MH3mP-72-28 N

93

HE SYNTHESIS

D. V. Hayes

&

F. I. Honea

DEVELOPMENT DIVISION

OCTOBER - DECEMBER 1971

Normal Process Development
Endeavor No. 213 & 203

Mason & Hanger-Silas Mason Co., Inc.

Pantex Plant
P. O. BOX 647
AMARILLO, TEXAS 79105
806-335-1581

operated for the
ATOMIC ENERGY COMMISSION
under
U. S. GOVERNMENT Contract DA-11-173-AMC-487 (A)

HE SYNTHESIS

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The purpose of this project is to develop, maintain, and use pilot scale (10-20 kg) synthesis of energetic binders, plasticizers and explosives.

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Endeavor No. 213 & 203
Acct. No. 22-2-44-01-213 & 04-203

HE SYNTHESIS

ABSTRACT

Existing supplies of bis-trinitroanisole and picryl hydrazine were used to make 2 kg of bis-hexanitrohydrazobenzene.

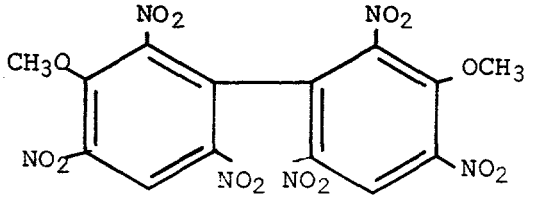
Development of the HNAB recrystallization process was temporarily stopped due to the need to produce a supply of the intermediate products (picryl chloride and HNHB).

Purchase orders for DINOL and DNPIA required for synthesis of AFNOL were awarded.

DISCUSSION

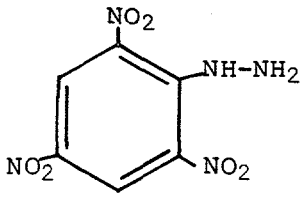
I. BIS-HNHB (BIS-HEXANITROHYDRAZOBENZENE)

Existing supplies of picryl hydrazine(*1*) and Bis-TNA(*2*) were used to make a 12kg batch of bis-HNHB (precursor to bis-HNAB).

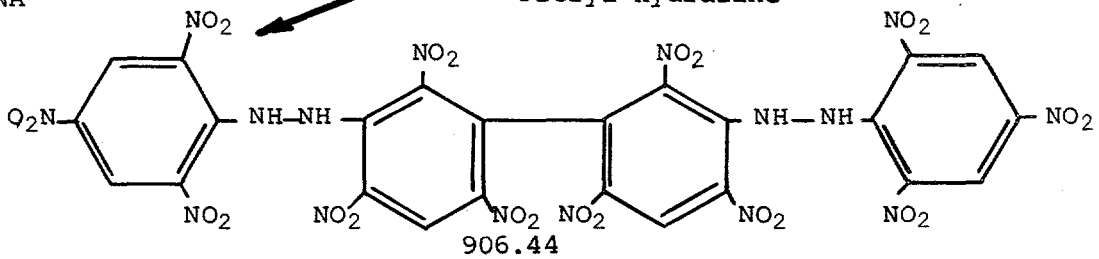


MW 484.25
Bis-TNA

+ 2



243.14
Picryl Hydrazine



906.44
Bis-HNHB

A solution of bis-TNA (6kg) and tetrahydrofuran (THF) (31 liters) was heated to 55 C in the 200 liter reactor. A solution of picryl hydrazine (6kg), THF (31 liters) and ethanol (62 liters) was then dumped into the reactor. This mixture

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(1) Synthesis of Picryl Hydrazine, D. V. Hayes and F. I. Honea, August 1970.

(2) HE Synthesis Quarterly Report, April-June 1971, D. V. Hayes and F. I. Honea.

was heated to 45 C and a slurry of 9700 g potassium acetate and 62 liters of ethanol was added rapidly to the reactor. The whole reaction mixture was heated to 55 C for one hour then allowed to cool overnight. The reaction mixture was added to a hydrochloric acid solution in the 200-gallon reactor and mixed about 2-1/2 hours. Again, the mixture was allowed to stand overnight in the reactor. During this time the product changed from a light brown powder to a sticky black tar. The melting range for this tar was 125 C to 185 C. The tar was recrystallized by dissolving in ethyl acetate and ethanol and precipitating in hexane. The product had a melting range of 160 to 185 C but the yield was only 2 kg. DTA gives no information because the product undergoes an exothermic decomposition when it melts (Fig. 1). Data from C H and N are shown in Table I. All batches were high in carbon and hydrogen but low in nitrogen content.

