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HE FORMULATION

A. G. Osborn
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DEVELOPMENT DIVISION

JULY - SEPTEMBER 1973
SANL NOS. 260-003 & -004

For
Lawrence Livermore Laboratory
Livermore, California

&

Normal Process Development
Endeavor Nos. 219 & 402

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The purpose of this activity is to produce HE formulations and perform studies of processing variables.

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ABSTRACT

PETN samples precipitated in the 3-liter continuous precipitation chamber and subjected to various drying methods and heat treatments were formulated into Extex and evaluated for extrudability in Production's standard extrusion test. Also, a control of Production precipitated PETN was included. Results are promising, with some samples extruding very nearly like Production materials.

Using an extrusion casting technique, three skid test parts have been made from a new LLL ECX, RX-08-CH. The 20% HMX, 62.5% potassium perchlorate and 17.5% Air Force binder formulation is resilient and very insensitive to the skid test. The manufacturing techniques are straightforward, no serious problems were encountered and all three parts had a density in excess of 99% of TMD.

Work is continuing on the processing and the rheological evaluation of the paste explosive, RX-08-DR. Ten batches were tested on the modified Haake apparatus. Also, the screw extruder is in the process of being rendered operable. Mock material is now being processed.

A 500-pound lot of RX-04-EK was blended from two 250-pound batches made in the 300-gallon kettle. The RX-04-EK which has a nominal composition of 96% by weight HMX and 4% Estane had an actual lot analysis of 95.88 ± 0.20% HMX.

DISCUSSION

Extex PETN

During the last quarterly period the work with the 3-liter continuous PETN precipitation chamber began to extend beyond process parameter studies involving just precipitation, into the area of the performance of the PETN in Extex. Although the most critical factor is firing performance, the area of interest now is extrudability: how to get Extex made from continuous precipitated PETN to extrude as well as Extex made from PETN produced by Production.

At various times in the past during the development of the continuous precipitator, samples of PETN have been made up into Extex and loaded into detonation velocity blocks and into Sunburst fixtures and test fired. All preliminary results indicate that there is no problem with firing.

Last quarter was the first time that materials were subjected to the Production extrusion test. Four combinations of process parameters were chosen which would yield lower surface area crystals which were made up into Extex and tested for extrudability in Production's standard extrusion test. The test is described in detail in the last quarterly report along with a photograph of a typical test block made with Mock LX-13. Unfortunately, extrudability was very poor, barely sufficient to even provide measurements. This was

somewhat of a surprise since the surface area of the PETN samples as precipitated were in the desirable range of 5000 to 6000 cm^2/g as measured by the FSSS, which is typical of Production's Extex PETN. It was thought that perhaps the freeze-dried crystals were somewhat more fragile than those obtained in Production's oven drying process, thus, the reason for a comparison done this quarter on the effect of drying techniques and heat treatments on the PETN after precipitation. Instead of merely freeze-drying—which is inherently desirable because it removes the water without alteration of the crystal—samples were also oven dried using the typical Production drying cycle, and samples were vacuum oven dried which has a potential Production application since they have a newly installed vacuum oven.

For uniformity the processing parameters used for Batch No. 3172-02 made last quarter were chosen for three batches made this quarter. The conditions are as follows:

3-liter continuous precipitation chamber
15% solution of purified PETN in Acetone
Acetone pump, output 1002 cc/min
Water pump, output 3288 cc/min
Agitation, 400 rpm

Samples from these batches were also subjected after drying to further heat treatment as shown in Table I, the 36-hour at 66 C and the 8-hour at 116 C. Photomicrographs of the crystals are shown in Figs. 1 and 2. Table I also includes surface areas and extrusion results. As noted in the results for the Extex made from the various samples of PETN from Batches 3261-01, 02 and 03, extrudability overall was not as good as typically obtained for Extex; however, it was much better and more promising than that initially obtained last quarter. The last two batches listed in the table are controls—one made with and one made without TF Freon from PETN precipitated by Production. This was the only time TF Freon was used in the initial mixing of PETN and Sylgard. These controls were made as somewhat of a check on our manufacturing process which involves hand mixing small batches, 200 to 250 grams, and then milling on the small laboratory 3 roll mill. As shown, the batch made with the Freon added was the most extrudable. This is typically experienced by Production. They have found that the use of Freon in the mixing process enhances extrudability.

