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HE FORMULATION

Engineering Order No. 504-005

A. G. Osborn

January, February, March, 1968

ATOMIC ENERGY COMMISSION
UNITED STATES OF AMERICA

DEVELOPMENT DIVISION

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MASTER

HE FORMULATION

This concerns the development and manufacture of explosives formulations. Production and quality parameters are determined; among these are viscosity, composition, particle size distribution, processing variables and raw materials, and their effect on operation, safety characteristics, producibility, and physical and explosive properties. Pastes, extrudables, and PBX's are among the formulations.

A. G. *Osborn*

Quarterly Report for January, February, March, 1968

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ABSTRACT

RX-09-CB and LX-07 were made to supply material for testing. Both were made in the 300-gallon kettle in 250-pound batches which were then blended into 1000-pound lots. An RX-09 with no plasticizer (HMX and DNPA) was made in the 30-liter reactor for special gap and friction studies.

Approximately 20 pounds of DNPOH, supplied by Aerojet, was converted to DNPA and polymerized by the emulsion polymerization process.

Work on high surface area PETN continued by precipitation recrystallizing two 10 kg batches; one to supply material for detonator applications to Mound Laboratory and the other to supply high surface area PETN to LRL for special applications. Surface area for this batch was 21,200 cm^2/gm. The detonator material had a surface area of 14,500 cm^2/gm.

A system duplicating the English method for achieving high surface area has been completed with the installation of the 8-inch Micronizer, and two preliminary trials of one pound each have been made. Surface areas were 20,900 and 14,900 cm^2/gm. The system is being modified slightly to eliminate the problems incurred during these trial runs and preparations are in process for making a 10 kg batch to be shipped to Mound.

PREVIOUS APPLICABLE WORK

Last quarter the ten experiments which were related to high surface area PETN included exploration of various purification methods and reprecipitation techniques. Reprecipitation included shock dilution techniques at low temperature, ball milling, conventional and ultrasonic spraying methods, and the vigorous mechanical action of the Cowles Dissolver to aid dilution. A ball milled sample of material shock reprecipitated, after being purified by LRL's charcoal technique, heat stabilized more rapidly at a higher surface area than other materials tested. Previously, much higher surface area PETN crystals have been obtained by various techniques; however, the problem has been their collection. Filtration was unsuccessful because the rates were too slow or the crystals were so small that they passed through the filter medium.

The production of sizeable quantities of PBX's to support LRL activities has been emphasized recently. Last quarter the 3000 pounds of RX-09 made included 1750 pounds of RX-09-BJ, 450 pounds of RX-09-BL, 250 pounds of RX-09-CB, 200 pounds of RX-09-BE and small preliminary batches of variants of RX-09 in the 30-liter reactor for gap and friction studies. Previously, batches of RX-09-AG were made for the purpose of comparing DNPA of various molecular weights made at different installations (Hummel, Aerojet, Naval Ordnance Station and Pantex). There were no outstanding variations which could be attributed to differences in the DNPA. Also various treatments, which included processing techniques, HMX particle size, composition, quantity of plasticizer, etc., were tried with

RX-09 to improve pressability; however, none of these treatments resulted in an improvement in pressed density.

DISCUSSION

Responding to the requirements for supplying larger quantities of explosives with short lead times, 3000 pounds of PBX's were produced this quarter in the HE Formulation Facility: 1000-pound lot of RX-09-CB and two 1000-pound lots of LX-07. The lots were made up by blending 250-pound batches which were processed in the 300-gallon kettle. The RX-09-CB was wet blended in the 300-gallon kettle while the LX-07 lots were dry blended. Wet blending of quantities approaching 1000 pounds is being discontinued in the kettle until the modifications to the shaft have been completed to stabilize the agitator. Table I includes processing data on the RX-09-CB and Table II the data on LX-07.