Table I. CH and N Data for Bis-HNHB

Element	Theoretical[a]	Sandia 10-15-2	Sandia 10-11-3	Pantex 1293-14-01 Sample 1	Pantex 1293-14-01 Sample 2
C	31.8	33.4	32.2	33.3	35.2
H	0.5	1.6	1.4	1.1	1.6
N	24.7	23.5	21.5	20.4	20.4
X[b]	43.0	41.5	44.9	45.2	42.8
Σ	100.0	100.00	100.0	100.0	100.0

[a] *Composition given as percent.*

[b] *The balance (should be oxygen) is found by difference.*

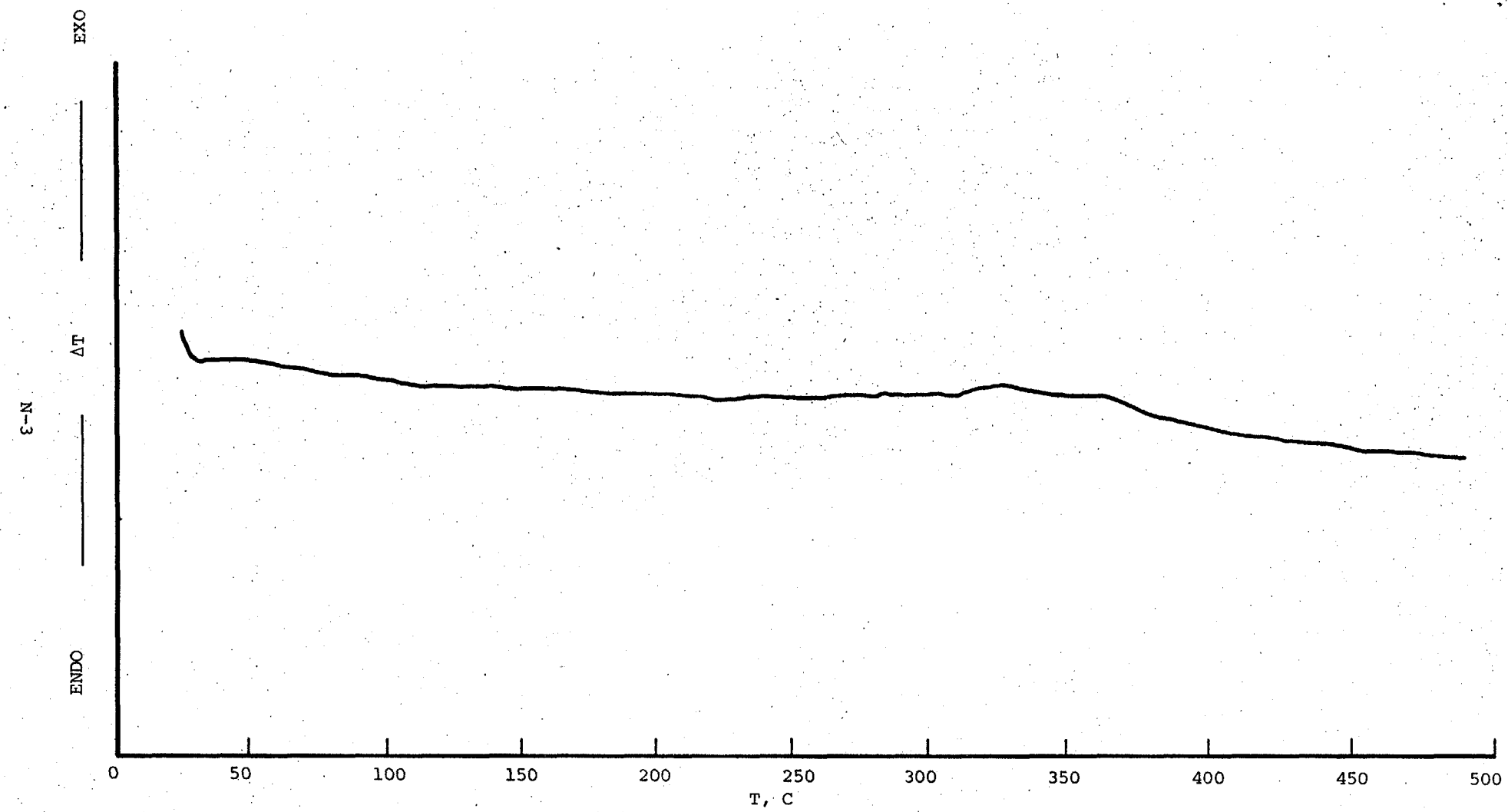
II. HNAB (HEXANITROHYDRAZOBENZENE)