As shown in the extrudability results the PETN made from the continuous precipitation process, although somewhat lower, compares very well to the PETN precipitated by Production. The next step to get a better, more direct evaluation or comparison of precipitation processes will be to supply Production with a larger quantity of PETN precipitated in the 3-liter chamber and then let them incorporate it into Extex and evaluate extrudability.

Table I

PETN Batch No.	Description	Surface Area FSSS (cm^2/g)	PETN/Sylgard Batch No.	Extrusion Length Down the Track Track Size Inches 0.015[b]	0.020[c]	0.030[d]
3261-01	Freeze Dried	5700	———			
	Plus 36 hrs at 66 C	4550	3271-01	0.50	0.66	1.44
	Plus 8 hrs at 116 C	1900	3274-01	0.56	0.82	2.37
3261-02	Oven dried, 36 hrs at 66 C	4600	3263-01	0.41	0.46	1.13
	Plus 8 hrs at 116 C	1800	3270-01	0.54	0.69	1.85
3261-03	Vacuum oven dried 20" at 66 C	4200	———			
	Plus 36 hrs at 66 C	4100	3271-02	0.49	0.61	1.44
	Plus 8 hrs at 116 C	1850	3274-02	0.45	1.30	2.15
1072-0814-23[a]	Oven dried, 36 hrs at 66 C	6200	3282-01	0.73	0.95	1.54
		6200	3282-02[e]	1.18	1.54	2.83

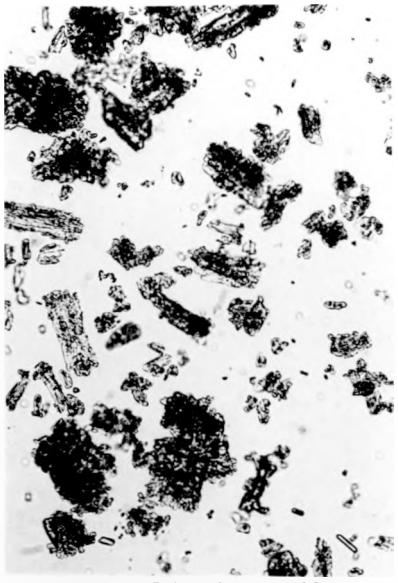
[a] *Production PETN*

[b] *For 0.015-inch track Typical Extrusion length: LX-13, 1.0-inch; Extex 0.8-inch.*

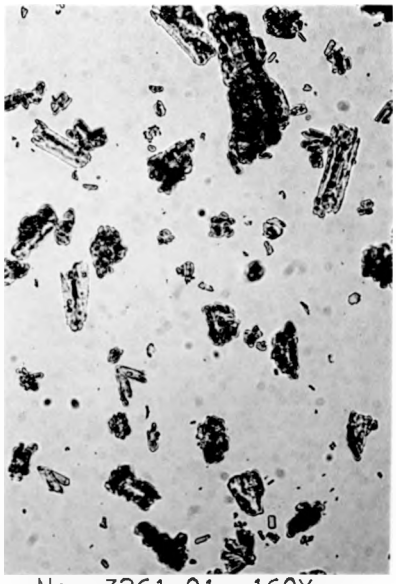
[c] *For 0.020-inch Track Typical Extrusion length; LX-13, 1.2-inch; Extex 1.0-inch.*

[d] *For 0.030-inch Track Typical Extrusion length; LX-13, 3.0-inch; Extex 2.5-inch.*

