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AUTHORITY
OSRD list 31 dtd 5-9 Aug 1946; OTS index dtd Jun 1947

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Progress Report on "The Preparation of Pentaerythritol" to September 1, 1943

by
Robert C. Elderfield

Report OSRD No. 1804
Copy No. 42
Date: September 16, 1943

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NATIONAL DEFENSE RESEARCH COMMITTEE

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Section 8.2

Progress Report on "The Preparation of Pentaerythritol"

Service Directive OD-58

Endorsement (1) Dr. Ralph Connor, Chief Section 8.2 to Dr. G. B. Kistiakowsky, Chief Division 8. Forwarding report and noting:

> "In connection with the work of Division 8 on OD-58, it seemed probable that the by-products formed with pentaerythritol might be important in determining the thermal stability of PETN and Pentolite. The initial research on this work, therefore, dealt with methods of preparation of pentaerythritol and methods for its analysis. This report describes these experiments, which were not, in themselves, significant but which contributed to the further study of this subject which has been reported in OSRD 1414 and will be further described in subsequent reports."

(2) from Dr. G. B. Kistiakowsky, Chief Division 8 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee. Forwarding report and concurring in the above endorsement.

This is a final report under Contract 8-194, OEMsr 224 with Columbia University.

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INTRODUCTION

It has been noticed on several occasions by those concerned that the quality, in particular the stability, of PETN and Pentolite is apparently adversely affected by the presence of impurities in the pentaerythritol used for the preparation of PETN. Information at hand concerning the nature of such impurities, and the specific effect of individual impurities is scanty and conflicting. The present report describes work directed toward the production of good quality pentaerythritol by variation in the experimental conditions and reactions used.

In available studies on the preparation of pentaerythritol (British Report A.C. 117; Org./Ex. 27; NDRC No. B-88; British Report, R.D. Woolwich D. 906; NDRC No. B-171; NDRC Serial No. 86), the yield of product has been arrived at by estimation of the amount present in solution at the end of the reaction and, with but a few exceptions, the quality of the product with respect to difficultly removable by-products has had no attention. In the present study the product has been isolated in all cases and its purity determined by a variety of methods.

DISCUSSION

Analytical Methods

A number of analytical methods have been used in the past for estimating the purity of pentaerythritol. The method finally adopted as standard in this work is the so-called benzylidene method described in detail in British Report A.C. 117; Org./Ex. 27. In order to secure satisfactory reproducible results slight modifications have been necessary. As finally worked out, the procedure is as follows:

A sample of between 0.4800 and 0.5200 g. of pentaerythritol (Note I) in a 125 ml. Erlenmeyer flask is dissolved in 5 ml. of water by warming, and the solution is cooled to room temperature. To this solution is pipetted 10 ml. of a solution made up by dissolving 20 ml. of freshly distilled benzaldehyde in 100 ml. of 87% alcohol (9.2 ml. of water added to 100 ml. 95% alcohol) and 20 ml. of hydrochloric acid, sp. gr. 1.16 (22.5 ml. of water added to 100 ml. of hydrochloric acid, sp. gr. 1.19. This reagent was made up fresh every second day. Within a few minutes, the benzylidene derivative of pentaerythritol separates. The tightly stoppered flask is allowed to stand for four hours (Note 2) at room temperature with occasional shaking. To the crystal mush is then added 30 ml. of petroleum ether (Skelly Solve B) and the mixture is shaken very vigorously by hand. The temperature of the mixture is then brought to 25°±1° (Note 3) and the precipitate of benzylidene derivative is filtered by suction on a tared fritted glass Gooch crucible and washed with 150 ml. of water. After drying for 1 hr. at 95° the precipitate is weighed. From the weight of the benzylidene compound the weight of pentaerythritol is calculated with the aid of the graph shown in Figure 1, (Note 4) and the percent of pentaerythritol in the sample is calculated. The accuracy is ±0.4 percent.

Note 1. It has been found that if the sample taken be outside this range, variable results are obtained.

Note 2. Four hours is the minimum time required to give satisfactory results.

Note 3. It is important that the precipitate be filtered at this temperature. Deviations therefrom give variable results. Chilling the crystal mush to 0° in ice as has been recommended by Wolfrom has been found to lead to variable results, caused apparently by varying time of filtration from determination to determination. In cases of slow filtration, the chilled solution warms up. This leads to low results by virtue of increased solubility of the precipitate. Since an arbitrary empirical correction for solubility is applied, it is therefore important to filter at the same temperature consistently.

