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PETN HOMOLOGS

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DEVELOPMENT DIVISION

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PETN Homologs

ABSTRACT

High purity nitrate esters of the pentaerythritols can be successfully synthesized from correspondingly high purity reagents. The latter are not commercially available, but may be purified through molecular distillation and/or fractional crystallization from xylene. The isolated products are ultimately saponified to reagents of high purity.

The nitration of high purity pentaerythritols using 97-100% nitric acid proceeds smoothly resulting in yields of the corresponding nitrate esters which are nearly quantitative.

Thin layer chromatography (TLC) indicates numerous satellite impurities present in all the pentaerythritol-tetranitrate (PETN) homologs with the exception of ultrapure PETN itself. Separation and isolation of these contaminants, from a high impurity concentrate, was achieved by liquid chromatography. IR spectra of these components suggests these compounds are the various homologs and pentaerythryl ethers with a mixture of hydroxyl and nitrate functional groups.

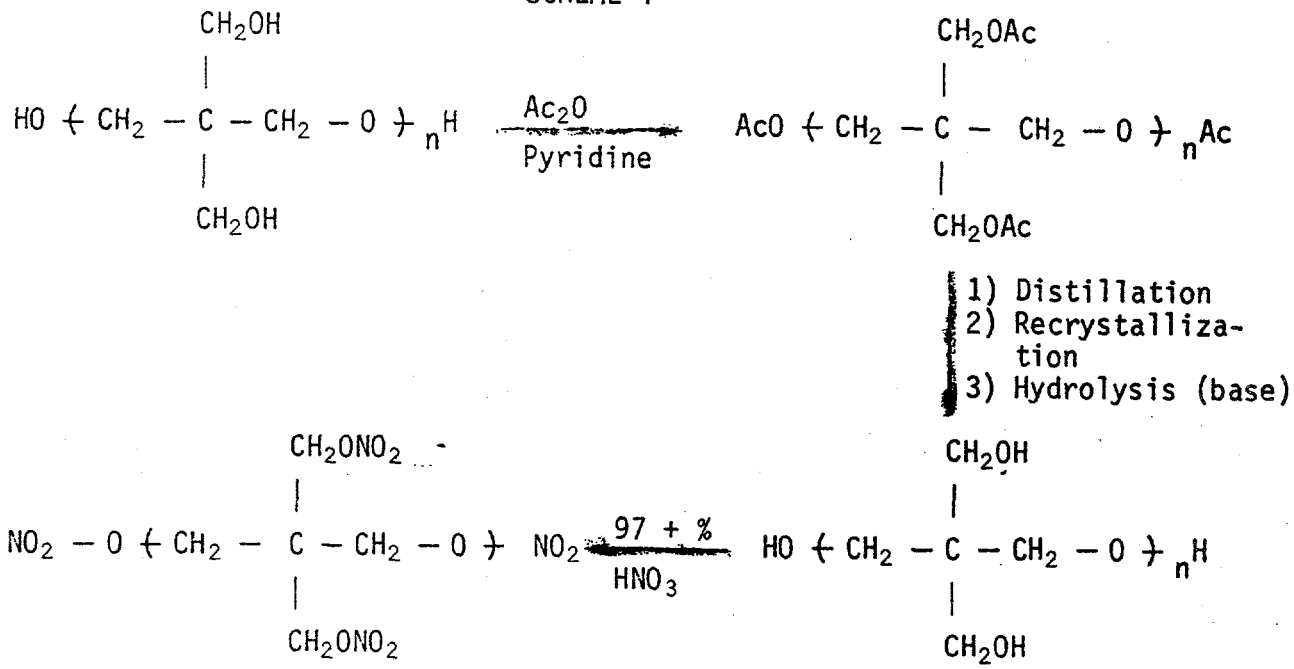
DISCUSSION

Pentaerythritol, PE, is prepared by the condensation of acetaldehyde and formaldehyde in the presence of an alkaline condensing agent. Other related hydroxylated products (dipentaerythritol, tripentaerythritol, etc.) are also obtained as by-products of the pentaerythritol reaction. These compounds have higher molecular weights than PE and are formed by etherifying one or more of the hydroxy groups of PE with other pentaerythritol residues.

Of the higher pentaerythritols, only dipentaerythritol and tripentaerythritol are commercially available, and neither of these reagents is of sufficient purity for most applications. Whenever these products are esterified, additional impurities are introduced. These additive impurities result from the partial esterification of the reagent and of its contaminants.

The general reaction route (Scheme 1) utilized in the synthesis of high purity nitrate esters of the pentaerythritols:

SCHEME 1



n = 2 Dipentaerythritol (DiPE)
n = 3 Tripentaerythritol (TriPE)
n = 4 Tetrapentaerythritol (TetraPE)

involves the conversion of the polyhydric alcohols to their respective acetate esters. The latter lend themselves to purification through distillation and recrystallization from xylene. Subsequently, the alcohols are reconstituted from the purified acetates by hydrolysis in alkaline solution, followed by nitration of the alcohols to yield the desired nitrate ester.

Dipentaerythritol-hexanitrate (DiPEHN) and tripentaerythritol-octanitrate (TriPEON) of excellent purity were synthesized by the above procedure. During the purification of the acetate esters, the residues from the molecular still and the extracts from the fractional crystallization process were isolated. These were found to contain a high concentration of tetrapentaerythritol-decaacetate (TetraPEDAc) along with numerous other impurities.

The TetraPEDAc was extracted from the impurity concentrate by repeated crystallizations from xylene. It was eventually nitrated into tetrapentaerythritol-decanitrae (TetraPEDN).

The remaining impurities were collectively hydrolyzed and subsequently nitrated. The yield consisted of a mixture of nitrate ester products. These were isolated by liquid chromatography and some characterization work was done on them.

TRIPENTAERYTHRITOL-OCTANITRATE (TRIPEON)

Nitration of commercial TriPE yields a reaction product consisting of PETN, DiPEHN, TriPEON, TetraPEDN and other impurities. Column chromatography promotes separation of these components, resulting in products of over 99% purity. Although high purity products can be obtained in this manner, quantity limitations prohibit the use of this technique in large scale production.

Column chromatography was used in an effort to isolate small samples of the components of crude TriPEON. Acidic, neutral and basic alumina columns were prepared by slowly sieving the dry aluminas in a 1 cm column partially filled with benzene. The columns were packed to a height of 16 cm and glass wool plugs were inserted. The benzene levels were adjusted to that of the adsorbent and one gram samples of crude TriPEON, dissolved in methylene chloride, were applied. The fluid level was adjusted to the level of the top of the glass wool. One hundred ml of benzene was then allowed to pass through each column. The elutant was then changed to 90% benzene, 8% dichloroethane and 2% acetone. Samples were periodically taken and tested for the presence of nitrate ester by a sulfuric acid solution of N,N-diphenylbenzidine.