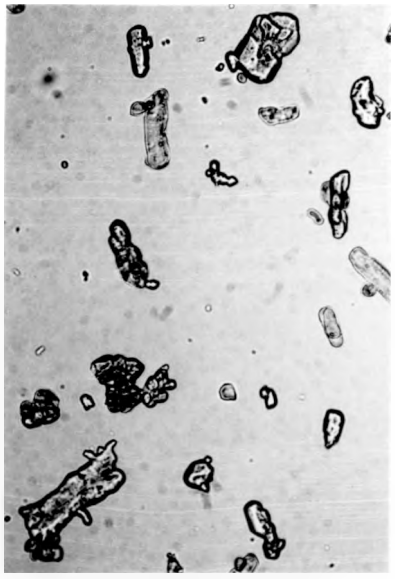
[e] *TF Freon used as fluidizing agent during initial mixing of PETN/Sylgard.*



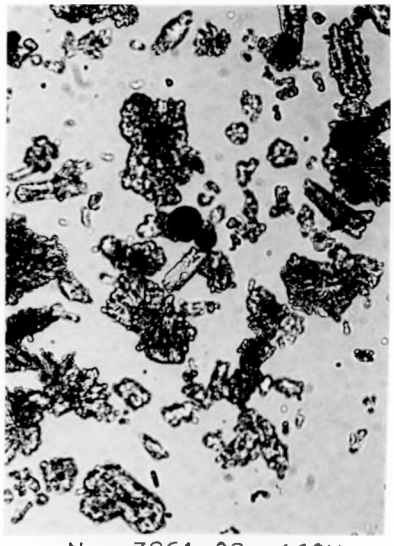
No. 3261-01, 160X
Freeze Dried
5700 cm^2/g



No. 3261-01, 160X
Freeze Dried Plus
36 hrs @ 66 C
4550 cm^2/g



No. 3261-01, 160X
Freeze Dried Plus
8 hrs @ 116 C
1900 cm^2/g



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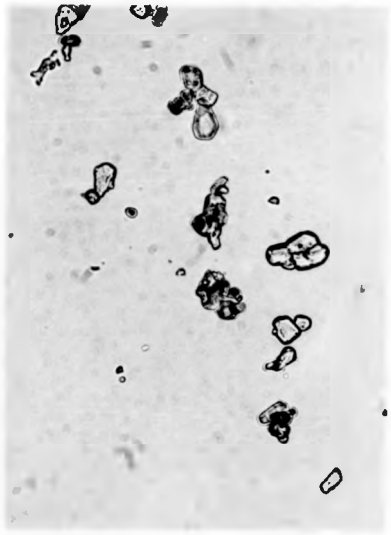
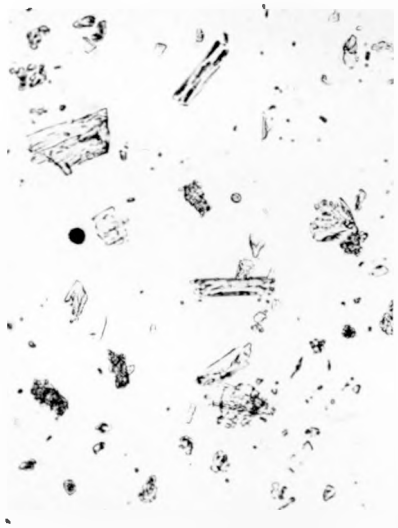
Oven Dried, 36 hrs
@ 66 C, 4600 cm^2/g