Note 4. This curve differs somewhat from a similar one given in British Report A.C. 117; Org./Ex. 27, and has been obtained by repeated analyses of mixtures of known composition.

The above procedure has been used in some 200 determinations, all done in duplicate. The results are within the limit given above.

Prior to the adoption of the benzylidene method an attempt was made to apply a conductometric method based on the report of Boeseken (Rec. Trav. Chim. 30, 400 (1911); Ber. 46, 2619 (1913)) that dipentaerythrityl ether does not increase the conductivity of a solution of boric acid whereas pentaerythritol does to a three or four fold extent. In several experiments, no significant difference in conductivity of boric acid could be noted on addition of either of the above substances.

We have also used the test nitration assay method and the spent acid stability method supplied by the DuPont Company in a few cases. In this method the yield and melting point of PETN is determined after a standard nitration and purification procedure. The spent acid is heated at 60° C. and the time to the appearance of gas bubbles on the walls of the tube is noted. The procedure is as follows:

Ten grams of finely powdered pentaerythritol is added to 46.8 g. of 95% white nitric acid at such a rate that the temperature does not exceed 32° C. with good stirring. External cooling is necessary. This takes about 10 min. The mixture is then stirred for an additional 10 min., cooled to 20°, filtered on a sintered glass funnel and sucked as dry as possible. The spent acid is treated as described below. The PETN is washed on the funnel with two portions of water, once with 5% sodium carbonate solution and finally with water. The crude PETN is dissolved in hot acetone (about 100 ml.) and 0.5 g. of anhydrous sodium carbonate is added. While still hot, 3 volumes of water are sprayed in to the well stirred acetone solution. After cooling to 20°, the PETN is collected and dried in a desiccator. The yield and melting point are determined.

The volume of spent acid is determined and 5 ml. are withdrawn, placed in a test tube and heated in a beaker of water at 60°±1°. The time in minutes to the appearance of gas bubbles on the walls of the tube is noted.

The remainder of the spent acid is drowned in 4 volumes of ice. After standing, the somewhat gummy precipitate is filtered on a tared fritted glass Gooch crucible, dried in a desiccator and weighed.

The comparative results of analyses of a number of samples of pentaerythritol by the three methods are given in Table I, in which the samples include synthetic mixtures, a commercial product supplied by DuPont, and several laboratory batches which are identified in Table II. It appears that some inconsistencies between the methods exist, from which we feel that the benzylidene method gives the only accurate indication of the percentage of pentaerythritol in a given sample. On the other hand, the spent acid stability may be decidedly misleading (compare Run 19a with PE-diPE containing 5% of di-PE). Likewise, the residue obtained on drowning the spent acid appears to be variable and is possibly influenced by the nature of the impurities present.

Table I.

Pentaerythritol Used	M.P. of P.E.	Yield of recrystal PETN (in points)	M.P. of PETN	Spent Acid Stability in min.	Spent Acid Residue (% of PE used)	Bzd. Anal.
Synthetic mixture contg. 5% di-PE.	252-4°	227	139.5-141.4°	25.0	4.6	—
Ditto contg. 10% di-PE	231-4°	201	139-141.5°	11.5	10.2	—
Run 20	246-52°	211	139.8-141.2°	7.5	5.6	88.8%
Run 19a	258-61°	228	140.3-141.3°	11.0	1.0	97.2%
Niacet Chem. Co. Lot No. 300-370 Nitrated at Repauno to PETN Lot No. 891.	255-8°	222	140.8-142°	7.0	4.4	95.1%
Run 14	256-8°	229	140.2-141°	3.0	2.4	92.3%
Run 21	236-48°	201	140-141°	15.5	7.4	87.3%
LFH No. 2	256-8°	219	139.5-140°	—	2.9	95%

EXPERIMENTS ON THE PREPARATION OF PENTAERYTHRITOL

A large number of experiments have been performed in order to ascertain the effect of the following variables on the quality of the PE produced: Order of addition of reactants, i.e., aldehydes to lime or lime to aldehydes; use of calcium oxide vs. calcium hydroxide; use of acetaldehyde as such or as aldol or crotonic aldehyde; use of formaldehyde as formalin or paraformaldehyde; influence of the so-called "second reaction" and the time elapsed after the onset of the "second reaction" before neutralization of the reaction mixture.