Fractions, of a volume equivalent to the weight of the adsorbent, were collected as soon as the nitrate esters were detected. Table I is a comparison of efficiencies of the different aluminas used. The basic alumina promoted no separation. The neutral alumina was limited to the isolation of one component, while the acidic support effected the isolation of ultrapure TriPEON and TetraPEDN.

In order to obtain quantitative data, a second set of columns was prepared using acidic and neutral aluminas. The columns were 1 cm in diameter and 20 cm long. Both columns were packed by sieving alumina into benzene. The columns were charged with crude TriPEON and eluted. The elutant was 90% benzene, 8% dichloroethane and 2% acetone. The volumes of the fractions collected were equal to the weight of the support in the columns.

The collected fractions were evaporated to dryness and weighed. The isolated fractions were evaluated by TLC. Figs. 1 and 2 show the results of this study.

A sample of the pure TetraPEDN isolated in the above manner was characterized by DTA (Fig. 3) and infrared spectra (Figs. 4-6). The data on DiPEHN and TriPEON are included for comparison purposes.

Extraction, crystallization, vacuum sublimation, and other techniques of purification of the TriPE reagent were tried and evaluated but no complete separation was obtained. The procedures discussed herein were found to be the most effective in obtaining TriPE of the desired purity. These involve the acetylation of commercial TriPE, fractional distillation of the resulting acetate, fractional crystallization of the acetate, and hydrolysis of the TriPEOAc enriched fractions. TriPE of 97% + purity was obtained from a commercial reagent of less than 88% purity as shown in Table II.

Table I. Comparison of Alumina Column Supports

Cumulative Volume Collected	Components Identified		
	Acidic Column	Neutral Column	Basic Column
120 ml	Mixture: Di & Tri	Mixture: Mono & Di	Mixture: Di & Tri
150	Pure Tri	Pure Di	Mixture: Di & Tri
180	Pure Tri	Mixture: Di & Tri	Mixture: Di & Tri
210	Mixture: Tri & Tetra	Pure Tri	Mixture: Di, Tri & Tetra
240	Mixture: Tri & Tetra	Pure Tri	Mixture: Di, Tri & Tetra
270	Pure Tetra	Pure Tri	Mixture: Di, Tri & Tetra
300	Pure Tetra	Mixture: Tri & Tetra	Mixture: Di, Tri & Tetra
330	Pure Tetra	Mixture: Tri & Tetra	Mixture: Di, Tri & Tetra
360	Pure Tetra	Mixture: Tri & Tetra	Mixture: Di, Tri & Tetra
390	Mixture: Tetra & Lower	Mixture: Tri & Tetra	Mixture: Di, Tri & Tetra
420	Mixture: Tetra & Lower	Mixture: Tri & Tetra	Mixture: Di, Tri & Tetra
450	Mixture: Tetra & Lower	No nitrate esters	Mixture: Di, Tri & Tetra

NOTE: Mono - pentaerythritoltetranitrate

Di - Dipentaerythritolhexanitrate

Tri - Tripentaerythritoloctanitrate

Tetra - Tetrapentaerythritoldecanitrate

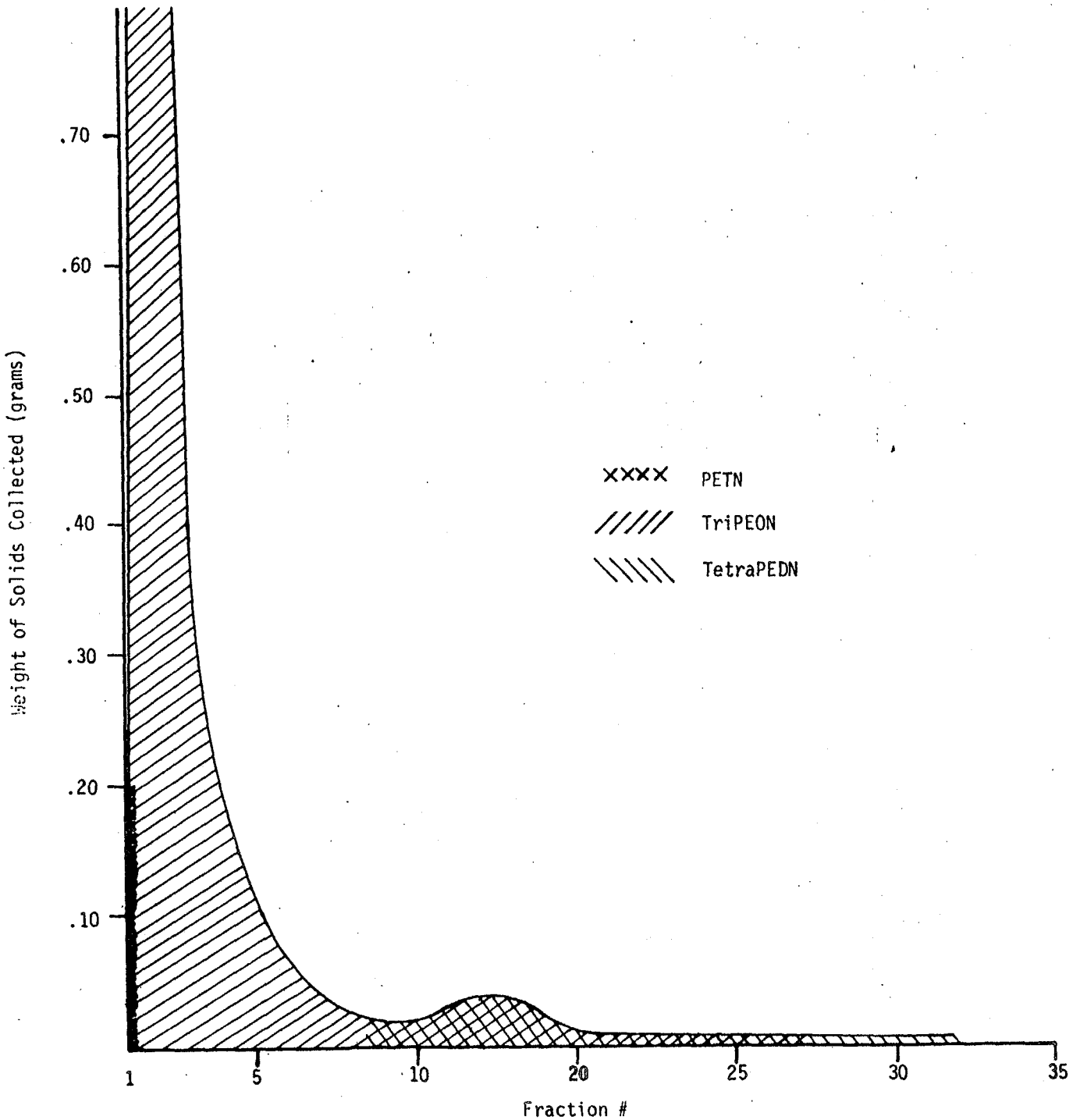


Fig. 1. Neutral Alumina Column (1 cm x 20 cm, 1.15g Crude TriPEON)