The first 250-pound batch of RX-09-CB made this quarter, No. 8018, required reworking because it was slightly low in DNPA and small white specks were visible throughout the batch. These white specks could have resulted from a deviation which occurred in the normal sequence of addition of material to the kettle.

Table I

RX-09-CB

Lot No.	HMX 93%		Binder 7%		Batch Wt. Pounds	Granulation								Bulk Density gm/cc
	3/4 Class A	1/4 Class B	4.6% DNPA	2.4% FEFO		Analysis Wt. %			Wt. % Retained on Sieve Size					
						HMX	DNPA	FEFO	4	12	20	40	PAN	
8018-114G-01	701-26	SR-1B-65	Lot 3 Aerojet	Aerojet	250	94.1	3.9	2.0	-	19	66	9	6	0.9
8019-114G-01	701-26	SR-1B-65	Lot 3 Aerojet	Aerojet	250	93.5	4.3	2.2	-	75	25	-	-	1.0
8019-114G-02	701-26	SR-1B-65	Lot 3 Aerojet	Aerojet	250	93.6	4.2	2.2	5	93	2	-	-	0.9
8022-114G-01	701-26	SR-1B-65	Lot 3 Aerojet	Aerojet	250	93.7	4.4	1.9	1	87	10	1	1	0.9
8023-114G-01[1]	701-26	SR-1B-65	Lot 3 Aerojet	Aerojet	250	92.5	4.9	2.6	-	42	52	6	-	0.9
8023-114G-02[2]	701-26	SR-1B-65	Lot 3 Aerojet	Aerojet	1000	93.2	4.4	2.4	3	79	16	2	-	0.9

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[1] *Rework of 8018-114G-01.*

[2] *Blend of 8019-114G-01, 8019-114G-02, 8022-114G-01, 8023-114G-01.*

Table II

LX-07

Lot No.	HMX (90%) Lot No.	Viton (10%) Lot No.	Batch Wt. Pounds	Analysis Wt. %		Granulation Wt. % Retained or Sieve Size				Bulk Density gm/cc
				HMX	Viton	4	12	20	40	
8066-104-02	700-10	Lot 18	250	90.8	9.2	35	63	2	-	.8
8067-104-01	700-10	Lot 18	250	90.6	9.4	36	61	3	-	.8
8071-104-01	700-10	Lot 18	250	90.1	9.9	25	72	3	-	.9
8072-104-01	700-10	Lot 17 & 18	250	90.0	10.0	21	74	5	-	.9
8072-104-02	700-10	Lot 17 & 18	250	90.2	9.8	21	74	5	-	.8
8073-104-01	700-10	Lot 17 & 18	250	89.9	10.1	23	70	7	-	.8
8073-104-02	700-10	Lot 17 & 18	250	90.7	9.3	22	70	7	1	.8
8074-104-01[1]	700-10	Lot 18	250	89.7	10.3	22	77	1	-	.9
71-10[2]			1000	90.2	9.8					
71-11[3]			1000	89.8	10.2					

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[1] *Rework of 8066-104-01*

[2] *71-10 dry blend of 8066-104-02, 8067-104-01, 8071-104-01, 8074-104-01*

[3] *71-11 dry blend of 8072-104-01, 8072-104-02, 8073-104-01, 8073-104-02*

The procedure for slurrying RX-09 which has become accepted as yielding the best product is as follows:

Step 1: Place 50 - 75 gallons of water in the kettle.

Step 2: Add buffers, 175 grams each of sodium acetate and acetic acid.

Step 3: Add HMX and stir for at least 30 minutes to insure that all particles are wet.

Step 4: Add the DNPA lacquer, FEFO and dye (mix for 30 minutes).

Step 5: Add extra ethyl acetate to saturate the water.

Step 6: Add balance of water to bring total to 175 gallons.

Step 7: Apply heat and vacuum to granulate the material.