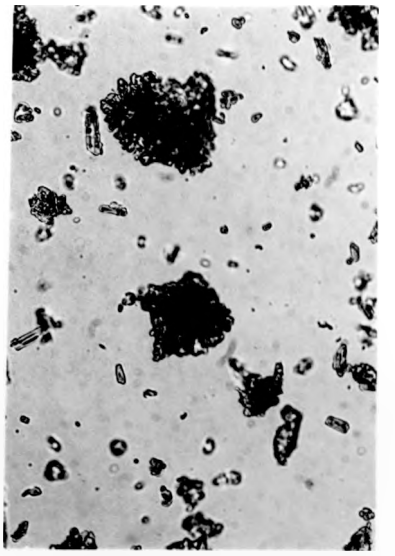


No. 3261-02, 160X
Oven Dried, 36 hrs
@ 66 C Plus 8 hrs
@ 116 C, 1800 cm^2/g

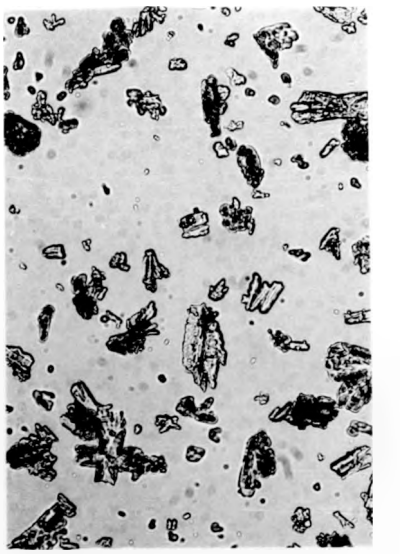


No. 1072-0814-23,
160X, Oven Dried
36 hrs @ 66 C
6200 cm^2/g

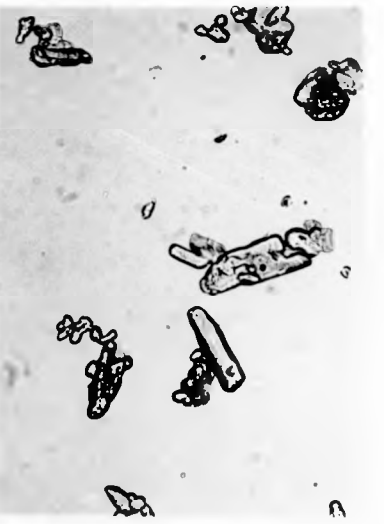
Fig. 1



No. 3261-03, 160X
Vacuum Oven Dried
20" @ 66 C 4200 cm^2/g



No. 3261-03, 160X
Vacuum Oven Dried
20" @ 66 C Plus
36 hrs @ 116 C
4100 cm^2/g



No. 3261-03, 160X
Vacuum Oven Dried
20" @ 66 C, Plus
8 hrs @ 116 C
1850 cm^2/g

Fig. 2

ECX (Extrusion Cast Explosive)

Three 11-inch diameter hemispherical skid test parts have been made by an extrusion casting technique from a new LLL HE, RX-08-CH. The parts were made using the 5-gallon Day Mixer and the large paste deaerator. RX-08-CH, consisting of approximately 20% HMX, 62.5% potassium perchlorate, and 17.5% Air Force binder, was cast under vacuum to a density of > 99% TMD. Results of the skid testing indicate the material to be insensitive since no reaction occurred at any of the skid test conditions. The RX-08-CH billets have much the same appearance as conventional HE; it is light tan in appearance and resilient as demonstrated by the fact that the parts do not break when dropped, but bounce. For details of the skid test see the report "Friction Sensitivity and Skid Test."

The exact composition of the RX-08-CH, is as follows by weight:

62.45%	- $KClO_4$	
20.00%	- HMX LX-04-1 Grade	
5.30%	- IDP (Emolein 2911)	isodecylpelargonate
10.90%	- PPG (P-2010)	polypropylene glycol
0.89%	- PAPI	polymethylene polyphenylisocyanate
0.15%	- HMDI	hexamethylene diisocyanate
0.30%	- TDI	toluene-2,4-diisocyanate
0.01%	- FeAA	ferric acetylacetonate

Other data are as follows:

Part No.	Shore A Durometer	Weight (lbs)	Density
3233	35-45	23.41	1.8577
3235	25-35	23.46	1.8700
3240	45-55	23.45	1.8671

A photograph of a skid test part is shown in Fig. 3. Also, the parts were radiographed. Small cracks visibly evident on the first two parts also showed up on the X-ray film. The third part appeared to be free of blemishes. The parts were cured overnight at 140 F in a recirculating steam oven under approximately 100 psi. For the first part, No. 3233, silicones were used as mold release agents and minor sticking occurred in the mold after cure. A different mold release, Epoxy Parfilm, Price-Driscoll Corp., was found which eliminated this. The second part, No. 3235, had the highest density. It was subjected to a somewhat higher pressure during cure; however, this may not necessarily be desirable since it apparently adversely affects the cure as shown by the reduction in the durometer.