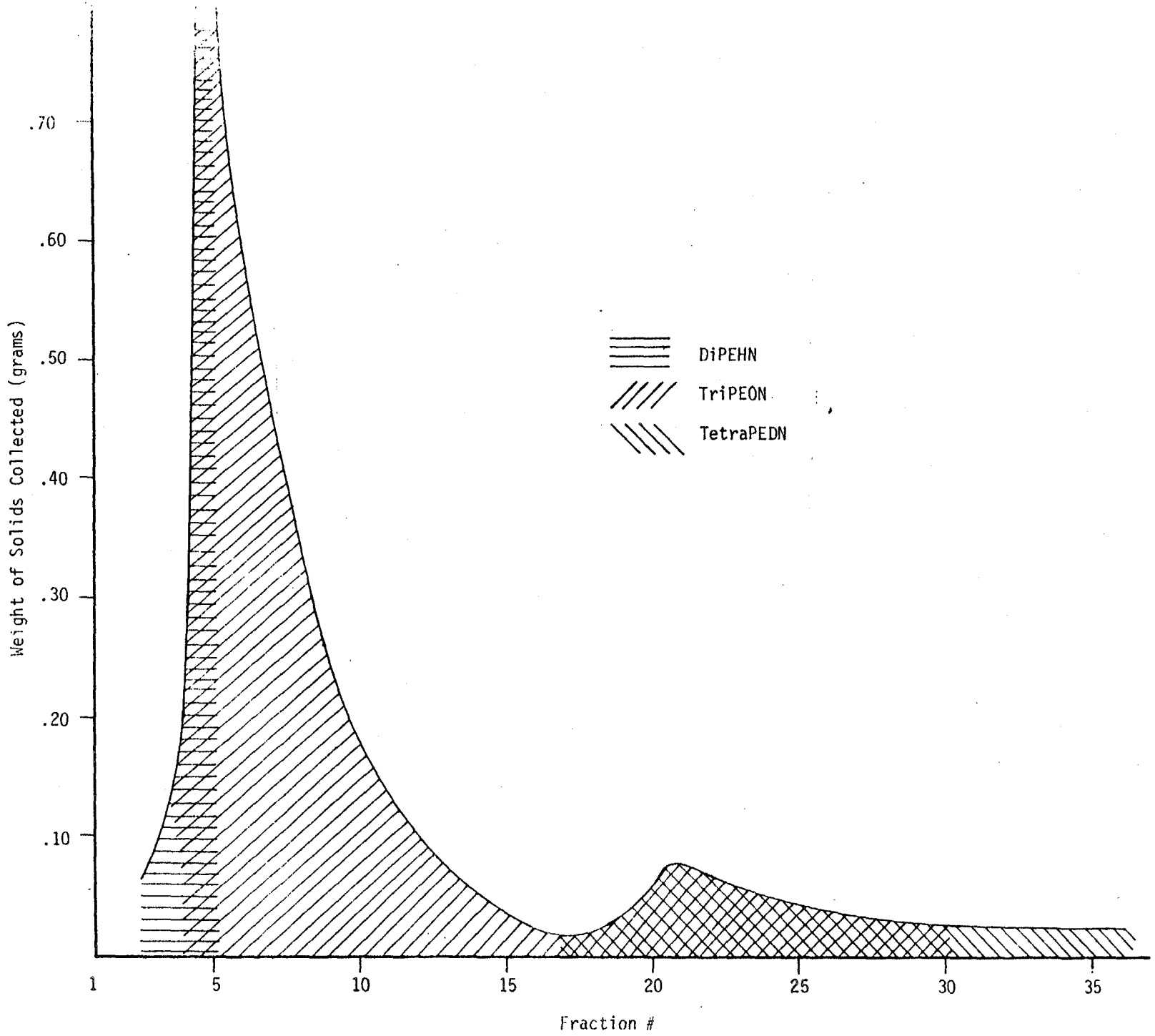


Fig. 2. Acidic Alumin Column (3 cm x 60 cm, 5.17g Crude TriPEON)