In all cases the method of working up the reaction mixture and of isolating the product was the same: Sulfuric acid equivalent to 96 percent of the calcium present was added to the well-stirred reaction mixture. After filtration and thorough washing of the precipitated calcium salts, the filtrate was concentrated under reduced pressure until excessive bumping caused by separation of PE prevented further concentration. After refrigeration, the PE was filtered off and the filtrate further concentrated until the final volume was about 4 percent of the original. A second crop of PE was removed and combined with the first. The crude PE was recrystallized once from the minimum amount of boiling water with use of decolorizing carbon. Yield, analyses and other data were taken on this once recrystallized material except as noted.

In all runs the proportions of reactants were kept constant and in the ratio of 5.5 mols of formaldehyde, 1 mol of acetaldehyde and 0.6 mols of lime in 1.5 L. of water. In cases where formalin was used the formaldehyde content was determined; when paraformaldehyde was used, it was assumed to be equivalent to 100 percent formaldehyde; aldol and crotonic aldehyde were assumed to be equivalent to 100 percent acetaldehyde. The runs were of three sizes, those through No. 17 except No. 14 being done in 3200 cc. of water, from 18 to 25 and No. 14 in 10 L. of water. In order to get a line on a still larger sized run, No. 26 was done in 52 L. of water.

The results of a number of typical runs are shown in Table II. P refers to paraformaldehyde, F to formalin, Ac to acetaldehyde, Al to aldol and Cr to crotonic aldehyde.

Comments

1. Order of addition of reactants: It appears from Runs 20 and 21 that addition of the mixed aldehydes to the lime water results in a somewhat higher yield of PE, but that the quality of the product is definitely lower.

2. Calcium oxide vs. calcium hydroxide: In all cases finely powdered lime was used, so that it presumably hydrated substantially instantaneously. No study of the use of lump lime was made.

3. Acetaldehyde vs. aldol vs. crotonic aldehyde: All three give good quality PE although the yield obtained with crotonic aldehyde is markedly less than with acetaldehyde or aldol. For convenience in handling, aldol is much to be preferred.

4. Paraformaldehyde or formalin: Without further work this point cannot be answered definitely, although tentatively it can be said that few differences arise from the use of one or the other with respect to quality. The yield is better with paraformaldehyde.

However, the use of paraformaldehyde does present one striking advantage from a practical point of view. Apparently the depolymerization of paraformaldehyde is accompanied by considerable absorption of heat, which reduces materially if not completely the refrigeration required to control the reaction when formalin is used. This is brought out by the details of Runs 22 and 23. In both cases the reaction was carried out in a 12-L. Pyrex precipitating jar, the mixture being well stirred mechanically and a coil of copper tubing was used for temperature control when necessary. 10 L. of water, 288 g. of aldol, 1080 g. of paraformaldehyde (or an equivalent amount of formalin) and 246 g. of calcium oxide were used. The lime was added to the mixed aldehydes gradually as indicated.

Time in min.	Temp. Run 22	Temp. Run 23	
0	27°	25°	Addition of lime started
2	23.5	24.5	
4	23	27	
6	24	30	
8	27	33	
12	35	42	
14	43	--	
16	46 -(lime all in)	48	
30	48.5	50.5	
40	48.3	51	-(lime all in)
45	---	59	
50	53 - 2nd reaction over added H_2SO_4	62 -	2nd reaction over added H_2SO_4

It is obvious that a much lower temperature prevailed in Run 22. While no cooling was necessary in either run, on a larger scale a run similar to Run 23 would probably require cooling. In Run 26, given in detail below, heating was necessary in order to raise the temperature sufficiently for the second reaction to start.

Run No. 26

Since this was the largest run attempted and can be expected to give some idea of what can be expected on a still larger scale, the record is given in detail.

The vessel was a 25 gal. crock equipped with good mechanical agitation and a copper coil for cooling or heating.

Materials:

52 L. water
5350 gm. paraformaldehyde
1500 gm. aldol (technical)
1279 gm. calcium oxide, powdered C.P.

The lime was added gradually to the slurry of aldehydes.

Time in Min.	Temp.	Remarks
0	22°	Start adding lime.
5	20	
10	21	All paraform had dissolved leaving a clear solution.
20	23	
30	23	
40	26	
50	31	
60	36	
70	40	lime all in.
75	41	- Steam put through coil.
90	49	- Steam turned off.
110	50	- Second reaction started.
115	53	
117	55	
120	55.5	- Stopped by adding H_2SO_4.