Approximately 44 kgs of HNAB were synthesized and are ready for recrystallization and heat treating. A summary of the intermediate products made this quarter are shown in Table II.

Table II. Summary of HNAB Intermediate Products

Picryl Chloride

Batch No.	Yield (kg)	% of Theoretical
1277-05-01	18.8	94.0
1292-05-01	18.7	93.5
1293-05-01	19.2	96.0
1294-05-01	19.5	97.5
1299-05-01	19.1	95.5
1300-05-01	18.9	94.5



N-3

Fig. 1. Bis-HNHB 1293-14-01

Table II. Summary of HNAB Intermediate Products (Cont'd)

Hexanitrohydrazobenzene (HNHB)

1312-10-01	18.0	90.0
1314-10-01	18.5	92.5
1320-10-01	19.0	95.0
1322-10-01	19.0	95.0

Recrystallization of HNHB

1327-10-01R	3.5	50.0
1333-10-01R	3.9	55.0
1335-10-01R	4.3	61.0
1341-10-01R	5.0	71.0
1342-10-01R	3.9	55.0
1343-10-01R	5.2	74.0
1349-10-01R	4.8	68.0
1350-10-01R	5.5	78.0

HNAB

1361-11-01	14.3	95.4
1362-11-01	14.5	96.6
1363-11-01	14.6	97.4

Six 20kg batches of picryl chloride were made with yields between 93 and 97%. Four batches of HNHB (20kg) were made with yields ranging between 90 and 95%. Eight 7kg recrystallizations of HNHB were made with yields between 50 and 78%. Three batches of HNHB were oxidized to HNAB with yields between 95 and 97% and a total production of over 44 kilograms. (The above work for Synthesis of HNAB is primarily funded by Sandia P.O. 58-0060.)

Data for HNAB 1281-11-01R which was completed last quarter (but the data was not complete) is compared to 1194-11-01R in Figs. 2, 3, 4 and 5, and Tables III, IV, V, and VI.

Purchase orders for DINOL (25 lbs) and DNPIA (50 lbs) were awarded to Aerojet. The expected delivery date is April 1, 1972. These materials will be used to make two 75 lb lots of AFNOL.

FUTURE WORK; COMMENTS; CONCLUSIONS

The HNAB produced will be recrystallized and heat treated to complete the study on recrystallization.

The bis-HNHB will be oxidized to bis-HNAB and this material will be recrystallized.

Existing quantities of triPEOA will be used to check out the molecular still. The purified triPEOA will be reconverted to triPEON.

Since the lab study on BTF synthesis is nearing completion, pilot scale work on this material can be started.

Lab scale work on nitration of TCB (trichlorobenzene) to TNTClB(trinitrotrichlorobenzene) will be started.