However, during the formulation of 8018, Steps 4 and 5 were reversed. The excess ethyl acetate for saturating the water was added out of sequence (before the lacquer was added) thus possibly having a pelletizing effect upon the HMX, preventing it from being thoroughly wet by the lacquer containing the green dye. Ethyl acetate, when present in excess quantities, is the only solvent used with HMX which has been noticed as causing the HMX to coalesce. The new analysis given in Table I for the rework, No. 8023, was satisfactory. Emphasis was placed on adhering to the proper sequence of addition for the remaining four batches of RX-09 processed.

Last quarter white cores which appeared inside green granules of a batch of RX-09-AG were partly responsible for changes in the slurry procedure resulting in the procedure given. The technique of adding only a part of the water, adding all ingredients, stirring, and then completing the fill with water, was adopted to prevent premature beading. Apparently, as the lacquer containing the binder and green dye was being added, the granules began forming prematurely before complete mixing of the lacquer with HMX. Thus, the slurry technique was modified slightly to eliminate this possibility by agitating initially at a low fluid level while there is still sufficient concentration of solvent for a true slurry.

Data on the individual batches of LX-07 are given in Table II. Lot analyses were 9.8% Viton for Lot 7110 and 10.2% Viton for Lot 7111. As mentioned the 1000-pound lots were dry blended. Only one batch, No. 8066-01, required reworking. Viton content was 9.1% which was 0.1% out of tolerance. After rework, Batch No. 8074-01 analysis was 10.3% Viton.

The slurry procedure, except for the application of heat and vacuum, was essentially the same as that used with the RX-09. All the ingredients were agitated at a low liquid level before the addition of the balance of the water and the subsequent granulation. Because of the higher boiling solvents, MIBK and NBA, used to make the Viton lacquer, 35-pound steam was used in the kettle jacket instead of 160 to 200°F controlled temperature water. For the RX-09 the water temperature was gradually increased from 160°F to 200°F to improve yield and retard hang-up in the kettle. The LX-07 procedure required maximum vacuum capabilities while the RX-09 procedure required only a partial vacuum.

DNPA

Interest in DNPA and problems related to its synthesis is increasing at Pantex since LRL has designated Pantex to be the purchasing agent for the conversion of approximately 30,000 pounds of Aerojet DNPOH to DNPA. In view of this, work related to the synthesis of DNPA has been resumed. Earlier, two 1-pound batches and one 4-pound batch were made in the 10 and 30-liter reactors. The 4-pound batch was approaching the capacity of the reactors. For this work the DNPA was synthesized starting with the basic raw materials. However, this quarter the starting material was DNPOH supplied by Aerojet. An attempt was made to convert approximately 20 pounds of DNPOH to DNPA. Because of the larger volumes of fluids, the larger vessels in the Formulation Facility were required.

The conversion progressed smoothly, except for a few problems, which can be easily rememdied. During the emulsion polymerization, for instance, the rotating drum used developed a leak and a part of the material was lost. Instead of having a yield approaching 20 pounds, only 14 pounds of usable material are available.

Basically, the procedure outlined in the report by LASL was used. The DNPOH is esterified using acrylic acid with polyphosphoric acid as the water scavenger.

It was found that the esterification could not be performed in the presence of ethylene dichloride, which is somewhat unfortunate because DNPOH as received from Aerojet is in a 30% solution in ethylene dichloride. In order to perform the esterification, the ethylene dichloride had to be completely stripped and a small amount of toluene added.

Table III contains data on the Pantex DNPA compared to LRL's purchase description which specifies the quality parameters for PDNPA synthesized using the DNPOH supplied from Aerojet as the starting material.

Nitrogen will be determined as soon as the repair parts for the Coleman Nitrogen Analyzer are received. The solubilities, physical state and color are satisfactory. Solution viscosity was somewhat low; however, by extending the polymerization time the relative viscosity can easily be increased. The IR corresponded to the standard except for three spurious peaks. Comparisons are being made with the IR's of the initial ingredients in an attempt to identify the peaks.