Fig. 3. RX-08-CH - Skid Test Hemisphere

An initial batch size of 30 pounds was used in the mixer and deaerator since this seems to be a reasonable quantity considering hang-up in the deaerator and fill lines. To very briefly review the procedure for making the ECX, the HMX, $KClO_4$ and Emolein are mixed in the 5-gallon Day Mixer for approximately 30 minutes with intermittent scrapedown. Then all of the other ingredients are mixed in for an additional 15 minutes. The mixture is then transferred to the 5-gallon paste deaerator where it is deaerated under vacuum, and then extrusion loaded into the skid test mold, also under vacuum. The mold is then detached from the deaerator and placed in the oven for curing. Air lines are attached to place the mold under pressure.

PEX (Paste Explosive)

In the last quarterly report it was reported that batches of PEX made in the Baker-Perkins and the Grenier Mixer were being subjected to rheological evaluations. These data have been obtained and are reported in Fig. 4. The processing particulars given in the last quarterly report are given again in Table II for information purposes, with the exception of Batch No. 2286, which was dropped because it was not tested for extrudability. As reported, the PEX is designated as RX-08-DR which is by weight, 76% HMX, 22% EDNP, and 2% Cab-O-Sil with trace amounts of ethylene glycol added as a thickening agent.

A total of 10 batches is included, seven 1 kg batches in the Baker-Perkins and three 100-gram batches in the Grenier Mixer. As shown in Table II, LX-04-1 special HMX was used. The HMX was oven dried except for two cases where it was freeze dried. The Cab-O-Sil/EDNP dispersion was prepared by two methods; one in the high shear blender and the other in the Grenier Mixer under vacuum. In one case ethylene dichloride was used as a fluidizing agent in the high shear blender to help disperse the Cab-O-Sil in the EDNP.

The rheological results are presented in Fig. 4 in two groups. The upper half of Fig. 4 contains the reciprocal viscosity curves obtained from the 1 kg batches mixed in the Baker-Perkins mixer. The solid lines indicate that the Cab-O-Sil/EDNP pre-mix was mixed in a high shear blender and the dotted lines indicate that the pre-mix was prepared in the Grenier Mixer under vacuum. The HMX was oven dried except for Batch 3180, curve 7 for which deagglommerated freeze dried HMX was used. As shown, the freeze dried material seems to have a better viscosity initially. Also, those batches made with the EDNP/Cab-O-Sil prepared in the Grenier, the dotted line curves 2 and 5, seem to have good viscosities

The curves obtained from the material mixed in the Grenier Mixer are shown in the lower half of Fig. 4 and verify a conclusion reached earlier regarding the differences between the two mixers; the Baker-Perkins does a better job of mixing.