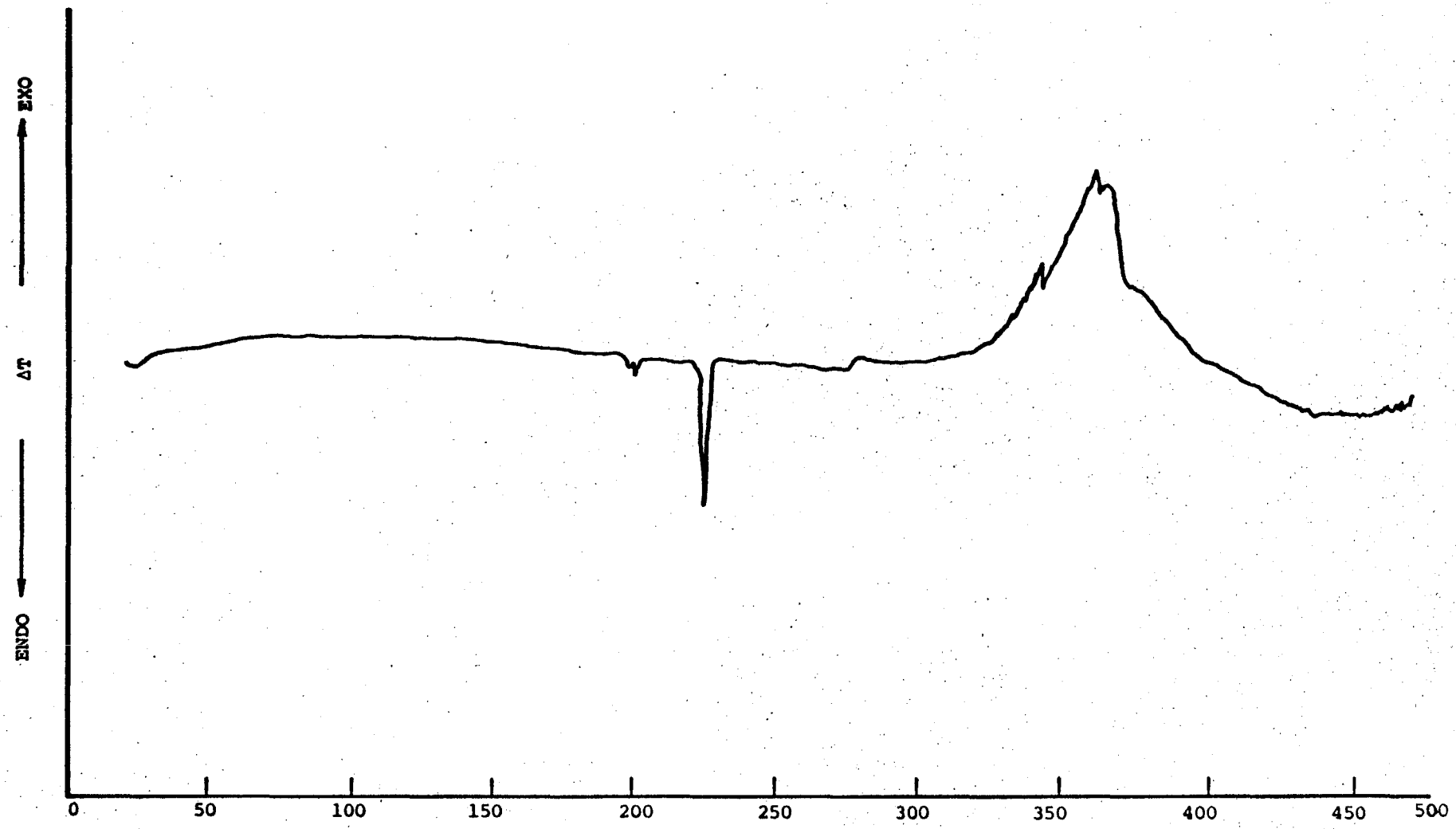


Fig. 2. Recrystallized HNAB 1281-11-01

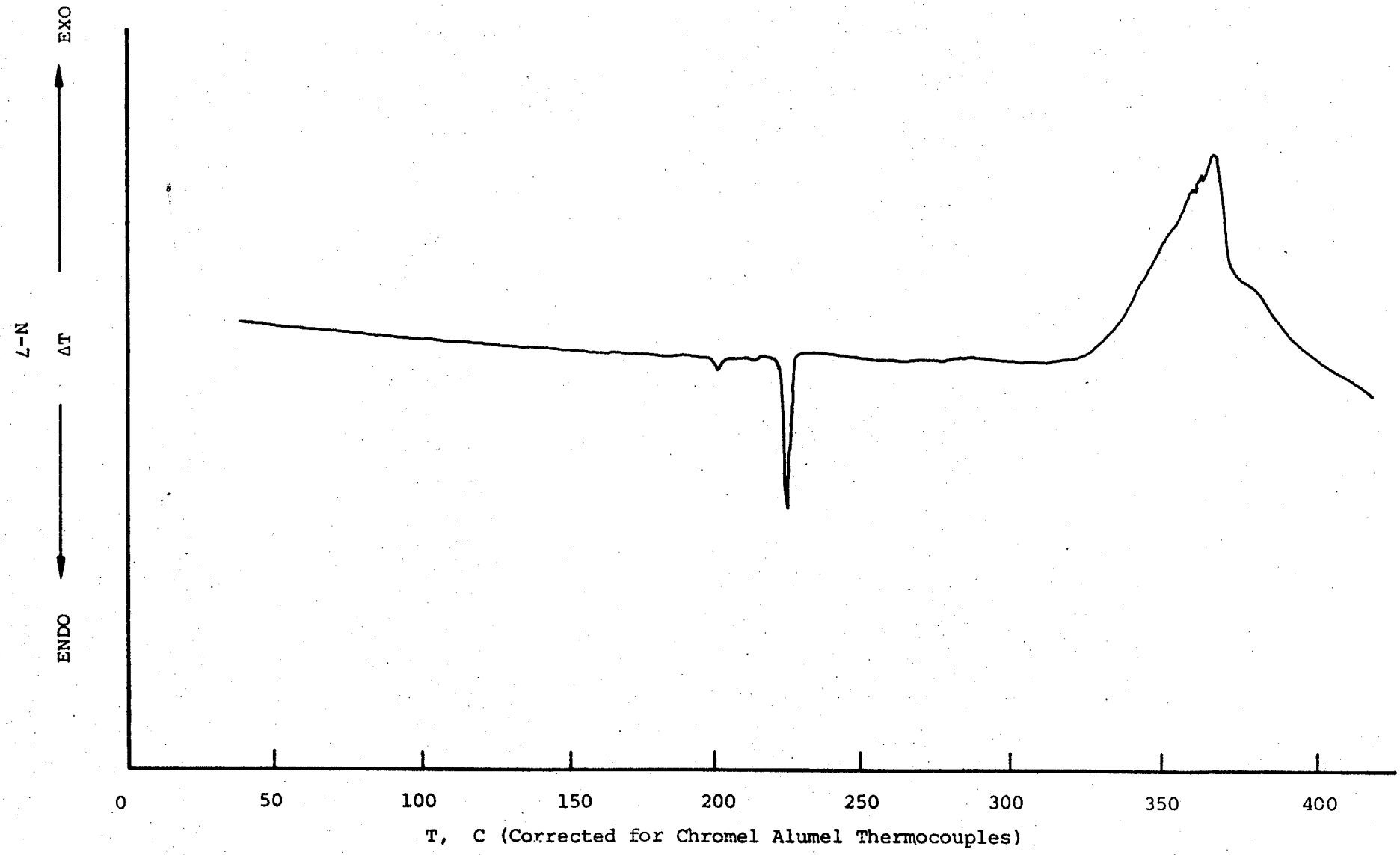


Fig. 3. Recrystallized HNAB 1194-11-01

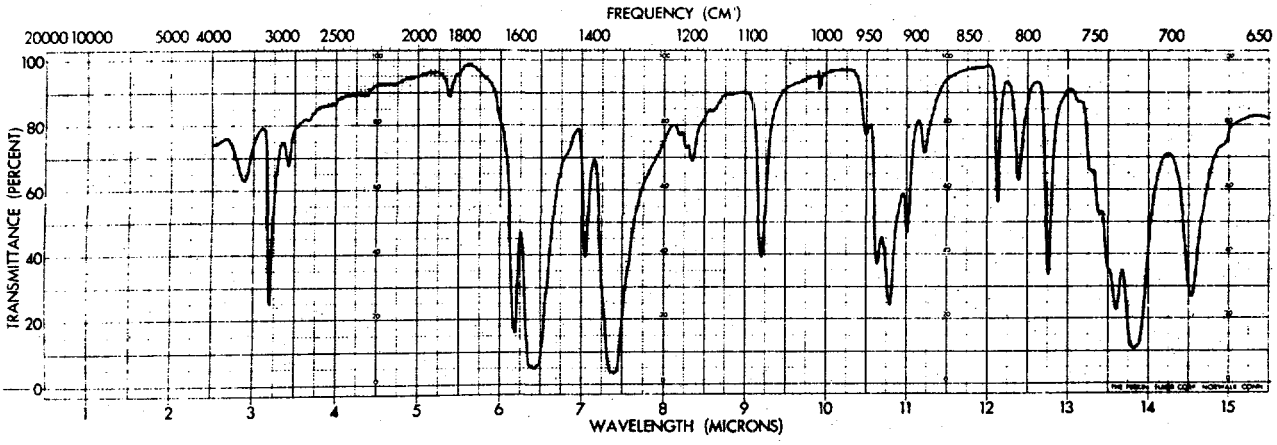


Fig. 4. Infrared Spectrum 1194-11-01

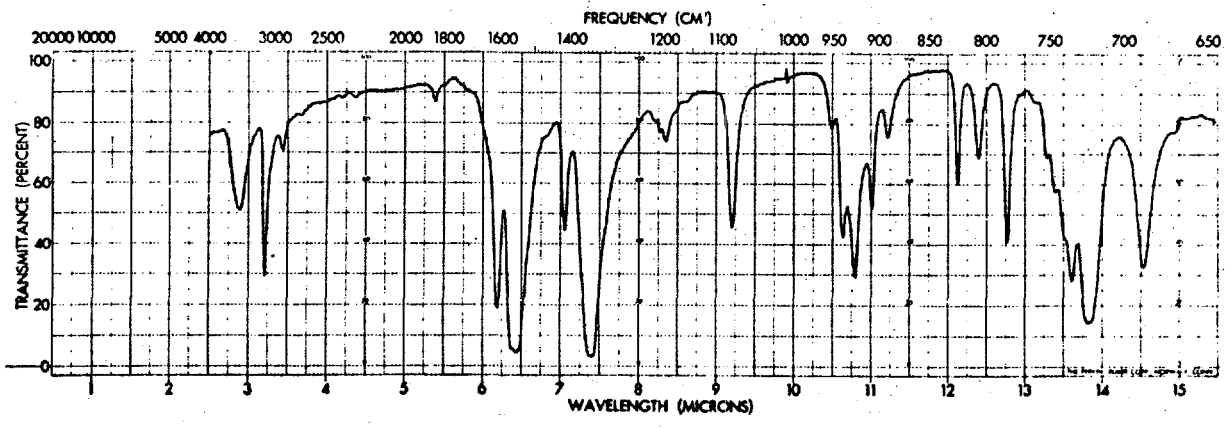


Fig. 5. Infrared Spectrum 1281-11-01

Table III. X-Ray Diffraction

HNAB 1194-11-01

