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HNS II Pilot Scale Studies And Production Trial Run

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DEVELOPMENT DIVISION

P.O. No. 03-2323 & 03-7008
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For
Sandia Laboratories
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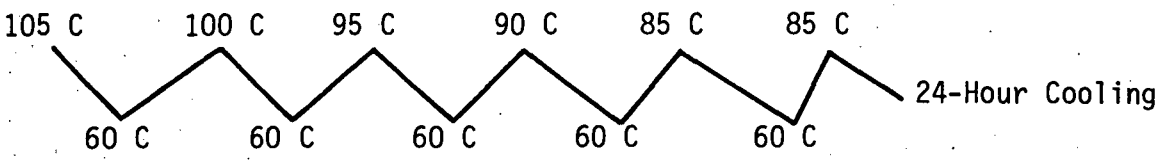
INTRODUCTION

HNS II (hexanitrostiblene) is to be produced for Sandia in the Pantex Synthesis Facility. HNS II is made by a recrystallization of HNS I in dimethylformamide (DMF). HNS I is dissolved in hot DMF, filtered, and entered into a heating and cooling cycle:

HEATING/COOLING CYCLE



After cooling the slurry is filtered followed by an acetone wash, crystal altering in a Cowles dissolver, and then final drying.

PROCESS PROCEDURE

The equipment used is described in the appendix, and the process schematic for the production scale recrystallization is shown in Fig. 1.

Prior to charging, the DMF was analyzed(*1*) to assure that it contained less than 0.5% water. Also, the HNS was analyzed for purity(*2*) and stability in hot DMF(*3*). The process is initiated by charging a measured amount of DMF to the 100-gallon reactor. A 5 μm solvent filter removes solid impurities from the DMF as it enters the reactor. Filtered DMF is also added to the 5-gallon reactor. A preweighed amount of HNS I is manually added with stirring to the DMF in the 100-gallon reactor. Both reactors are then heated to 105 ± 2 C. The hot DMF is transferred through the 5 μm solution filter and into the 200-gallon reactor in order to heat the lines and filter thus reducing crystallization in the initial DMF/HNS solution transfer. The DMF/HNS solution is then transferred to the 200-gallon reactor. The solution filter removes undissolved HNS and insoluble particles. Nitrogen pressure (10 - 25 psig) is used to transfer the hot DMF. The solution is received in a nitrogen atmosphere in the 200-gallon reactor. Two charges from the 100-gallon reactor are required to fill the 200-gallon reactor. The solution is then reheated to 105 C and the recrystallization initiated. When a cycle temperature peak is attained, it is maintained for 15 minutes before heating or cooling the solution to the next temperature. Fifty rpm agitation is used during the cycling. No agitation is used during the cool down period. After cooling, the slurry is stirred at 100 rpm for 5 minutes. Then the agitation is increased to near its maximum (240 rpm) for 25 minutes. This breaks up the agglomerates that had been observed in the bench scale runs. The crude HNS II is isolated in the filter press. The filtrate is retained in the 200-gallon receiver until it and the filter cake are examined. The 200-gallon reactor is flushed with acetone which was premeasured and passed through a 5 μm solvent filter before it entered the 200-gallon reactor. The acetone reslurries the small amount of holdup left in the vessel. This acetone/HNS slurry then

follows the cycled material into the filter. The crude HNS II is partially dried by applying 120 C steam (15 psig) to the heating frames and applying vacuum to the filter cake for 45 minutes. This results in a fairly dry (10 to 20% moisture) cake that can be handled easily. The cake is removed from the filter, and then packaged in conductive polyethylene bags.

To clean the colored solvents from the crude HNS, the material is slurried in acetone in a 100-gallon mix tank. The solvent is pre-measured, filtered, and transferred into a nitrogen atmosphere. The acetone/HNS II slurry is then stirred at 180 rpm for an hour with no heat. The same filtration procedure is repeated to isolate the HNS II. After partially drying the product it is placed in conductive polyethylene bags. A sample of the material is slurried in a miniature crystal altering process using a Waring blender. This determines if the HNS II can pass the bulk density specification (*4,5*). If satisfactory, the HNS II is slurried in the Cowles Dissolver for crystal altering.

