HNS CRYSTALLIZATION STUDIES

Jacob Sandoval

DEVELOPMENT DIVISION

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Normal Process Development
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ABSTRACT

An investigation into the crystallization of HNS from DMF solution was undertaken to determine the effects of seeding, agitation, concentration, cooling rate, and related physical factors on the particle characteristics and bulk density of the resulting crystal aggregates. Through selective parameter control, a product of moderate bulk density was obtained. The length to width ratio can be adjusted through hydraulic attrition.

INTRODUCTION

Crystallization of a solute from its solution is promoted when an orderly arrangement of molecules is effected, permitting them to deposit from a super-saturated solution in a definite geometric configuration characteristic of the material.

An investigation on the crystallization of 2,2',4,4',6,6'-hexanitrostilbene (HNS) from solution in n,n-dimethylformamide (DMF) was undertaken to evaluate the effect produced on the HNS crystal habit when some of the crystallization parameters were altered. Along with this, it was also desired to establish an ideal set of parameters which would repeatedly induce crystallization of a desired particle size and bulk density when similar conditions were employed. No effort was made to evaluate other solvents, although as noted later, the effectiveness of acetonitrile, as a diluent, was considered.

In this study, the following parameters were considered: concentration (solute to solvent ratio), temperature (110 C to ambient), cooling rate, stirring rate, and seeding.

EXPERIMENTAL

The equipment and instruments employed in this study consisted of:

1. 3-Neck, Round Bottom Flask, 250 ml
 - a. Thermometer, Hg; Thermocouple
 - b. Stirrer, glass; 2 blade (Teflon, 1/2")
 - c. Stirrer Control; Fisher Dyna-Mix
 - d. Tachometer; Photolastic Inc.
 - e. Recorder; Varian, A-25
2. Hot Plate; Corning PC 351
 - a. Oil bath
 - b. Thermocouple
 - c. Stirrer, Lab.; 2 blade (Stainless Steel 1")
 - d. Stirrer Control; Variac - Power Stat

3. Temperature Programmer; F&M Scientific 240

- a. Line Follower; Mosely, H/P - 7500A
- b. Recorder; Mosely, H/P - 17501A

Since solution concentration was one of the factors under consideration, the solubility of HNS in DMF was established. Four solubility values, in grams per 100 grams of DMF, of HNS I Lot No. 4-357-XHNS-1-02 were determined. These values are listed in Table I and plotted in Fig. 1. DMF boils at 153 C, but because it begins to darken and decompose at approximately 120 C, the dissolution of HNS in all the crystallization endeavors was limited to temperatures below 115 C.

Table I. Solubility of HNS (g in 100 g of DMF)

Temperature (C)			
<u>26</u>	<u>59</u>	<u>100</u>	<u>115</u>
1.34	2.91	7.66	11.43

HNS I, Lot No. 4-357-XHNS-1-02 was used in the first two experimental runs; thereafter, Chemtronics HNS-I Lot 66-48 was employed. A saturated solution in DMF of the latter product was prepared and filtered hot to remove fibers and other insoluble impurities. The precipitated HNS was collected and dried for subsequent recrystallization studies.

Throughout this study the heating and cooling rates were programmed. Pre-determined masses of HNS and volumes of DMF were introduced into a 250 ml round-bottomed flask and heated at temperatures below 115 C until solution of the HNS was promoted. The effects of seeding, agitation, recycling, cooling rates, and solution concentration on the resulting crystalline crop were investigated. A summary of the test conditions and some of the test results are tabulated in Table II.

Except for one sample, Chemtronics HNS II, Lot 66-47 was used exclusively as the seeding agent where seeding was involved. The inoculating material was first cleansed by dissolution (10 g/100 g solvent) and recrystallized from DMF.

From Table I a saturated HNS/DMF solution at 115 C contains 11.4 parts solute to 100 parts solvent, by weight. In all of the experimental runs, at the same temperature, the solute to solvent ratio was kept at 8.5/100 and 8.7/100; consequently, these solutions had to undergo cooling to their saturation point before crystallization commenced. As the temperature of a solution drops, its saturation point changes. Fig. 2 is drawn from information extracted from the HNS solubility curve, and shows the percentage composition of an HNS solution as its temperature drops from 115 C to ambient (10 C steps).

H-4

Fig. 1. Solubility of HNS in DMF (g HNS/100 g DMF)