Table III

PDNPA

Test	Specified	Actual
Nitrogen Content	13.2 to 13.9	Not determined
Solubility	99.9% soluble in acetone & ethylene-dichloride	OK
Insolubility	<1.0% in water	.6% OK
Volatile	<1.0% at 60°C under 25 in Hg	.2% OK
Relative Viscosity	1.2 or greater	1.18 (low)
Infrared Spectrum	Conform to Standard	Three spurious peaks
Physical State	Powder, free flowing	OK
Color	White with 37778 to 37875	OK

PETN

Supplementary to the different methods already developed at Pantex for achieving high surface area PETN for detonator applications, another method is now available which makes use of an 8-inch Micronizer. It will permit an exact duplication of the English technique for achieving high surface areas. Preliminary runs were made in the Micronizer and two 10 kg batches were made using techniques developed earlier and discussed more in detail in previous quarterly reports. The various techniques previously developed include: (1) the purification of the starting PETN by the English method which involves the double recrystallization of PETN from hot saturated solutions by chilling prior to its shock reprecipitation (Pantex method) in cold alcohol/water; (2) purification by charcoal (LRL's technique) prior to reprecipitation in cold solution; (3) ball milling; (4) conventional spray and ultrasonic spray of an acetone/PETN solution directly into both a nitrogen atmosphere and into water; and (5) using the high speed blades of the Cowles Dissolver to disperse the PETN solution into water.

The two 10 kg batches of PETN were processed this quarter, No. 8064 and No. 8092, used the Pantex technique of reprecipitation at low temperatures in the 300-gallon kettle. TriPEON was added to No. 8064 which will be used for special pressing applications at LRL. The starting material for No. 8092 was purified by the English technique; it will be used for detonator applications.

Current planning for detonator material studies provides for three 10 kg batches to be sent to Mound Laboratories for evaluation; one using the English purification by double recrystallization combined with the Pantex method of shock reprecipitation at low temperature, another using this same technique except performing an additional step of ball milling on the material produced, and the third using the Micronizer to duplicate, as nearly as possible, the English technique.

Work is progressing on duplicating the English method for achieving high surface area. Two preliminary trial runs have been made with the Micronizer of one pound of material each. Modifications are in progress to eliminate the problems incurred and preparations are being made for producing 10 kg of material in a single continuous run.

A comparison of the two trial runs is detailed in Table IV. The setup included a small 5-gallon pressure tank for the PETN acetone feed, a 30-gallon pressurized kettle for the water feed, a 100 psig air supply, and a vacuum filter of Teflon over glass to collect the PETN. A 600-gallon vacuum receiver was used to apply vacuum to the filter buggy which was located directly under the Micronizer. As noted in Table IV, Batch No. 8046 had the higher surface area although the dilution ratio was lower than for Batch No. 8047. For this batch, however, nitric acid was used to adjust the pH of the water. Although a pH of 3 was desired, the run was made with pH of 2.2. These runs were made strictly for the purpose of becoming familiar with the operation of the Micronizer and to ascertain problems, thus the pH was not readjusted to 3. Also it was difficult to precisely control the flow rates as noted by comparing the differences in

Table IV

Batch Number	8046-304H-01	8047-304H-01
Surface Area (cm^2/gm)	20,900	14,900
Acetone/PETN flow (800 ml/minute)	738	525
Percent of desired flow rate (%)	92	72
Water Rate (2273 ml/minute)	1,770	2,170
Percent of desired flow rate (%)	78	96
Dilution Ratio water to acetone (2.8/1.0)	2.4/1.0	3.8/1.0
Water	Deionized	Deionized
Water (pH)	7.0	2.2[1]
Air Pressure (psig)	83	83