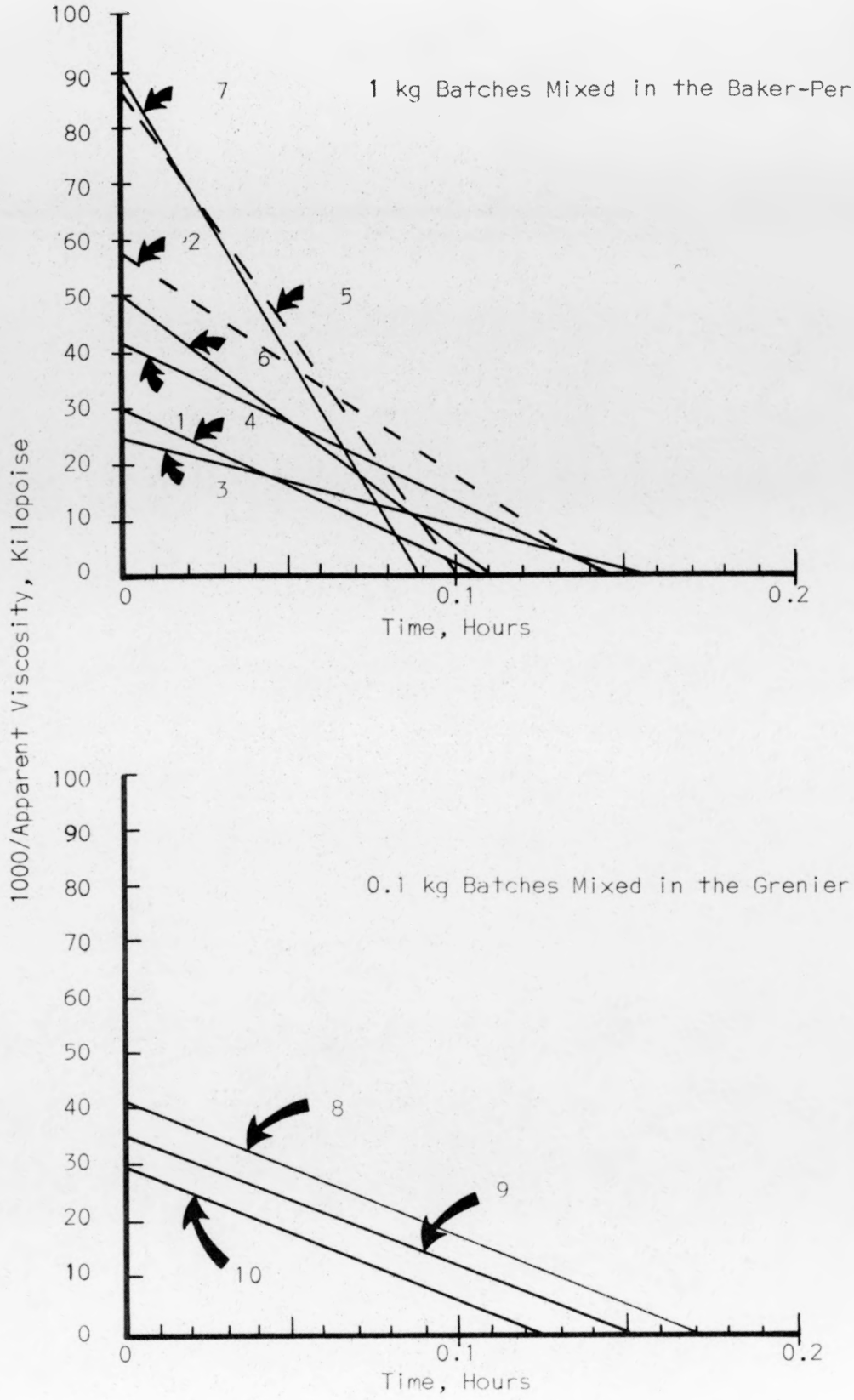


Fig. 4. Reciprocal Viscosity Plot of RX-08-DR at Shear Rate of 3.31 sec^{-1} Elevated

Table II. Processing Studies of RX-08-DR Paste Explosives
Nominal Composition

(Wt. %, 76 HMX/22 EDNP/2 Cab-O-Sil with 0.06% Ethylene Glycol)

Description	Batch No.	Mixer	Batch Size (kg)	Vacuum (μ)	Mix Time (min)	Curve No.	Comments
LX-04-1 HMX Special Oven Dried	3164	BP[a]	1.0	> 6000	30	1	EDNP/Cab-O-Sil Mixed in Blender
LX-04-1 HMX Special Oven Dried	3165	BP[b]	1.0	> 6000	30	2	EDNP/Cab-O-Sil Mixed Under Vacuum in Grenier
LX-04-1 HMX Special Oven Dried	3173	BP	1.0	> 6000	30	3	EDNP/Cab-O-Sil Mixed in Blender
LX-04-1 HMX Special Oven Dried	3176	BP	1.0	> 6000	30	4	EDNP/Cab-O-Sil Mixed in Blender with EDC Fluidizing Agent[b]
LX-04-1 HMX Special Oven Dried	3177-01	BP	1.0	> 6000	30	5	EDNP/Cab-O-Sil Mixed Under Vacuum in Grenier
LX-04-1 HMX Special Oven Dried	3177-02	BP	1.0	> 6000	30	6	EDNP/Cab-O-Sil Mixed in Blender
LX-04-1 HMX Special Freeze Dried	3180	BP	1.0	> 6000	30	7	EDNP/Cab-O-Sil Mixed in Blender
LX-04-1 HMX Special Freeze Dried	3184-01	G	0.1[d]	3700	45	8	EDNP/Cab-O-Sil Mixed in Blender PEX Stiff
LX-04-1 HMX Special Oven Dried	3184-02	G[c]	0.1	3500	45	9	EDNP/Cab-O-Sil Mixed in Blender PEX Stiff
LX-04-1 HMX Special Oven Dried	3186	G	0.1	3400	45	10	EDNP/Cab-O-Sil Prepared in Blender PEX Stiff