The filtrate from the calcium salts was worked up as described above, except that because of the amount of material it was necessary to concentrate in batches. The yield of not recrystallized material was 2850 g. or 64 percent. This was recrystallized from 8 L. of water yielding 1523 g. of PE which melted at 258-9° and assayed 95.5%. The mother liquors were concentrated and gave 824 g. more PE which melted at 248-54° and assayed 91%. A third crop of material melting at 228° and weighing 450 g. was obtained on further concentration of the mother liquors.

5. The "second reaction": It appears to be quite definitely established that unless the second reaction takes place, the quality of the PE suffers very greatly and the yield decreases. While the chemistry involved in the second reaction is obscure, the fact remains that in no case where the second reaction was not allowed to take place, was a satisfactory product obtained. It is recommended that, if opportunity presents itself, a detailed study of this reaction be undertaken.

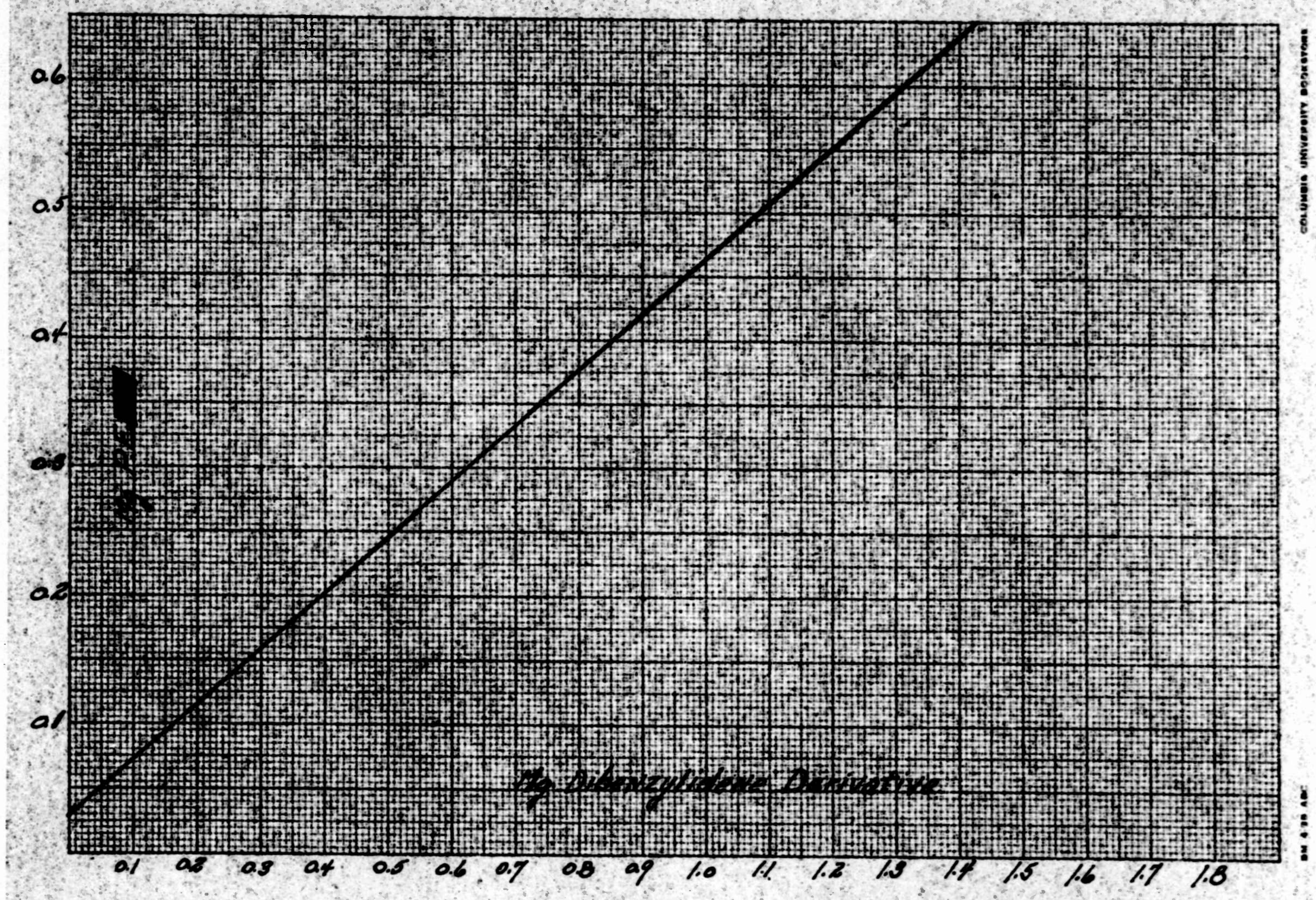
The time elapsed after the onset of the second reaction until working up appears to be relatively unimportant. The reaction is characterized by a sudden rise in temperature followed shortly by the development of a yellow color in the reaction mixture. It makes little difference whether the reaction is worked up a few minutes later or as much as two hours later.