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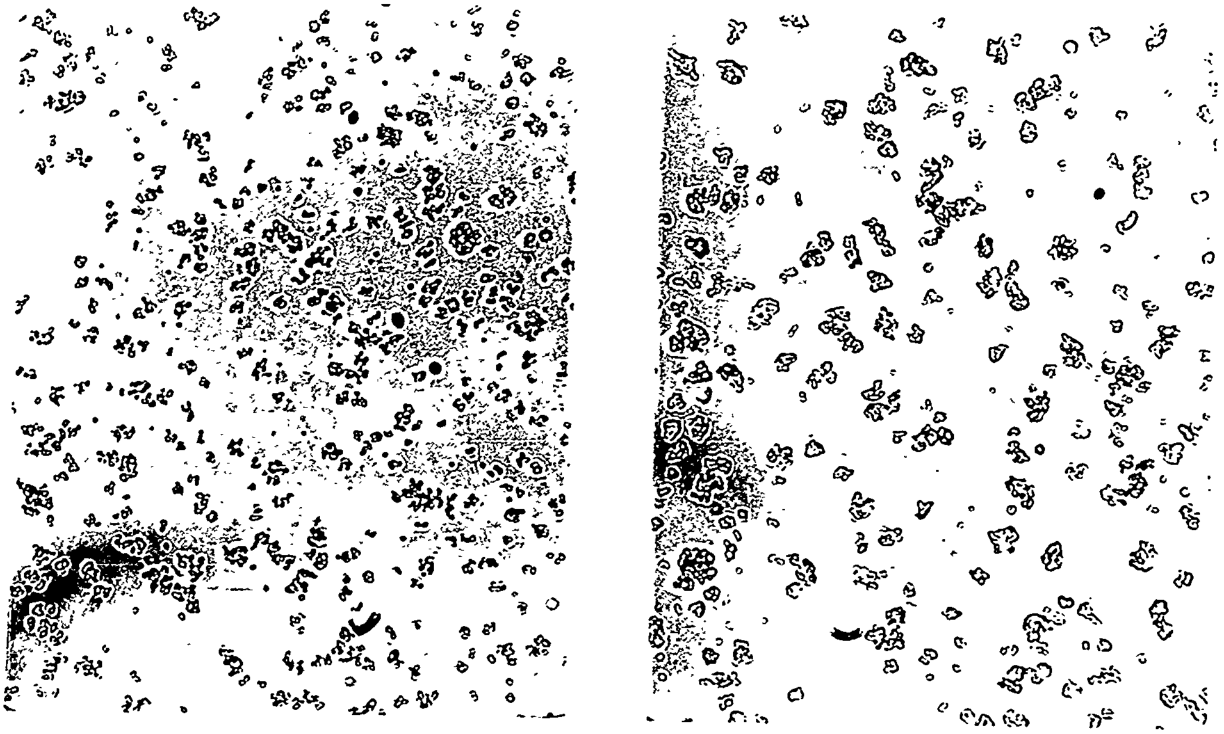
[1] *Adjusted with nitric acid.*

flows and their variation from the desired flow. Attempts to preset and calibrate flow by adjusting and balancing a needle valve against tank head pressure is not practical. The flow will not remain constant over any period of time. The system is being modified by the addition of flow meters. Also larger addition vessels will be used to permit uninterrupted operation and larger air lines and filters are being installed to increase the air pressure at the grinding chamber from 83 to 100 psig.