SCALE-UP STUDIES

The first pilot scale batch using this process was a scale-up study in a 50-gallon glassed steel reactor. This batch was necessary to determine if the desired crystal form could be produced with the cyclic process in the Pfaudler reactors. Laboratory and bench scale systems did not have geometries or agitation systems similar to these pilot plant reactors.

The same 5- and 100-gallon reactors were used for the pre-heat DMF and for dissolving the HNS. The 50-gallon cycle reactor is described in the appendix. It is very similar to the 200-gallon reactor that is to be used for production batches. Also, the filtration was identical to that of the full scale process; however, a reduced number of filter frames were used. A 30-gallon glassed steel mix tank replaced the 100-gallon mix tank in this small run for the acetone slurry.

The first 50-gallon scale-up run was synthesis Lot No. 6142-07-01R. Chemtronics HNS I was supplied by Sandia. The following quantities were used:

10.34 kg HNS I[a]

2 litres DMF in 5-gallon reactor
157 litres DMF in 100-gallon reactor

0.066 kg/litre in 100-gallon reactor
0.065 kg/litre in cycle reactor

The temperature cycling required 5-3/4 hours. An average of 71 minutes was needed to complete one cycle. After a 24-hour cool down, the HNS II slurry had cooled to 32 C. The average cooling rate was 2.33 C/hour.

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[a] *97.5% HNS, 2.5% dipicrylethane (DPE), and 0.06% DMF insolubles*

Ninty-five litres of acetone was required to rinse the hold-up from the reactor and transfer line. There was a recovery of 6.64 kg of crude HNS II with an analysis of:

HNS	99.83%
TNB	Trace
DPE	Trace
DMF Insolubles	∿ 0.04%

Prior to the final acetone slurry, a miniature crystal altering check was made. The results were:

Time in Blender (sec)	Bulk Density (g/cc)
0	0.328
7	0.456
10	0.522
14	0.581

The crude was then slurried in 100 litres of acetone at 180 rpm for an hour in the 30-gallon mix tank, and filtered. After partially drying the HNS II was packaged to await crystal altering in the Cowles dissolver. A total of 5.68 kg of product, representing a 56.3% recovery, was obtained.

Another small cyclic recrystallization batch was made. The equipment and procedures were identical to the batch just described. A lot of Teledyne (batch process) HNS I was furnished by Sandia for this work. A total of 4.77 kg HNS I was cycled in 74 litres of DMF (0.065 kg/litre). The Waring blender bulk densities were satisfactory. The analysis of the HNS I and resultant HNS II were:

	HNS I	HNS II
% TNB	Trace	Trace
% DPE	2.9	Trace
% HNS	97.06	99.83
% DMF Insolubles	0.023	0.015

A total of 2.27 kg of HNS II, representing a 48% recovery, was packaged to await crystal altering.

PILOT PLANT PRODUCTION BATCH

This larger pilot scale run utilized the vessels that will be used in the production of HNS II. This batch was synthesis Lot No. 6156-07-01R and used the same Chemtronics HNS I lot as the 10.34 kg scale-up study. The following quantities were used:

	1st Charge	2nd Charge
litres DMF in 5-gallon reactor	7.5	7.0
litres DMF in 100-gallon reactor	340.0	280.5
kg HNS I	22.5	18.6
kg HNS/litre DMF in 100-gallon reactor	0.066	0.06
Total Charge in 200-gallon reactor	41.1 kg HNS I 635 litres DMF 0.065 kg/litre	

Temperature cycling required 6-3/4 hours. An average of 85 minutes was needed for each cycle. After 59.5 hours the HNS slurry had cooled to 28 C. The initial cooling rate (before approaching ambient temperature) was 2.25 C/hour. A total of 190 litres of acetone was used to flush the reactor and transfer line and rinse the HNS II in the filter. A yield of 27.7 kg of crude HNS II was obtained. After partial drying, this crude HNS II was slurried in 280 litres of acetone in a 100-gallon mix tank. A yield of 25.67 kg of product (62% recovery) was packaged in polyethylene bags to await Cowles dissolver processing. Crystal altering of samples in the Waring blender was compared with those in the scale-up studies. Prior to the Cowles dissolver, the HNS II had an analysis of:

HNS	99.56%
DPE	0.43%
Bulk Density	$\sim$ 0.35 g/cc

The Cowles dissolver is described in the appendix. Crystals are altered in the dissolver by a combination of hydraulic attrition and particle impingement. The HNS II (both Chemtronics batches) was weighed and charged into the 0.483 m diameter, 0.53 m high, clean stainless steel baffled container. Approximately 37 litres of filtered, distilled water and 1 litre of methanol were then added to the container and gently agitated to wet the crystals. The impeller was lowered into the container and gently turned by hand to ease the positioning of the impeller. The lid was fastened and the dissolver was operated for a total of 7 minutes under the conditions described in the appendix. The dissolver was stopped after 1 minute and a sample of approximately 0.03 kg was taken. Samples were also taken after 2, 3, 4, 5, 6 and 7 minutes operation, with the results listed in Table I below:

Table I

Time (min)	Bulk Density (Mg/m^3)
1	0.526
2	0.529
3	0.547
4	0.579
5	0.612
6	0.551
7	0.532

The material was then poured into a batch buggy containing a clean Tetko 15 μm nylon filter cloth, the water was drained off and the HNS II was dried in a steam heated oven at 107 C for 18 hours.

DMF insoluble impurities were found in the HNS II. Therefore, 28 kg of the HNS II was washed to remove foreign inclusions in the HNS.

Equipment used is described in the appendix. A schematic of the process is included in Fig. 2. The process consists of dividing the HNS lots into two portions and washing each portion with acetone and then with TF Freon. The two portions are then combined in a large container equipped with a 15 μm filter and bottom drain. A 420 μm wire cloth screen is used to separate any extremely large particles. A siphon hose connected through a trap is used to remove "floaters" as they come to the top. After allowing the slurry to stand with gentle vibration for 1-1/2 to 2 hours the bottom drain is opened and the Freon is drawn off by vacuum. The cake is then placed on a filter bag and the bottom part of the cake is cleaned off. The material is dried in a steam heated oven at 107 C for 16 hours. The HNS II is then placed in clean bags and X-rayed for inclusions. After being checked for inclusions the HNS II is then packaged in 0.45 kg bottles.

The final analysis of the HNS II is given in Table II and is compared to the Navy WS5003F(*4*) specification. A total of 17 kg was shipped to Explosive Technology.

COMMENTS, CONCLUSIONS AND FUTURE WORK

The recrystallization, crystal altering, and washing processes all went smoothly; however, the resultant HNS II did not meet all of the specifications. The 20-minute vacuum stability test, the pressure densities, and the DMF insoluble particles were not at acceptable levels. The vacuum stability is believed to be related to the use of TF Freon since the material met the vacuum stability specification prior to its use. The pressure density, as a test for repeatibility, is not considered a problem at this time.

Simple vessel washing by steaming and solvent rinsing did not give the vessel cleanliness needed for this material. Extensive work has since been performed to reduce the number of inclusions.

G. L. Clink(*6*) has shown that the dipicrylethane impurity and some small amounts of the HNS decompose in hot DMF. To insure that any insoluble decomposition products are not included in the final HNS II, a prewash of the HNS I has been added to the process.

This consists of digesting the incoming HNS I in DMF at a moderate temperature for 4 hours. A ratio of 0.2 kg crude HNS I per litre DMF is used. The digestion is run at 75 C with mild agitation in the 100-gallon glassed steel reactor. After cooling, the material is filtered in the filter press, as described before, and vacuum dried. Hot water (50 - 80 C) has replaced the steam as the heating medium for the filter. This reduces the temperature extremes on the HNS in an effort to eliminate

decomposition. Also, due to the lower temperature, additional time will be required for the partial drying in the filter. The incoming HNS I will be cleaned by this process until it is at least 99% pure as determined by LC(2). In most cases only one digestion will be required. A total of 63 kg of HNS I can be run in each cleanup process and will require 2 - 3 shifts of work.