Table II

Run No.	Mode of Addition	Yield	M.P.	Bzd Assay	Temp. at which 2nd Reaction Began	Time after onset of 2nd Reaction to stopping.
5	$P+Ac \rightarrow Ca(OH)_2$	---	234-5°	---	58°	20 min.
6	$P+Ac \rightarrow Ca(OH)_2$	Nil.	---	---	Stopped before 2nd reaction began.	
8	$F+Ac \rightarrow Ca(OH)_2$	27%/(I)	Not isolated		" "	" " "
9	$Ca(OH)_2 \rightarrow P+Ac$	---	242°	---	50°	20 min.
12	$Ca(OH)_2 \rightarrow F+Ac$	---	240°	---	51°	35 min./(2)
13	$Ca(OH)_2 \rightarrow P+Al$	59%	256°	---	47°	35 min.
14	$Ca(OH)_2 \rightarrow P+Al$/(3)	61%	256-8°	92.3%	51°	1 hr. 50 min.
15	$CaO \rightarrow P+Al$	55%	256-8°	90.6%	51°	1 hr. 35 min.
16	$CaO \rightarrow P+Ac$	57%	246-9°	---	51°	35 min.
18	$CaO \rightarrow F+Al$	33%	258°	90.0%	50°	50 min.
19	$CaO \rightarrow P+Al$	61%	254°	89.9%	50°	5 min.
19a/(4)			258-61°	97.2%	---	---
20	$P+Al \rightarrow Ca(OH)_2$	65.5%	246-52°	88.8%	48°	6 min.
21	$F+Al \rightarrow Ca(OH)_2$	68%	236-48°	87.3%	50°	5 min.
22	$CaO \rightarrow P+Al$	57%	248-52°	89.9%	50°	5 min.
23	$CaO \rightarrow F+Al$	43%	256°	96.7%	51°	5 min.
24	$CaO \rightarrow F+Ac$	67%		93.0%	55°	2 min.
25	$CaO \rightarrow F+Ac$	58%		93.3%	53°	12 min.
23	See details elsewhere.					
L-4	$CaO \rightarrow P+Cr$	32%	256-8°	95%	52°	35 min.

Notes to Table II

1. Crude product was slimy and could not be readily recrystallized. Yield was determined in solution.
2. Hydrochloric acid used to neutralize instead of sulfuric.
3. Twice usual concentration of all reactants.
4. Material from Run 19 recrystallized a second time.

Mg Dibenzylidene Derivative
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TITLE: Progress Report on "The Preparation of Pentaerythritol" to September 1, 1943

AUTHOR(S): Elderfield, Robert C.
ORIGINATING AGENCY: Columbia University, New York, N. Y.
PUBLISHED BY: Office of Scientific Research and Development, NDRC, Div 8

ATI- 29922
REVISION (None)
ORIG. AGENCY NO. (None)
PUBLISHING AGENCY NO. OSRD-1804

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
Sept '43	Confd'l	U.S.	Eng.	16	graphs

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The quality, and in particular the stability, of PETN and Pentolite is adversely affected by the presence of impurities in the pentaerythritol used for the preparation of PETN. A description is given of the work directed toward the production of good quality pentaerythritol by variation in the experimental conditions and reactions used. Experiments on the yield of pentaerythritol have shown that, the addition of the mixed aldehydes to the lime water results in a somewhat higher yield of PE, but that the quality of the product is lower. Aldol is preferred to acetaldehyde and crotonic aldehyde for ease of handling, and the yield obtained with acetaldehyde and aldol is greater than that obtained with crotonic aldehyde. The yield was found to be greater with paraformaldehyde than formalin although there were few differences with respect to quality.

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DIVISION: Ordnance and Armament (22)

SUBJECT HEADINGS: Explosives - Production (34511); Explosives - Development (34504.7)

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AD-B803 014

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List 31 dtd Aug 5-9, 1946
by on 4 Aug 49