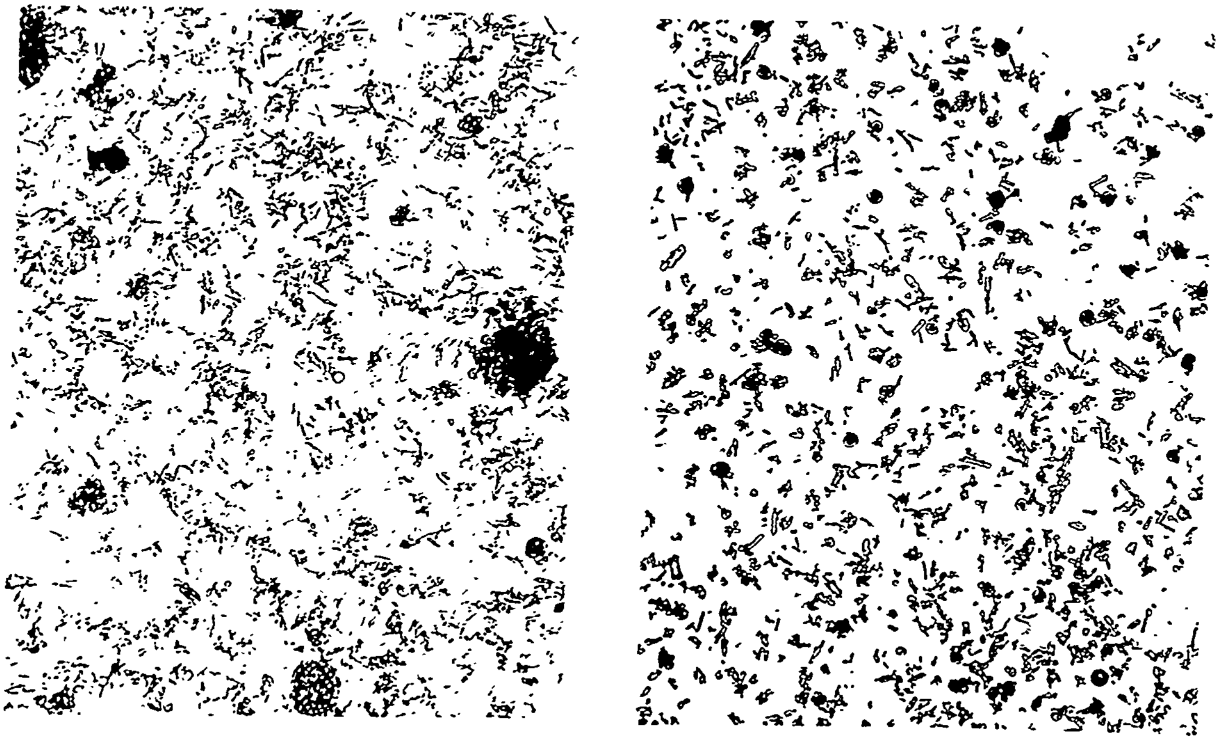
Photomicrographs of PETN crystals from the Micronizer batches and the other two PETN batches processed this quarter are given in Fig. 1 for the purpose of comparing crystal shapes rather than sizes since the magnifications are somewhat random.

The 10 kg batch No. 8092, intended to be the 10 kg batch used for the detonator studies at Mound, which was a combination of the English purification plus the Pantex reprecipitation, was to be essentially a duplication of batch No. 7286 made last quarter except, hopefully having a higher surface area. The reprecipitation temperature for the batch this quarter was even dropped an additional 20°F over that used last quarter to -40°F. However, the surface area of 14,500 cm^2/gm was not nearly as high as expected. This possibly may be easily explained by another difference between the batches made this quarter and last quarter; the drying cycle. The material last quarter was dried under vacuum almost entirely which would mean that probably the low temperature caused by evaporation at low pressures would stop or greatly retard crystal growth, while this quarter's batch, No. 8092, was dried at ambient temperature by using a slight vacuum to force



Batch 8046 20,900 cm^2/g
1.412 Oil 500x

Batch 8047 14,900 cm^2/g
1.412 Oil 500x



Batch 8064 21,300 cm^2/g
1.412 Oil 260x

Batch 8092 14,500 cm^2/g
1.412 Oil 235x

Fig. 1

filtered room temperature air through the filter cake for removing moisture. This batch might possibly be an ideal candidate for ball-milling. As reported last quarter from a ball milling experiment, it was found that milling broke the needle-like crystals resulting in a more rapid stabilization at a higher surface area. Since batch No. 8092 has a lower surface area than desired and, based on preliminary aging trials, will not stabilize at a surface area of 6000 cm^2/gm or higher, ball milling may be the only alternative to salvage the lot. During the purification of the PETN for this lot (the refluxing of a hot saturated acetone solution with subsequent chilling to 32°F) with du Pont military specification PETN Lot No. 9-25, a slight off-color pink tint became apparent in the acetone, both before and after chilling. We were unable to determine the cause of the discoloration even using control samples and subjecting small samples to various treatments. Because of the question of the off-color, the Extex reprecipitated PETN was then used as the starting material.