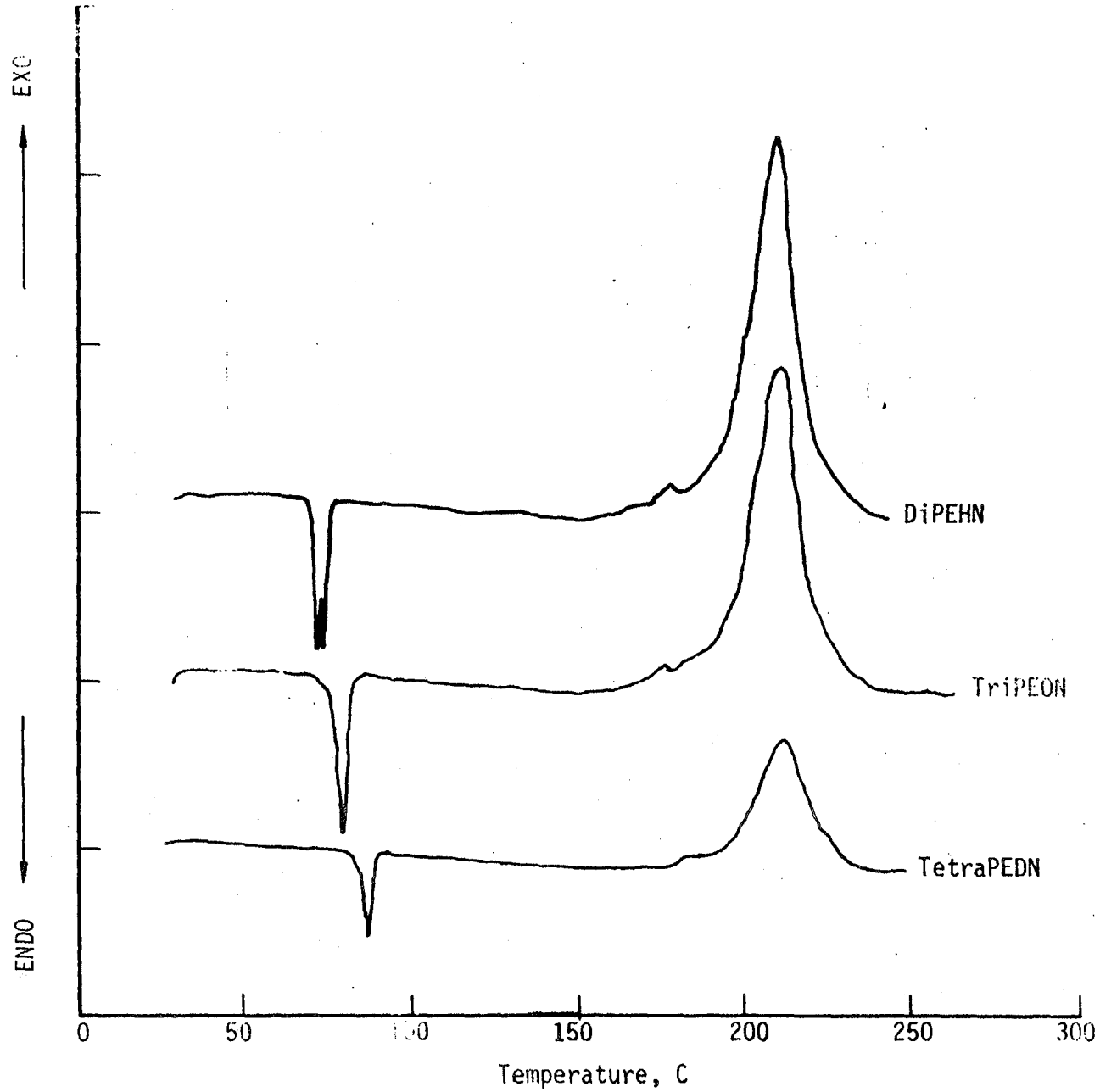


Fig. 3. DTA's of DiPEHN, TriPEON & TetraPEDN

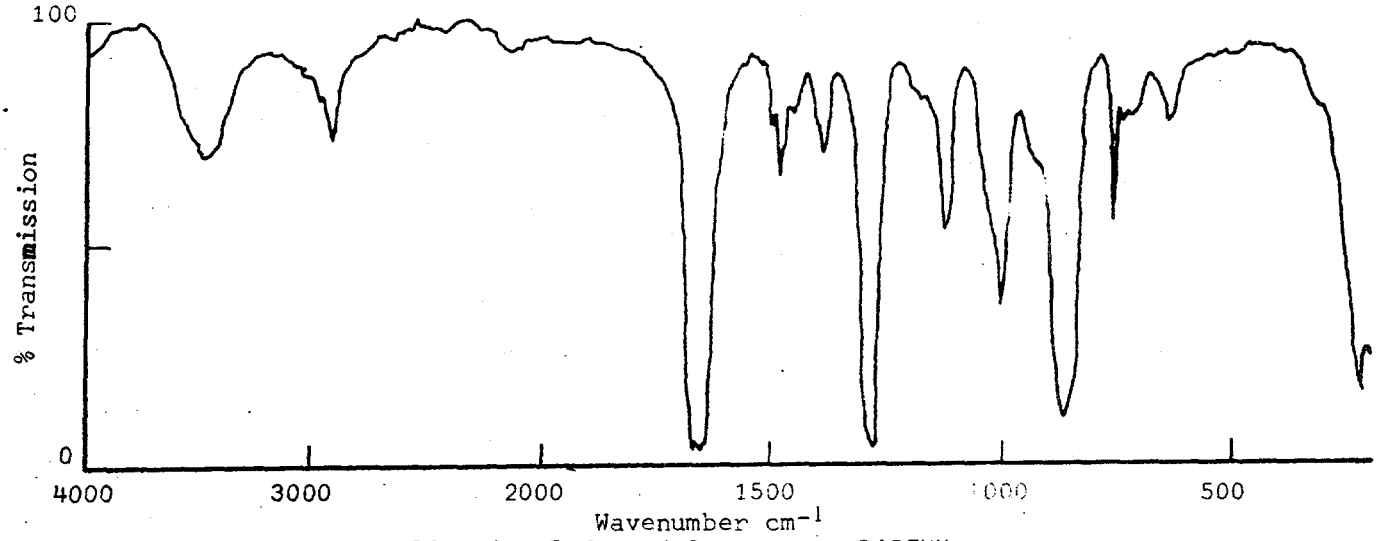


Fig. 4. Infrared Spectrum - DiPEHN

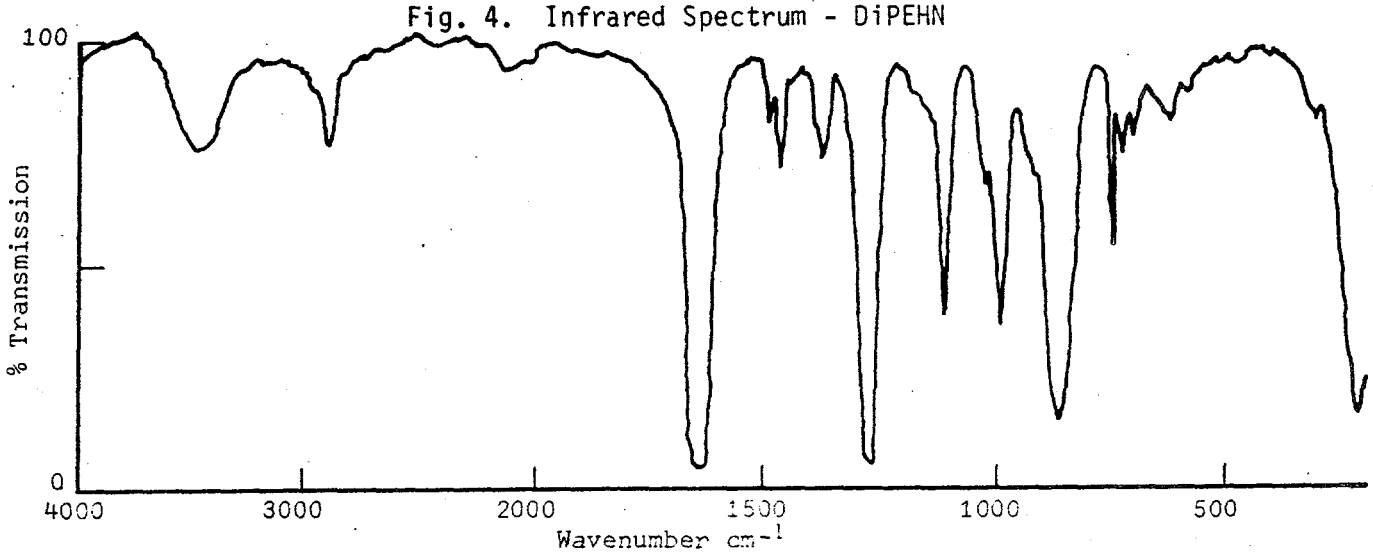


Fig. 5. Infrared Spectrum - TriPEON

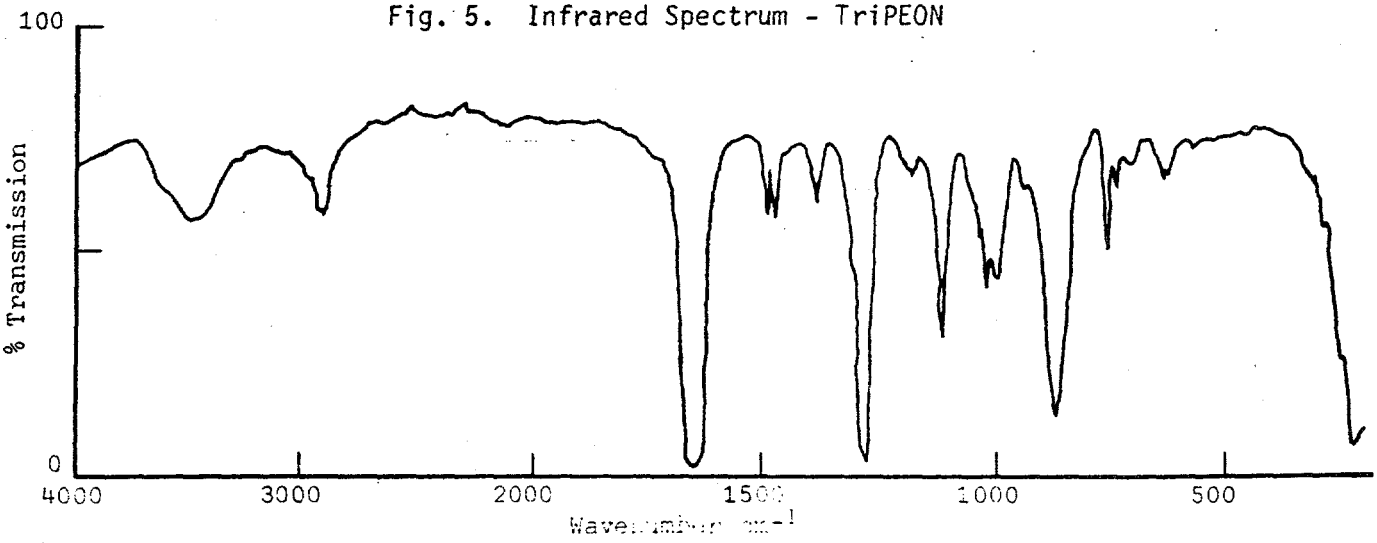


Fig. 6. Infrared Spectrum - TetraPEDN

Table II. Gas Chromatographic Determination of Tripentaerythritol*

	Sample Size µℓ	MonoPE %	diPE %	triPE %	tetraPE %	bisPE Monoformal %
TriPE (Shelf Reagent)*	-	-	1.8	87.7	13.3	1.1
TriPE (Hydrolyzed from Acetate Distillations)						
Sample 1	20	-	1.28	97.8	-	0.52
Sample 2	20	0.33	1.50	97.4	0.31	0.43
SAmple 3	20	0.24	3.43	96.3	-	-

**Total composition exceeds 100%; values given as reported.*

Numerous procedures are available for the acetylation of TriPE(*1*). Esterification has been promoted by adding the reagent to an excess of glacial acetic acid with sulfuric acid as the catalyst; from a mixture of glacial acetic acid and acetic anhydride with sulfuric acid; from acetic anhydride using pyridine as the catalyst.

The best yields of the acetate were obtained when TriPE was reacted with acetic anhydride in the presence of pyridine.

TriPE (1 mole) was added, with stirring, to a mixture of pyridine (6 moles) and acetic anhydride (12 moles) at a temperature below 30 C. The slurry was then refluxed for three hours, cooled and poured with vigorous stirring into 8X volumes of crushed ice. The crude acetate was collected and washed twice with hot water.

Distillation of the acetate and collection of the desired fractions can only be promoted from clean material. The crude acetate must be free of all unspent reagents, moisture and/or organic solvents.

The acetate may be filtered and washed while in an ethyl ether solution; however, the moist crude acetate is only moderately soluble in ethyl ether and large volumes of the solvent are required to effect solution. Understandably, safety considerations discouraged the use of ethyl ether and an alternative procedure using acetone as the solvent was developed. The crude acetate was dissolved in acetone and filtered. The solution was then neutralized with dilute hydrochloric acid. The acetate was allowed to settle, collected and redissolved in acetone. To the solution was added dry sodium carbonate (1 gm/100 g acetate) and the mixture stirred for 15 minutes. The mixture was then filtered and the acetate was precipitated from solution by the addition of water. The precipitate was redissolved in minimum acetone and the solution was shaken with anhydrous sodium sulfate (5 g/100 ml solution) for 15 minutes and refiltered to remove the drying agent. The filtrate was poured, with vigorous stirring, into 8X volumes of precooled petroleum ether. The ensuing precipitate was gathered and dried under vacuum at 50 C.