Many steps were initiated to make sure that the equipment and chemicals are cleaned thoroughly. The foreign inclusions found in the first HNS II were of all types—metallic, plastic and mineral. The process valves and lines and the reactor ports were disassembled, checked for corrosion or dirt and reinstalled or replaced as necessary. The 304 SS filter press had been used in previous operations which involved filtration of a chloride containing slurry. The filter had a "rusty" appearance. The filter was sandblasted to provide a clean stainless steel surface. Filters were installed to filter all nitrogen, air, and vacuum release lines leading into the reactors. Also, the two solution filters (Fig. 1) have been changed. The Filterite filter elements (PS5X10) have been replaced with Pall Elements (ACS 1001RZ) which are rated to eliminate 98% of all 1.5 μm particles. Also, jacketed canisters have been received from Pall. These will eliminate the need of the 5-gallon reactor and the preheat DMF to warm the filters.

A wash cycle has been incorporated into the operating procedure. Two filters are installed in the process lines. Then the vessels are filled completely with wash solvent (DMF). The wash solvent passes completely through the system as does the HNS slurry. Then the in-line filters are removed and the residue is screened and the particles larger than 10 mils are counted. If a total of more than 100 particles are found on the two filters the wash cycle is repeated. This wash cycle will be run when an out of spec lot (DMF insolubles test) is found in a continuous sequence of batches, after any maintenance on wetted surfaces and at the startup of a sequence of batches. The wash cycles will require additional processing time. The first cycles required 6 - 8 shifts to obtain a filter analysis below 100 particles. With experience and with the other improvements discussed above the time required should be reduced.

Two recrystallizations have been run with these improvements. One lot, No. 6231-07G-001, recrystallized a mixture of miscellaneous tailings and rejected HNS that remained from other Pantex HNS work. A total of 34 kg of this HNS was used in the 4-hour DMF digestion. The second batch, 6234-07G-01, began with 45.5 kg (100 pounds) of Chemtronics HNS. Both resultant lots were within specification for vacuum stability and pressure density. The DMF insoluble particles were reduced to the level shown below.

	Sample			
	A	B	C	Avg
Lot 6231-07G-001				
Retained on 60-mesh screen	3	1	5	3
Retained on 40-mesh screen	1	1	0	0.67
Lot 6234-07G-001				
Retained on 60-mesh screen	7	5	3	5
Retained on 40-mesh screen	0	2	1	1

For future HNS recrystallizations the DMF insoluble particles will be further reduced by lowering the number of particles accepted in the wash cycle and by maintaining all of the process improvements discussed above.