Target - Cu, $\Theta_1 = 0$, $\lambda_1 = 1.5418$

Line	S_1	dhkl	Qhkl	I/I_0
1	14.35	6.17	0.02625	10
2	14.70	6.03	0.02754	30
3	15.25	5.81	0.02963	15
4	16.05	5.52	0.03279	5
5	16.55	5.36	0.03486	2
6	16.95	5.23	0.03655	2
7	17.42	5.09	0.03859	20
8	18.58	4.78	0.04385	100++
9	20.15	4.41	0.05150	65
10	20.75	4.28	0.05457	55
11	21.92	4.05	0.06082	100
12	23.32	3.81	0.06873	100
13	23.90	3.72	0.07214	20
14	25.88	3.44	0.08438	30
15	26.62	3.35	0.08918	20
16	27.00	3.30	0.09170	50
17	27.55	3.24	0.09540	3
18	28.05	3.18	0.09883	40
19	28.42	3.14	0.10140	3
20	29.80	3.00	0.11125	4
21	30.55	2.93	0.11679	30
22	31.38	2.85	0.12321	20
23	32.22	2.78	0.12956	30
24	32.87	2.72	0.13470	3
25	33.57	2.67	0.14033	60
26	34.75	2.58	0.15006	40
27	35.40	2.54	0.15554	3
28	36.50	2.46	0.16503	10
29	37.52	2.40	0.17404	5
30	41.60	2.17	0.21219	20