The dried TriPEOAc was heated gently until it melted and while still fluid was poured into 10X volumes of ethyl ether to which had been added carbon black and magnesium sulfate (0.5 and 20 g respectively/100 g acetate). The slurry was filtered over a steam heated funnel. The solvent was stripped under vacuum and the powdery acetate was readied for distillation.

Purification of the acetate was promoted through fractional distillation. The richest TriPEOAc fraction was collected at a temperature of 285 ± 5 C and a pressure of 0.025 mm. A typical distillation monitored for temperature, pressure and distillate yields is shown in Table III. The composition of each of the distillate fractions was evaluated by TLC. It is to be noted that fraction No. 8 which was the largest fraction, was also the richest in TriPEOA. Further concentration was effected by fractional crystallization from xylene. The isolated fraction was freed of solvent and readied for hydrolysis.

Table III. TriPEOA Fractional Distillation

(80.56 gm distilled from 90 gm starting material)

Fraction	Temperature (C)	Pressure (mm)	Wt. Distillate (gm)
1	20 - 260	0.005	0.10
2	260 - 270	0.005	0.08
3	270 - 275	0.005	0.63
4	275 - 278	0.005	0.58
5	278 - 280	0.005	0.78
6	280 - 284	0.005	0.96
7	284 - 288	0.005	3.03
8	288	0.005	40.50
9	289	0.010	14.50
10	290	0.015	17.50
11	290 - 292	0.025	1.50
12	292 - 198	-	.40
t Residue	-	-	-

Saponification of TriPEOAc into TriPE is a highly efficient operation. Based on the starting acetate, hydrolysis yields average 95% of theory. Hydrolysis was effected in an alcohol solution of either sodium hydroxide or potassium hydroxide in a ratio of 12 moles alkali to 1 mole of the acetate.

The mixture was refluxed over a water bath for two hours. The product was cooled and poured into a large volume of cold water. After the product gathered, it was collected and washed with hot water then dilute sulfuric acid. The TriPE was rinsed with hot water until neutral, given one final rinse with acetone, collected and dried under vacuum at 50 C.

Synthesis of high purity TriPEON can be successfully promoted from correspondingly high purity TriPE(*2*,*3*). The reaction of the purified TriPE with 99% HNO_3 proceeded smoothly. The resulting nitration product was recovered from solution by drowning the mixture in a large volume of ice water.