[a] *Baker-Perkins, Mixer Bowl Volume - 6.3 Liters*

[b] *Ethylene Di Chloride*

[c] *Grenier, Mixer Bowl Volume - 1.3 Liters*

The test used for evaluating the viscosity of the material has been discussed more in detail in the previous reports. It is a modified Haake apparatus. A median shear rate of 3.31 sec^{-1} was used as noted in Fig. 4. Also, it was noted that separation occurred and was more pronounced at certain shear rates; nonetheless it did occur at all shear rates.

It is apparent from these data that the rheological curves are not clearly definitive as to the effect of changes in processing. The rheological test is in the preliminary stage of development and more work is being done to finalize the test and evaluate its repeatability. Recently an Instron has been purchased and received and will be used in viscosity determinations.

A new capability for processing and loading PEX's is being developed. Several runs using mock material were made this quarter on the Sterling 1-inch screw-extruder. This mock, composed of 70% Pentex and 30% Sylgard 182, was chosen to simulate several of the newer PEX's. It has the consistency of peanut butter when mixed on the Baker-Perkins Mixer.

The extruder is a single-screw hydraulically-powered 1-inch diameter extruder, fully jacketed for steam heating or water cooling. It has a length to diameter ratio of 24 to 1. The hydraulic motor is rated at five horsepower at 1000 psi and 1750 rpm. The motor is connected to the screw through a right angle 10:1 gear reducer. The motor speed is monitored remotely by the Air-Pax tachometer with magnetic pickup. The barrel is supplied with a vent and two vent plugs, one solid and one hollow. The solid plug is the one we are using at the present time. The hollow plug is for use when devolatilizing the product. The barrel also has two locations for thermocouples, one near the vent plug and the other near the end of the barrel. The thermocouples are connected to a recorder in the control bunker.

The operation of the extruder appeared to be very simple at first glance, however, several problems were encountered. The mock was loaded into a hopper with a 1-inch square opening in the bottom. The material flowed somewhat, but some pressure had to be applied to make it continue to flow. This pressure was applied with a ram made from a 2-inch x 2-inch frame. Further work indicated that the mock had sealed off the feed section and the screw was running dry when no pressure was applied. The light pressure applied worked to some extent, but another problem occurred. The mock was forced back up into the feed hopper due to the unevenly applied pressure.

A possible solution to the feed problem involves the use of a hydraulic or pneumatic ram type device which will apply an even pressure to the surface of the material in the hopper. Another method is to use an auger mounted above the feed hopper and feeding into the feed throat of the extruder (this method is used to feed dry plastics but could be adapted to our use by using a nylon auger).

The extruder appears to do a good job of mixing and deaerating this material. One short run involved the addition of a small sample of hand-mixed mock that was a darker red than the main material. This sample had several white specks in it due to the incomplete hand mixing. When this material was run through the extruder the mock appeared as a very dark pink with no white spots in the material. The material was very smooth and had no visible cavitations. The lack of any white areas indicated most of the larger lumps were broken up.

The extruder was then stopped and a different material, Viton B rubber, was forced into the feed hopper for cleaning. This material forced most of the mock Extex out of the barrel. Later some 1/8-inch diameter polyproypylene balls were put through the extruder to assist in cleaning the screw. The Viton B and polypropylene were not affected much by the extruder even when 15 psi steam was turned onto the jacket.