After the double purification by heating with subsequent chilling, collection of crystals, a 10% solution was made with 10 kg of PETN and placed in a 200-gallon addition tank. Then 60 gallons of hot absolute alcohol, a ratio of 2:1 alcohol to acetone, was placed in the tank. Then, through a polyethylene line with an in-line filter before a spray nozzle, the solution was added to 275 gallons of -40°F alcohol/water. At -40°F 165 gallons of alcohol with 110 gallons of water are required to prevent freezing. The reprecipitated PETN was then collected in two filter buggies lined with cotton filter material. Distilled water was also added to the buggies to aid filtration by warming the solution, thus decreasing its viscosity, plus further diluting the alcohol/acetone. The filter cake was not disturbed on the filter cloth to prevent the loss of an excessive amount of PETN through the filter medium. Then as mentioned, the PETN was air dried.

A similar procedure was used for making the other 10 kg batch of PETN, No. 8064, recrystallized this quarter to provide LRL material for special studies. A 7.86% acetone solution of PETN containing 1% triPEON and alcohol, in a ratio of 3.8:1, alcohol to acetone, was added to 165 gallons of 32°F water in the 300-gallon kettle. This material was collected on the Teflon glass filter since a short filtration time was not critical. Although the Teflon glass greatly retards flow rate, it was thought that the triPEON would retard crystal growth for the extended filtration time.

This batch was dried under vacuum. Surface area was 21,200 cm^2/gm. For ascertaining pressability since LRL is interested in that aspect of the material, three pellets were pressed to densities of 1 gm/cc, 0.9 gm/cc, and 0.8 gm/cc. All of the pellets held together rather well and seemed to have sufficient strength to withstand a reasonable degree of light handling.

FUTURE WORK; COMMENTS; CONCLUSIONS

The mild success achieved in the first two Micronizer experiments seems to indicate great potential in making high surface area PETN. An apparent problem appeared to be the 300 cfm at STP which is injected into the Micronizer at 100 psig. This seemed beyond our capabilities until it was discovered that the 8-inch Micronizer required only 130 cfm at STP while the larger 12-inch English model required 300 cfm at STP.

Also it was understood that a baffle used to control the residual time of PETN in the grinding chamber was to be omitted from the Micronizer. Upon examination of some photographs of the English Micronizer system brought to Pantex by H. Golopol of LRL, it was discovered that this baffle should have been installed. Thus it should be possible to easily achieve much higher surface areas.

With the 3000 pounds of PBX manufactured this quarter, the total quantity of PBX made, including last quarter, is now 6000 pounds. If warranted, production quantities could be produced in the HE Formulation Facility.

Although individual batch size has been 250 pounds in the 300-gallon kettle, the size could be increased to 300 or possibly in some cases 350 pounds depending upon the slurry characteristics of the particular binder used. It would depend upon the ease with which the granules form. In the case of RX-09 the granules form easily.

Also, with some modification of the agitator shaft, large lots can again be blended in the 300-gallon kettle. Wet blending has certain advantages over dry blending.

As it is the agitator speed can not be increased to the point necessary to keep 1000 pounds of PBX circulating in the kettle. The shaft is slightly out of line and the agitator stabilizing bushings are beginning to show wear.

A design has been completed increasing the shaft diameter and method of securing it; however, the kettle will not be pulled out of service until the demand for its services subsides.