One part TriPE was added slowly, with stirring, to 8 parts 99% nitric acid at a temperature of -25 to 0 C. The reaction was stirred for an additional hour at -5 to 0 C. The product was drowned by pouring it over 8X volumes of crushed ice and allowing it to stand undisturbed for two or three hours. The water was decanted from the crude TriPEON which gathered as a solid granular cake. The cake was rinsed copiously with water, crushed under water and collected. The solids were then digested in eight times their weight of 1% ammonium carbonate solution for several hours, then filtered, washed freely with water, given successive rinses in ethanol and ethyl ether, and dried. The crude TriPEON was then taken up in minimum acetone and anhydrous sodium sulfate was added to the solution and stirred. The drying agent was removed by filtration and the filtrate was poured into 5X volumes of precooled ethanol from which the TriPEON precipitated.

Occasionally, after digestion in ammonium carbonate, it was necessary to dissolve the crude TriPEON in acetone and treat the solution with dry sodium carbonate to completely free the product from the acid. When carbon dioxide ceased to evolve, the solution was filtered and introduced into water to precipitate the product. The precipitate was collected, redissolved in a minimum volume of acetone and shaken with anhydrous sodium sulfate. The drying agent was removed by filtration and the solution was poured into 5X volumes of precooled ethanol from which the TriPEON precipitated. This product had no true melting point but liquified at 65 to 68 C.

Purification of the crude TriPEON was promoted by crystallization from either absolute alcohol or chloroform. One part TriPEON (by weight) was introduced into 25 parts absolute alcohol and stirred over a steam bath. Heating was continued for 10 minutes after boiling commenced. The hot solution was suction filtered and set aside to cool slowly. A 90% yield was obtained. The crystallization crop consisted of clusters of needles with a melting point of 79 - 80 C. Crystallization from chloroform yields a granular crop of prism-like crystals, MP 81 - 82 C. One part TriPEON was dissolved in 80 parts hot chloroform. The hot solution was suction filtered over a steam heated funnel, the filtrate transferred into a beaker and cooled to 0 C. The solution was kept at this temperature for one or two hours and then the crystalline product was collected. A 35% yield was obtained. Examination, by TLC, of the crystal crops from the ethanol

and the chloroform crystallizations indicates both products to be of approximately the same purity.

DIPENTAERYTHRITOL-HEXANITRATE, DIPEHN

There are several procedures for the production of DiPEHN; however, none of these yield a product of high purity unless the starting reagent is of superior quality. High purity DiPE is not available commercially, consequently it must be purified in order to obtain a high purity nitration product.

Techniques for the purification of DiPE were patterned after the procedures developed from the production of high purity TriPE(4). These involved the acetylation of commercial DiPE, fractional crystallization of the resulting ester from xylene, and saponification of the crystallized fraction to DiPE.

The acetylation reaction was effected in a four-necked round-bottomed flask equipped with a thermometer, two water-jacketed condensers and a mechanical stirrer. Reagent grade DiPE (1 mole) was introduced slowly at room temperature to a mixture of acetic anhydride (8 moles) and pyridine (4 moles). The slurry was heated rapidly ($\sim$ 4 C/min) to 90 C, and then very cautiously until the reaction was initiated. On activation ($\sim$ 105 C) the reaction became very vigorous liberating much heat. All external heat was removed and was not reapplied until after the activity subsided. Refluxing was then promoted for two hours. The reaction flask was emptied over eight volumes of crushed ice from which precipitated a soft amber colored cake.

The dipentaerythritol-hexaacetate, DiPEHAc, was collected and washed repeatedly with water until neutral. It was then taken up in hot xylene, filtered over a steam heated funnel and set aside to permit crystallization. After the DiPEHAc had been recrystallized twice from xylene, it was collected and dissolved in hot ethanol, treated with decolorizing carbon and filtered. On crystallization, the product was collected and dried. TLC evaluation of the crystalline substance indicated a product of high purity.

Saponification of the DiPEHAc was promoted by refluxing with sodium hydroxide in alcoholic solution using a ratio of 9 moles alkali to 1 mole of the acetate. The mixture was refluxed over a water bath for two hours. At the termination of the reflux period the reaction product was poured into a large volume of cold water and allowed to settle. The excess fluid was decanted and the precipitate was collected by filtration. After successive washes with hot water and dilute sulfuric acid the DiPE was rinsed with hot water until neutral, given one final acetone rinse and collected. The product was then dried under vacuum and readied for nitration.

DiPEHN is prepared by the action of pure nitric acid ($\geq$ 97%) on DiPE. A number of variations in the nitration procedures were investigated. A typical synthesis of DiPEHN from DiPE and nitric acid follows.

DiPE, 4.5 grams (0.018 mole), was added slowly, with stirring, to 27 grams (0.428 mole) of 97% nitric acid which has been cooled to 0 C. While the DiPE was being introduced the temperature was maintained between 0 and 5 C. The

reaction was then stirred for one hour at 0 ± 5C. The crude DiPEHN was separated from solution by drowning over eight volumes of crushed ice. The acid-ice water mixture was decanted and the DiPEHN, a soft spongy mass, was digested in a large volume of a 1% ammonium carbonate solution for several hours.

The DiPEHN was gathered and washed with water until neutral. It was then collected by filtration and taken up in acetone. Solid anhydrous sodium sulfate was added to remove water from the solution. The drying agent was removed by filtration.

DiPEHN is extremely soluble in acetone but may be separated from this solvent by pouring the solution into cold ethyl alcohol. The solution was poured into eight volumes of vigorously stirred ethanol from which 4.7 grams of crystalline product was collected. The mother liquor was reduced to half volume and an additional crop of crystals (1.5 g) was gathered. The DiPEHN was recrystallized from ethanol and it yielded a product with an identical melting point (75 C).

TETRAPENTAERYTHRITOL-DECANITRATE, TETRAPEDN

Tetrapentaerythritol-decaacetate, TetraPEDAc, was successfully extracted from a mixture of the acetic acid esters of poly-pentaerythritols. This product was hydrolyzed and subsequently synthesized into tetrapentaerythritol-decanitrate, TetraPEDN.

Purification of DiPE and TriPE was promoted from their acetate esters through molecular distillation and through fractional crystallization from xylene(*5*,*6*). The residues from the molecular still and the extracts from the crystallization process were saved and these provided a rich source of TetraPEDAc. This was laboriously isolated through repeated fractional crystallization from xylene and ultimately converted into high purity tetrapentaerythritol-decanitrate, TetraPEDN.

Whenever DiPEHAc or TriPEOAc are hydrolyzed, the resulting products consist of minute white crystals. This was not the case when TetraPEDAc was saponified; instead, a spongy off-white cake of no crystalline structure was obtained. Repeated washings with water or organic solvents failed to remove this grayish tinge.

Saponification of the TetraPEDAc was promoted in alcoholic solution using a ratio of 12 moles of sodium hydroxide to 1 mole of the acetate. The slurry was refluxed over a water bath for two hours and then poured over 8X volumes of crushed ice. The hydrolyzed product was gathered and washed successively with hot water and with a 2% sulfuric acid solution. The product was rinsed with water until neutral, given one final acetone rinse, collected and dried.