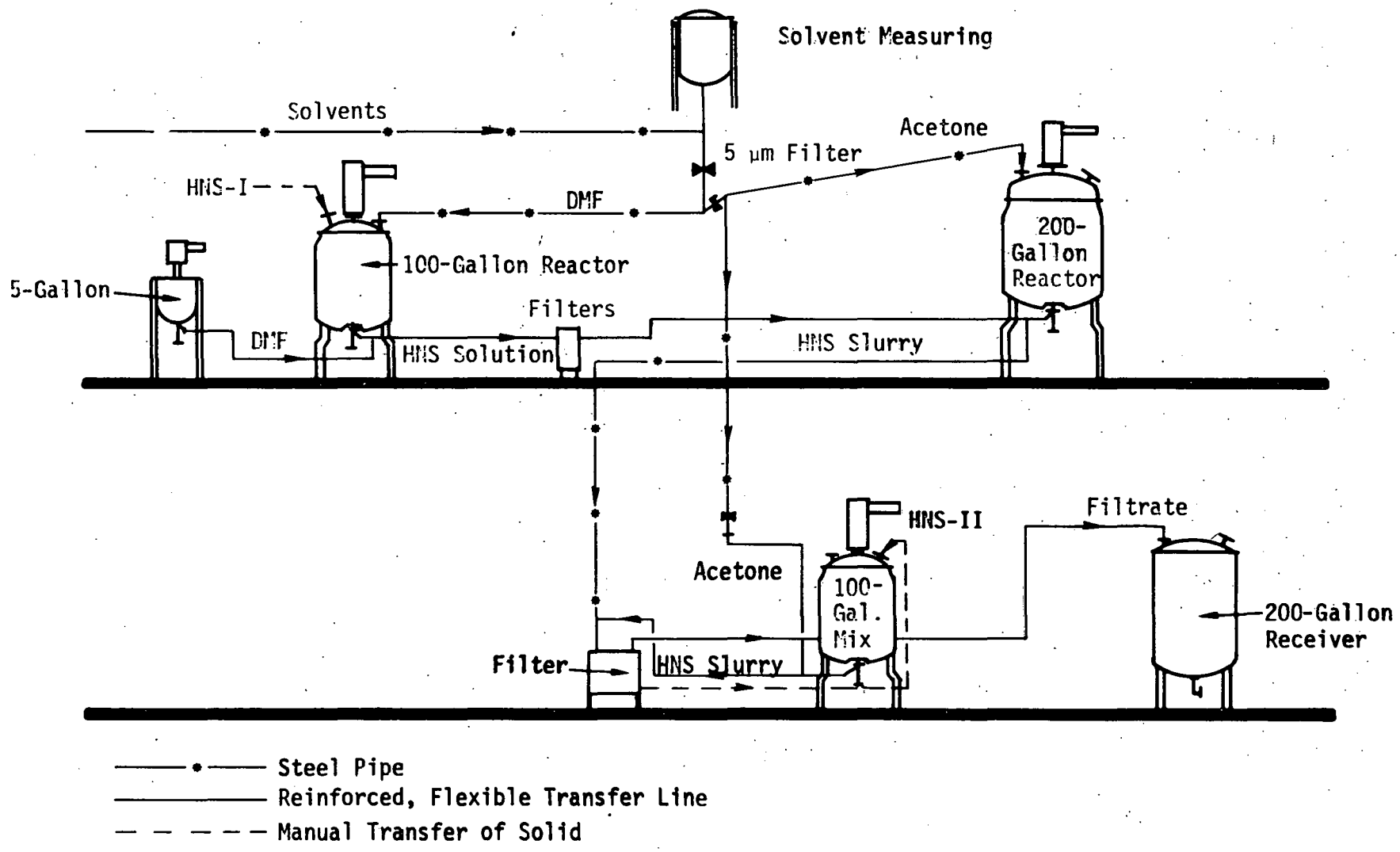

Fig. 1. HNS I to HNS II Recrystallization

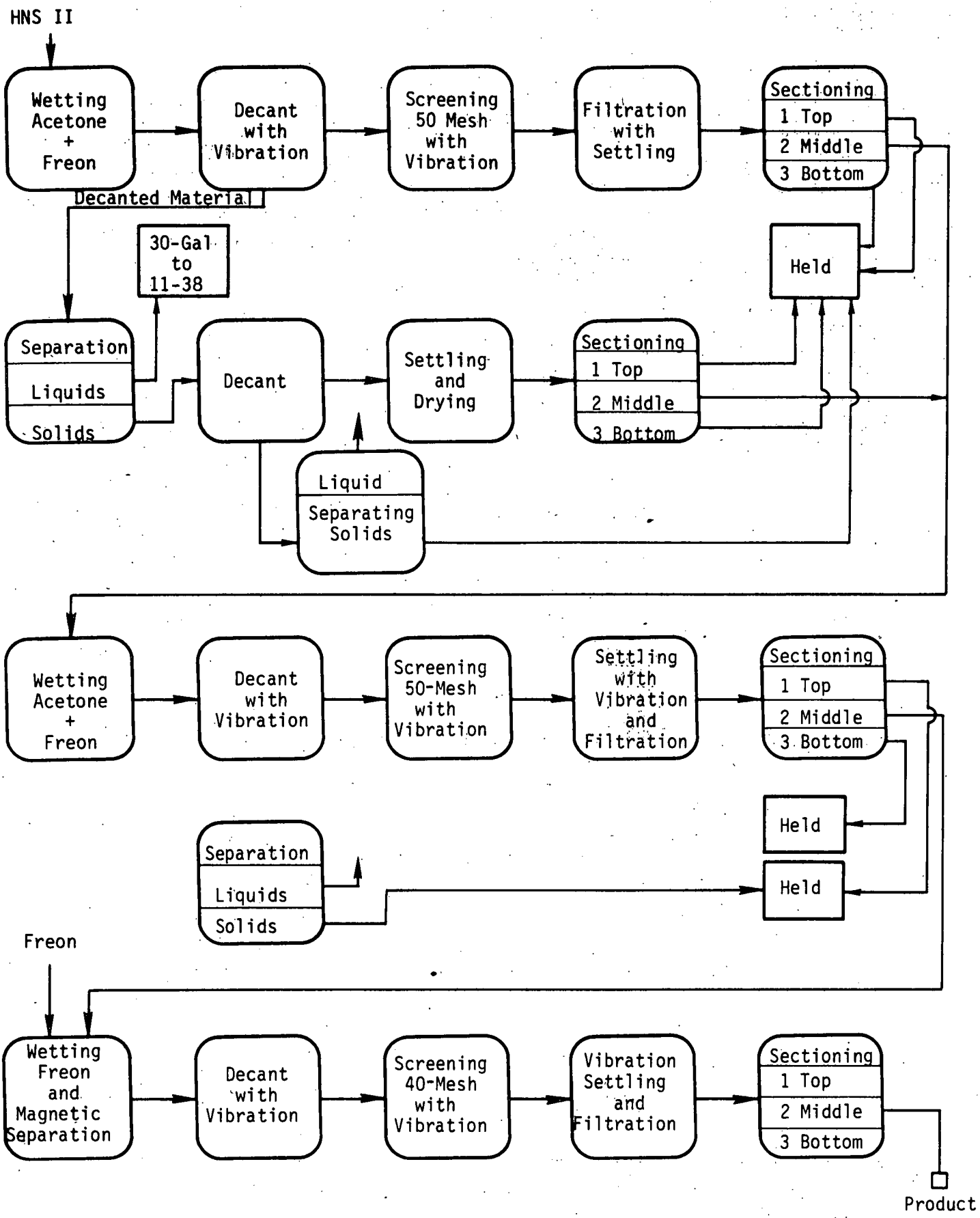

Fig. 2. HNS II Flow Sheet for Clean Up

Table II. Analytical Results for HNS IIA Lot 6161-137-01

	Specification Limits	Sample No. A	B	C	D	Avg.
Melting Point (C)	314.14 Min	315.4	316.0	315.4	315.8	315.7
Melting Point Range (C)	1.1 Max	0.5	1.1	0.9	0.8	0.83
DMF Insolubles (Wt. %)	0.03 Max	0.023	0.023	0.017	0.020	0.025
Surface Moisture (Wt. %)	0.05 Max	0.009	0.004	0.002	0.002	0.004
Water Solubles (Wt. %)	0.03 Max	0.02	0.005	0.002	0.005	0.003
Vacuum Stability						
First 20 Minutes (mℓ/g)	0.06 Max	1.32	1.22	1.17	1.38	1.27
Additional 120 Minutes (mℓ/g/hr)	0.6 Max	0.38	0.41	0.39	0.41	0.40
Bulk Density (g/cc)	0.45 Min	0.55	0.55	0.56	0.56	0.56
DMF Insoluble Particles						
Retained on 60-mesh screen	5.0 Max	10.0	11.0	11.0	11.0	10.5
Retained on 40-mesh screen	NONE	0	0	2.0	1.0	0.75
Conductivity Test 10^{-6} mhos	3.25 Max[b]	1.11[a]	1.12[a]	1.10[a]	1.04[a]	1.09[a]
Pressure/Density						
3 kpsi	1.30 Min	1.2754	1.2749	1.2713	1.2744	1.2740
16 kpsi	1.56 Min	1.5257	1.5259	1.5291	1.5252	1.5265
32 kpsi	1.62 Min	1.6029	1.6012	1.5996	1.5991	1.6007
Liquid Chromatograph Analysis						
(% TNB)		0	0	0	0	0
(% DPE)	No Spec.	T	T	T	T	T
(% HNS)		99.8	99.9	99.9	99.9	99.9
Sensitivity and Output						
(a) Gap Width (db) @ 1.6407 g/cm^3	4.996 to 5.796					5.465
(b) Average Indentation (mils)	49.0 Min					49.1

[a] *Must be less than the equivalent conductivity of 1 ppm NaCl*

[b] *One ppm NaCl conductivity x 10^{-6} was 3.25*

REFERENCES

1. G. L. Clink, The Content Effect of Water in N,N-Dimethylformamide on the Recrystallization of HNS, MHSMP-76-5P (1975).