At present the extruder has no die or breaker plate attachment. The breaker plate provides back pressure on the material to keep it fluid. The die then forms the material into the desired cross-section. The lack of a die and breaker plate causes the material to come out in an intermittent stream. A die is being manufactured and should be installed soon.

Historically ECX's and paste HE's are prepared by batch mixing operations which tend to trap air in the material which must be later removed by a deaeration operation adding to the handling and to the cost of the product. An extruder would have a significant advantage from the standpoint of a continuous Production process. From talking with several extruder and multi-screw processing machine manufacturers, it appears that the extruder has the capability of eliminating at least the deaeration step. Judging from the experiments conducted at Pantex so far this could be confirmed. The extruder as mentioned above does appear to mix well and the product is visually clear of bubbles. With suitable dies and molds it should be possible to produce parts free of cavitations. Experience in other industries, such as those manufacturing solid rocket fuels, bears this out.

Future experiments will determine the feasibility of feeding two streams, one of binder and the other of powder in either dry condition or in a suitable carrier, to see if the two mix well enough in the extruder to get a good product. Other projects include fabrication of a non-metallic barrel so there will be no possibility of metal-to-metal contact. The possibility of using a continuous feed will also be investigated. Other runs will further test capabilities and operating parameters for extrusion. The extruder will also be tested for different feed mechanisms and deaeration techniques.

PBX Processing

A variation of the HMX Estane PBX, the RX-04-EK with 4% Estane 5702-F1 binder, was made this quarter for skid test evaluation. Processing data, including compositions, bulk densities, and granulations are given in Table III for the two 250-pound batches of the RX-04-EK and the 500-pound blend of the two batches. As shown, the composition of final blend of 4.12 ± 0.02% was very close to the desired nominal.

Table III. PBX Processing Data

Batch No.	Batch Size	Actual Comp. Binder (%)	Bulk Density	Granulation % Retained Sieve Size			
				4	12	20	40
3207	250	4.31 ± 0.11	0.9	4	90	6	TR
3208	250	4.10 ± 0.06	0.9	2	93	5	-
3212[a]	500[a]	4.12 ± 0.20	0.9	3	92	5	-

[a] *Blend of 3207 and 3208*

FUTURE WORK, COMMENTS, CONCLUSIONS

The extrusion results reported for the Extex made from PETN precipitated in the 3-liter continuous chamber, though not quite as high as desired, are very encouraging, indicating that potentially the extrudability is on the order of conventional Extex or LX-13. The results of the two control batches made from Production precipitated PETN seems to substantiate this somewhat, with one being less extrudable and one being more extrudable than some of the samples made from our PETN precipitated in the 3-liter chamber.

Production normally uses Freon as a fluidizing agent during the initial mixing of the PETN Sylgard for making LX-13 but not for making Extex. Typically, their experience with the Freon is that it extrudes somewhat better, which as shown in the results appears to be the case. However, one other possibly important anomaly in the testing at this point was noted which could have a significant bearing on all of the results. The placement of the HE in the extrusion die was different; it was placed so that the quantity of HE directly under the loading ports was greater than for the other tests. Even so, after extrusion the HE spreads to a thin layer approximately 1/8-inch across the face of the Adiprene extrusion diaphragm. For the next series of tests the quantity of HE will be increased from the 200 to 250 g, to 350 to 400 g to insure an adequate quantity of material to the extrusion ports. Also, this should minimize the effect of tilt in the extrusion diaphragm which would also affect the supply of HE to the extrusion ports.

Work will also continue on the processing and evaluation of the extrudability or viscosity of the paste HE's. Although the work done thus far is not clearly definitive as to the effect of processing variables it has pointed out areas warranting further work. One area which will be concentrated on is the testing or evaluating of the viscosity in the Haake test to establish the reliability and repeatability of the test. Also, work will begin on the new Instron machine. As better testing methods become available the study of the effect of processing variables will become more meaningful.