Table IV. X-Ray Diffraction

HNAB 1281-11-01

Target - Cu, $\theta_1 = 0$, $\lambda_1 = 1.5418$

Line	S_1	dhkl	Qhkl	I/I_0
1	14.35	6.172	.02625	10
2	14.72	6.018	.02762	40
3	15.30	5.791	.02982	20
4	16.10	5.505	.03300	5
5	16.57	5.350	.03494	5
6	16.97	5.225	.03663	3
7	17.45	5.082	.03872	10
8	18.60	4.770	.04394	100++
9	20.20	4.396	.05175	95
10	20.75	4.281	.05457	55
11	21.92	4.055	.06082	20
12	23.35	3.810	.06891	90
13	23.90	3.723	.07214	35
14	24.27	3.667	.07436	2
15	25.92	3.437	.08463	25
16	26.55	3.357	.08872	2
17	27.07	3.294	.09217	40
18	27.50	3.243	.09506	3
19	28.10	3.175	.09917	45
20	28.60	3.121	.10266	4
21	29.80	2.998	.11125	5
22	30.65	2.917	.11754	40
23	31.40	2.849	.12321	30
24	32.25	2.776	.12980	30
25	32.85	2.726	.13454	2
26	33.65	2.663	.14098	50
27	34.82	2.576	.15064	10
28	36.40	2.468	.16415	15
29	37.55	2.395	.17431	10

Table V. Random Sample for Impurity Particle Distribution

HNAB 1194-11-01

Bottle No.	View A	View B
27	8 > 0.005 4 > 0.002	8 > 0.005 10 > 0.002
19	3 > 0.005 12 > 0.002	3 > 0.005 14 > 0.002
14	7 > 0.005 10 > 0.002	10 > 0.005 11 > 0.002
3	3 > 0.005 8 > 0.002	1 > 0.005 10 > 0.002
34	9 > 0.005 9 > 0.002	3 > 0.005 4 > 0.002
42	2 > 0.005 7 > 0.002	2 > 0.005 13 > 0.002
51	2 > 0.005 14 > 0.002	2 > 0.005 10 > 0.002
62	2 > 0.005 10 > 0.002	2 > 0.005 15 > 0.002
66	2 > 0.005 11 > 0.002	4 > 0.005 20 > 0.002
75	2 > 0.005 15 > 0.002	2 > 0.005 11 > 0.002

Table VI. Random Sample for Impurity Particle Distribution

HNAB 1281-11-01

Bottle No	View A	View B
10	8 > 0.005 15 > 0.002	8 > 0.005 16 > 0.002
20	7 > 0.005 21 > 0.002	7 > 0.005 24 > 0.002
22	6 > 0.005 32 > 0.002	5 > 0.005 33 > 0.002
24	9 > 0.005 23 > 0.002	10 > 0.005 21 > 0.002
51	4 > 0.005 18 > 0.002	4 > 0.005 14 > 0.002
61	6 > 0.005 20 > 0.002	6 > 0.005 18 > 0.002
71	5 > 0.005 16 > 0.002	4 > 0.005 16 > 0.002
81	6 > 0.005 10 > 0.002	6 > 0.005 10 > 0.002
91	7 > 0.005 22 > 0.002	9 > 0.005 20 > 0.002
101	4 > 0.005 18 > 0.002	3 > 0.005 24 > 0.002
111	7 > 0.005 17 > 0.002	5 > 0.005 18 > 0.002
121	7 > 0.005 14 > 0.002	7 > 0.005 13 > 0.002
131	5 > 0.005 16 > 0.002	4 > 0.005 11 > 0.002
141	10 > 0.005 4 > 0.002	10 > 0.005 4 > 0.002
151	4 > 0.005 11 > 0.002	4 > 0.005 9 > 0.002