isotacticity	85%

The isotactic PVA was nitrated using the following nitrating agents: nitric-sulfuric acid; anhydrous nitric acid and acetic anhydride; anhydrous nitric acid and phosphorous pentoxide.

A mixture of 90 parts nitric acid (98%) and 10 parts concentrated sulfuric acid was used. The ratio of mixed acid to PVA was 10 to 1 and the nitration was conducted at 0°C. The PVA was added slowly with vigorous stirring to avoid localized heating and possible oxidation. The mixture was stirred for an additional 30 minutes after the PVA was added. The product was obtained by pouring the reaction mixture into a vigorously stirred mixture of crushed ice and water, collected on a filter, washed with water, and stored under water for stabilization.

Ten parts of anhydrous nitric acid were used with 1 part isotactic PVA, and the reaction was run at -20°C while the PVA was slowly added to the stirred acid. The mixture was stirred for 1 hour after addition of the PVA. The product was obtained by pouring the mixture into crushed ice and water with vigorous stirring. It was collected, washed with water, and stored under water for stabilization.

Using acetic anhydride and anhydrous nitric acid, 1 part isotactic PVA in 10 parts of acetic anhydride was added slowly as a slurry to 5 parts anhydrous nitric acid with vigorous stirring at -15°C. When the addition was completed, the stirred reaction mixture was allowed to warm to 15°C and stirring was continued for 30 minutes at that temperature. The mixture was poured into crushed ice and

water. The product was collected, washed with water, and stored under water for stabilization.

A mixture of 80 parts 98% nitric acid and 20 parts phosphorous pentoxide was used with isotactic PVA. The PVA was dissolved in phosphoric acid in the ratio of 1 to 10 and the solution was poured slowly into the vigorously stirred acid at a temperature of 0°C. The ratio of nitrating acid to PVA-phosphoric acid solution was 10 to 1. After the addition, the mixture was stirred for an additional 30 minutes. The product was separated from the nitrating acid by filtration, poured into ice water, stirred vigorously in the ice water, and stored under water for stabilization.

The isotactic PVN was stabilized using two different methods. The first involved dissolving the PVN in acetone and then pouring the solution into a 0.5% sodium carbonate solution, with vigorous stirring, to precipitate the PVN. The product was then washed and dried in a vacuum oven at 65°C for 4 hours. It was white and very tough and fibrous in nature. The second method involved vigorously stirring the PVN in water heated to about 97°C on a steam bath and adding enough 0.5% sodium carbonate solution to maintain the pH at 7. The PVN was stirred at this temperature for 3 hours. After cooling, it was washed and the boiling process was repeated. After the second boil, the product was collected, washed and vacuum dried as in the first method. The product was cream colored and had the same tough, fibrous character as the material precipitated from the acetone and water mixture.

RESULTS

Table 2 lists the properties of isotactic PVN prepared by each nitration method and stabilities for corresponding stabilization methods.

Table 2. Properties of Isotactic PVN.

Nitrating agent	%N	Softening* temp. °C	134.5°C heat test (min)	
			Acetone	Boil
H ₂ SO ₄ /HNO ₃	14.7	66	30+	15
Anhy. HNO ₃	15.0	70	30+	18
HNO ₃ /(AcO) ₂ O	15.2	75	30+	25
HNO ₃ /P ₂ O ₅	14.9	73	30+	24

*

Determined using DSC at heating rate of 2.5°C/min.

The softening temperatures for the isotactic PVN are higher than those observed for PVN prepared from regular PVA (ref 2). This increase is attributed to an increased crystallinity in the isotactic PVN polymer. The method of stabilization did not affect the softening point.

The best method for stabilizing the isotactic PVN was by precipitation from acetone in dilute carbonate solution. The water boil method did not work as well.

CONCLUSIONS

Incorporating stereoregularity into PVN increases its softening temperature.

Stabilization of isotactic PVN to a level comparable to that of nitrocellulose can be achieved only when the polymer is dissolved and reprecipitated.

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