2. Pantex Standard Operating Procedure No. 6-1719, HNS Analysis by Liquid Chromatograph.

3. B. D. Faubion, Mason & Hanger Tech Note No. PXD-24-76.

4. J. M. Holovka, Navy Material Specification No. WS5003F, Sandia Laboratories (July 29, 1975).

5. Pantex Standard Operating Procedure No. 6-1724, HNS Bulk Density.

6. G. L. Clink, Thermal Stability of Hexanitrostilbene (HNS) in N,N-Dimethylformamide (DMF), MHSMP-76-5Q (1975).

APPENDIX

CYCLIC RECRYSTALLIZATION EQUIPMENT

Equipment	Manufacturer	Capacity	Serial No./Series	Auxiliary Equipment
Reactor, Glassed Steel	Ceramic Coating Co.	5-Gallon	5-8953	3-bladed, retreat "S" impeller, "H" baffel/thermowell, steam heating, 27 C water cooling
Reactor, Glassed Steel	The Pfaudler Co.	100-Gallon	E168-0593/"P"	3-bladed, retreat "S" impeller, "H" baffel/thermowell, steam heating, 27 C water cooling
Reactor, Glassed Steel	The Pfaudler Co.	200-Gallon	E168-0590/"EM"	3-bladed, retreat "S" impeller, "H" baffel/thermowell, steam heating, 27 C water cooling
Press, Filter - 304 Stainless Steel	D. R. Sperry & Co.	12-Inch	X17925/RC	Steam for heating plates, 27 C cooling water, 0-22 inches Hg vacuum
				Nylon filter media - Tetko No. HD3-5, Filter Media backing - Sperry No. 1 Cotton Duck
Receiver, Glassed Steel	The Pfaudler Co.	200-Gallon	E168-0596	
Mix Tank, Glassed Steel	The Pfaudler Co.	100-Gallon	E168-0589/"P"	3-bladed, retreat "S" impeller
Reactor, Glassed Steel	The Pfaudler Co.	50-Gallon	E168-0598/"P"	3-bladed, retreat "S" impeller, "H" baffel/thermowell, steam heating, 27 C water cooling
Mix Tank, Glassed Steel	The Pfaudler Co.	30-Gallon	E168-0591/"P"	3-bladed, retreat "S" impeller
Filters, 304 Stainless Solvent and Solution	Pall Trinity Corp.		VCS1001	Pall Filter Element No. ACS1001RZ (Removes 98% of 1.5 μm particles)
	Filter Corp.			Filterite Element No. PS5X10 (Removes 90% of 5 μm particles)
Process Transfer Lines				SS Braided, Teflon lined hose 304 and 316 SS pipe (solvent charging and Teflon lined steel pipe

CRYSTAL ALTERING EQUIPMENT

Cowles Dissolver Model 5 VTV	Cowles	C128	Variable speed drive (2000 -4500 rpm), "8-inch" sawtooth blade, 0.483 μm diameter baffled stainless steel stock pot, Tachometer, 2.2 kw electric motor
Stainless Steel Stock Pot			Impeller diameter/vessel diameter (d/D) ratio - 0.449, impeller positioned at 0.113 μm (0.25 x D) from container bottom
			Impeller speed - 76.67 π radians/second (2300 rpm)
			Operating time - 1 minute
			0.453 μm diameter, 0.53 μm high, equipped with 4 each 12 μm wide 0.5 μm long baffles welded in place at π/2 radians (90°) apart. Baffles are welded so they are 0.01 μm from vessel wall

FOREIGN INCLUSIONS WASHING EQUIPMENT

Tetko 15 μm Nylon Filter Bag	0.453 μm diameter x 0.559 μm high from Tetko filter cloth No. HD3-5.
Stainless Steel Container	0.453 μm diameter x 0.534 μm high uses a 0.03 μm diameter stainless steel outlet on bottom.