TetraPEDN is prepared by reacting TetraPE with nitric acid. A typical synthesis of TetraPEDN follows:

TetraPE, 25g (0.051 moles), was introduced at 0 ± 5C, with stirring, into 166g (2.63 moles) of 97% nitric acid. After the addition, the reaction was stirred for an additional hour at 0 C to 5 C. The reaction product was poured over 8X volumes of crushed ice and allowed to settle. The ice water was decanted and the product was covered with 400 ml of a 1% ammonium carbonate solution and digested for several hours. The solidified cake was crushed and collected. The washed product weighed 37.8g (78.8% yield). This was taken up in minimum acetone, filtered, and the filtrate dropped into 400 ml of cold ethanol from which 35.9g of recrystallized TetraPEDN was collected.

A purity of 90 to 95% is indicated by TLC evaluation. The contaminants are unknown, but these are indicated to be compounds of higher molecular weight than TetraPEDN. All efforts at further purification proved fruitless.

Impact sensitivity (drop hammer) values were determined for PETriN, DiPEHN, TriPEON, and TetraPEDN. These values are tabulated in Table IV.

Approximately 100 grams of TetraPEDN was synthesized. Large-scale production of TetraPEDN does not appear practical at this time. TetraPE, the prime reagent in the synthesis of this PETN homolog, is not commercially available. Condensation of TetraPE from pentaerythritol is ineffective and costly since the resulting condensate is a mixture of poly-pentaerythritols, difficult to separate. Isolation and purification of TetraPE as promoted during this investigation is too expensive to permit large-scale production of TetraPEDN.

SATELLITE IMPURITIES

The balance of the impurity concentrate, from which TetraPEDAc was extracted, was hydrolyzed and subsequently nitrated. TLC evaluation of the resulting mixture of nitrate esters showed 6 compounds above the origin, along with a heavy residue remaining at the point of application. Four of the compounds were identified, by comparison with known samples, as PETN, DiPEHN, TriPEON, and TetraPEDN. The portion of this sample which elicited the greatest interest was the product located immediately below TriPEON on the TLC chromatogram.

Separation of the components were achieved by liquid chromatography using a 40-inch by 2.1 mm diameter silica gel column. The elutant systems used were mixtures of tetrahydrofuran (THF) and n-heptane. The separations were followed by the U.V. detector. Fractions were collected over a period of time corresponding to about 80% of the total quantity of each peak. The head and tail portion of each peak were discarded.

The initial separations (Fig. 7A) were made using a 50% THF in n-heptane mixed elutant. Three fractions were taken (A_1, A_2, and A_3) each of which was shown by TLC (Figs. 8A and 8B) to contain more than one compound. PETN, DiPEHN, TriPEON, and PETriN were present in the original sample but were not found in any of the fractions collected. Therefore, they must have come through the column with the elutant front. Approximately 40 samples were injected at the above mentioned conditions in order to isolate sufficient sample for further identification.

Table IV. Impact Sensitivity Values

(cm)

	DiPEHN		TriPEON
12A	20; σ = 0.02	12A	26; σ = 0.02
12B	25; σ = 0.07	12B	28; σ = 0.10

	TetraPEDN		PETriN
12A	51; σ = 0.02	12A	Some smoke at 285 cm
12B	35; σ = 0.05	12B	No smoke at all at 285 cm

(PETN 12A is 10 to 20 cm; 12B is 40 to 60 cm.)

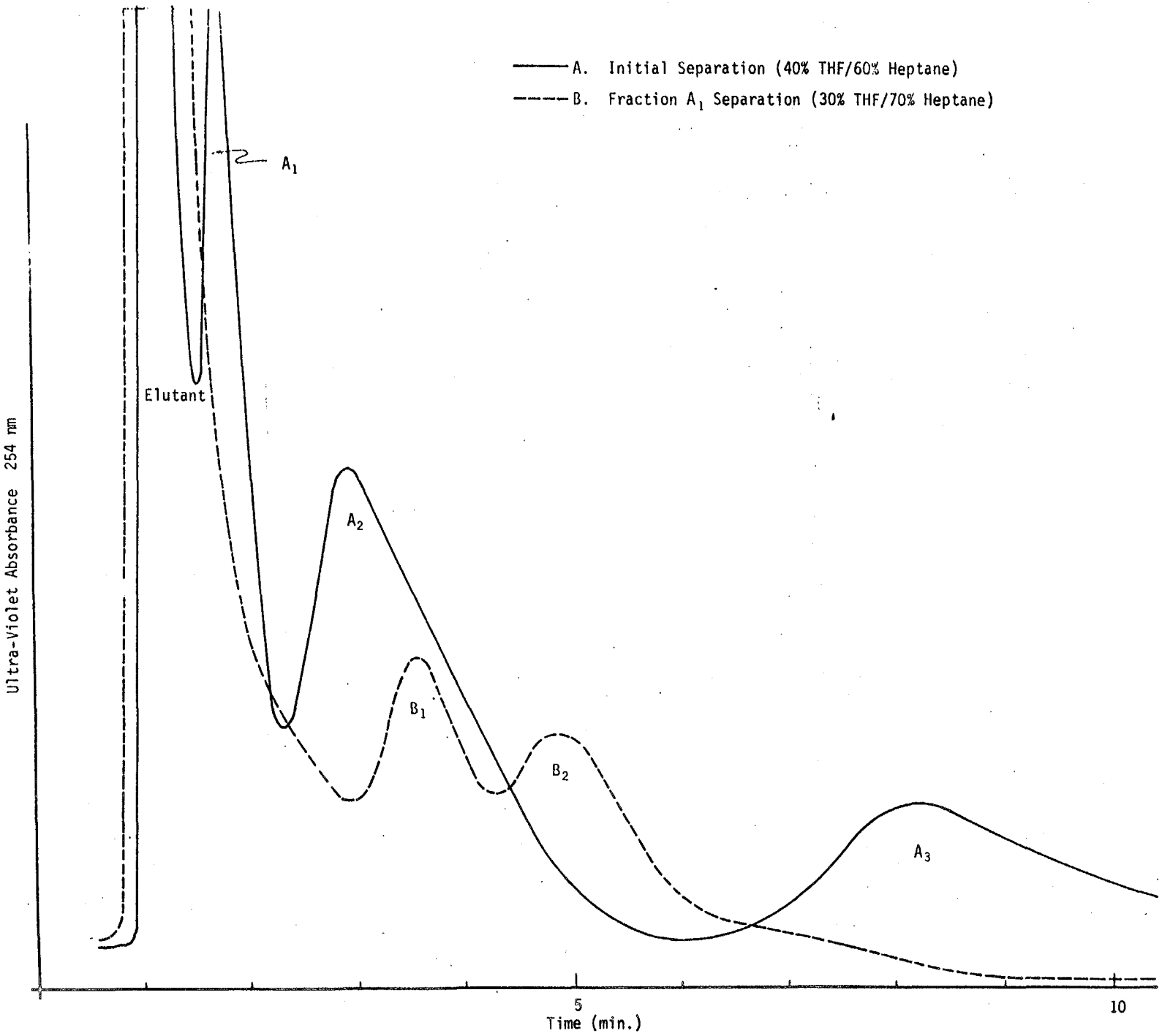


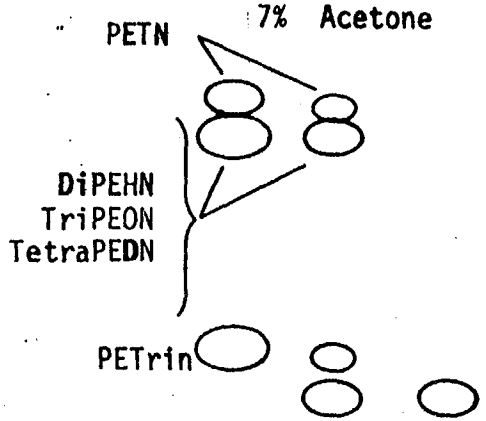
Fig. -7. Liquid Chromatograms

A

TLC #1

Plate Zn Loaded Silica Gel G

Elutant: 81% Benzene
12% Dichloroethane
7% Acetone

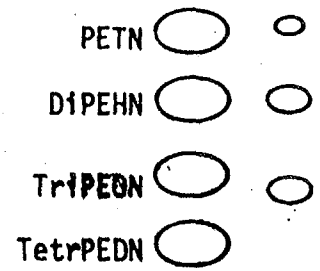


B

TLC #2

Plate Zn Loaded Silica Gel G

Elutant: 85% Benzene
13% Dichloroethane
2% Acetone



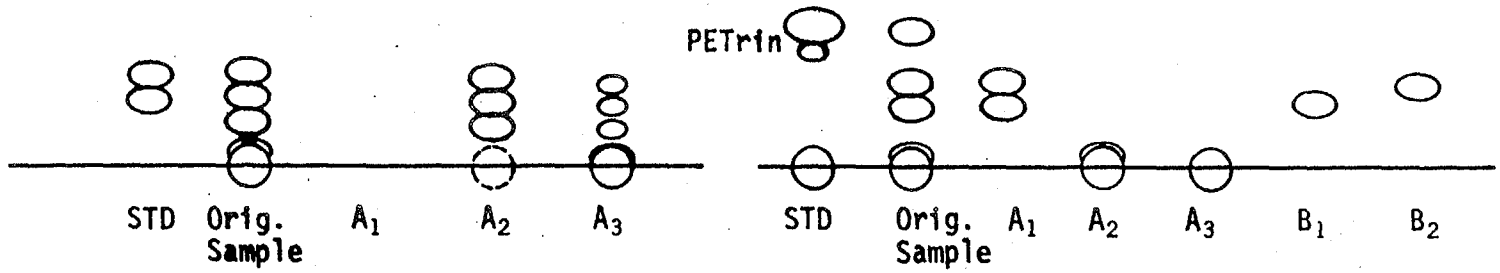


Fig. 8

The fraction identified as A_1 showed a single spot in TLC when eluted with a 81:12:7 benzene, dichloroethane, acetone mixture (Fig. 8A). Fraction A_2 was composed of at least four components, a minor spot at the origin and three spots of near equal intensity above the origin. Fraction A_3 had a minimum of five components, the major one being near the origin. Fractions A_2 and A_3 appear slightly cross-contaminated.

When the fractions were eluted with a 85:13:2 mixture of benzene, dichloroethane, acetone (Fig. 8B) fraction A_1 showed two components to be present where only one had been previously detected. Fractions A_2 and A_3 remained near the origin with no observable separations.

Of the four subgroups (Fig. 7A) the first, containing those components passing with the elutant front, was discarded. The multicomponent fractions A_2 and A_3 were saved for future use. Fraction A_1, the two component fraction, was further processed.

Further separation of fraction A_1 was attempted using the same chromatographic columns as previously described but varying the elutant composition. It was found that if the THF concentration, in the THF/n-heptane system, was reduced to 25%. None of the constituents of the sample below PETriN were moved through the column in one hour. If the concentration of THF was as high as 35% the A_1 fraction would not separate into the two components present as indicated by TLC. The separation of the two components was achieved by using 30% THF (Fig. 1B). Some overlap was observed but by taking narrow fractions fairly pure components were isolated. The TLC (Fig. $8B_1$ and $8B_2$) showed only a small amount of impurities remaining with the sample and this remained at the origin.

The solvents were removed from the sample at 60 C under vacuum. Concentrates B_1 and B_2 were wax-like materials, slightly off-white. Their infrared spectra were identical, when sample sizes and instrument sensitivity are considered. The spectra had bands at 2.75 and 2.90μ attributed to the presence of hydroxyl groups; at 8.95μ thought to be an ether linkage, and strong bands at 7.1 and 7.9μ assigned to nitrate ester groups. This evidence leads one to believe that the compounds are pentaerythryl ethers with a mixture of hydroxyl and nitrate ester functional groups. Mass spectrometry indicated the two compounds to be made up of similar skeletal and functional constituents but present in different proportions.

CONCLUSION

This study was initiated with the object of developing a method for large-scale production of TriPEON. Through the procedures discussed herein, over 30 pounds of high purity (> 97%) product were synthesized from commercial grade (< 85%) tripentaerythritol. The successful synthesis of TriPEON generated the subsequent production of DiPEHN and TetraPEDN. This effort satisfied the initial interest in the nitrate esters of the pentaerythritols and no further investigation into the isolation and synthesis of additional homologs was pursued.

Evaluation of the nitration products of pentaerythritol or of the poly-pentaerythritols by thin layer chromatography, TLC, usually reveals the presence of several contaminants in varying concentrations. Their presence, in relation to the known components, is always indicated in the same location on the chromatograms.

Some of these satellite impurities have been isolated and found to be PETN homologs. Others, presumed to be related to the parent compound, remain to be isolated and characterized.

Column chromatography was found effective in separating TriPEON and TetraPEDN from a mixture of nitrate esters of the pentaerythritols; however, an ideal column, capable of promoting additional separation was not obtained.

Liquid chromatography is an effective tool in the separation and isolation of additional homologs. A better understanding of the source of impurities and the effect of processing variables may be achieved by utilization of liquid chromagraphy as an analytical tool.

The large-scale production of high purity TriPEON, DiPEHN and TetraPEDN does not appear economically practicable at this time. The difficulties encountered in the isolation of high purity products and the expense involved in the purification process, warrant judicious scrutiny before large-scale production is undertaken. Until high purity reagents become commercially available, at a reasonable cost, the large-scale production of the PETN homologs cannot be economically promoted.

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