Table II. Summary of HNS/DMF Crystallization Parameters

Sample No.	HNS	HNS/DMF Ratio	Stirring Rate (rpm)	Cooling Period (hrs)	Seed (%)	Recovery (%)	Initial Bulk Density	Final Bulk Density	Comments
HNS-5-1	4-357-XHNS-1-02	8.3/100	225	5.0	-0-	78	0.21		Solution cooled 85 C/5 hrs. Light fluffy hairlike crystals.
HNS-6.5-1	4-357-XHNS-1-02	8.3/100	225	6.5	-0-	-0-	0.30		Solution cooled 85 C/6.5 hrs. Stirred at ambient overnight.
HNS-24-1	66-48	8.3/100	225	24.0	-0-	58	0.21		
HNS-24-2	66-48	8.3/100	225	24.0	6 (6.5 hr Run)	78	0.37	0.51	Blender treated; 5 sec.
3 HNS/DMF	66-48	8.0/100	225	4.5	6 (66-47)	81	0.22	0.39	Blender treated; 5 sec.
4 HNS/DMF	66-48	8.0/100	225	4.5	-0-	84	0.15	0.35	Blender treated; 5 sec.
5 HNS/DMF	66-48	8.0/150	225	4.5	20	69	0.22		
6 HNS/DMF	66-48	8.0/150	225	20.0	6	74	0.33		
7 HNS/DMF	66-48	8.0/150	300	20.0	6	76	0.38	0.50	Blender treated; 5 sec.
8 HNS/DMF	66-48	8.0/100	225	4.5	-0-	96	0.29		Binary solvent system, DMF with 15% dioxane.
9 HNS/DMF	66-48	8.0/150	225	24.0	6	81	0.15		Binary solvent system, DMF with 15% dioxane.
10 HNS/DMF	66-48	8.5/180	200	24.0 No Heat	6	83	0.46		16% acetonitrile added.
11 HNS/DMF	66-48	8.5/166.5	300	20.0	3	80	0.35		10% acetonitrile added.
12 HNS/DMF	66-48	8.0/150	No Stir	No Heat	6	75	0.21		Mechanical failure. Contents left undisturbed 90 hours.

Table II. (Cont'd)

Sample No.	HNS	HNS/DMF Ratio	Stirring Rate (rpm)	Cooling Period (hrs)	Seed (%)	Recovery (%)	Initial Bulk Density	Final Bulk Density	Comments
13 HNS/DMF	66-48	8.0/100	700	Recycle	-0-	67	0.45	0.63	Blender treated; 5 sec. Cycled 5 times 100-70 C, 3 g HNS added during cycle.
14 HNS/DMF	66-48	7.0/100	400	Recycle	6	57	0.46	0.71	Blender treated; 5 sec. Cycled 8 times 98-70 C.
15 HNS/DMF	66-48	8.0/100	600	Recycle	-0-	60	0.38	0.65	Blender treated; 15 sec.
16 HNS/DMF	66-48	8.0/100	300	5.0	6	80	0.17	0.46	Blender treated; 10 sec.
17 HNS/DMF	66-48	8.0/100	400	20.0	6	81	0.35	0.37	Fine feathery particles. Blender treated; 5 sec.
18 HNS/DMF	66-48	8.0/100	300	44.0	6	80	0.40		
19 HNS/DMF	66-48	10/160	325	4.0	-0-	81	0.51	0.65	35 ml acetonitrile added in 8 minutes. Blender treated; 5 sec.
20 HNS/DMF	66-48	8/100	No Stir	20.0	6	70	0.51	0.71	Cooled 100 - 67 C/20 hrs. 67 ambient/3 hrs. Blender treated; 5 sec.
21 HNS/DMF	66-48	10/100	300	5.0 Recycle	-0-	75	0.48	0.71	6 cycles.* Blender treated; 5 sec.
22 HNS/DMF	66-48	8/100	No Stir	20.0	6	78	0.35	0.67	Cooled 100 - 73 C/10 hrs; 73 C/6 hrs. Machine failure. Blender treated; 5 sec.
23 HNS/DMF	66-48	8/100	300	Recycled	6	86	0.34	0.54	Line follower failure. 95 C/16 hrs, Cycled x 5. Blender treated; 5 sec.

*Temperature Cycle:

<u>High</u>	<u>Low</u>	<u>HNS Added</u>
108	72	-
105	78	2 g
107	65	2 g
105	78	2 g
103	67	-
97	55	-

Fig. 2. Fraction of HNS in Solution as a Function of Temperature

The low solute content at or near ambient temperature explains why crystallization is limited at the lower temperatures. The addition of a diluent (e.g., water, methanol, acetonitrile, etc.) promotes the precipitation of HNS from its DMF solution, and is recommended as a means for recovery of the HNS from the mother liquor.

In this study, seeding of the test solution with 6% to 20% inoculating material failed to alter the crystal habit of HNS. Inoculating material for all tests was Chemtronics HNS II, Lot 66-47. Neither was there any definite evidence that seeding had any influence on the crystal growth or bulk density. Inoculation of the test solution initiated the inception of the crystallization process at a higher temperature, but this may be attributed to the increase in solute concentration.

With a few exceptions cooling of the test solutions was promoted from the dissolution temperature to ambient at cooling rates ranging from approximately 20 C/hr (uncontrolled) to 3 and 4.5 C/hr (controlled). As the cooling time was extended, a marked increase in the product bulk density was realized indicating it to be a function of the cooling rate.

Agitating the contents of the crystallization flask appeared to have a dual effect on the crop produced. It is desirable to stir at a sufficient rate of mobility to preclude the precipitating solid from collecting into a mass at the bottom of the container. The agitation should be slow enough to allow the formation of crystal nuclei, yet rapid enough to keep the formation of nuclei at a minimum. Such a stirring rate permits the formation of large crystals at the expense of minute particles. The problems encountered in controlling this prerequisite, which is influenced by temperature, concentration and cooling rate, eliminate stirring as a controllable factor.

Two samples were prepared for evaluation of the effect of "No-Agitation" on the crystalline crop. Both samples were seeded with 6% seeding material and the cooling was programmed from the dissolution temperature to ambient over a 20 hour period (approximately 4.5 C/hr). Instrument malfunction in each resulted in the disruption of the cooling rate.

During one test the line-follower jumped course to a slower cooling rate resulting in a temperature drop of 38 C over a 17 hour period. Course correction was made and the cooling continued to ambient (~ 3 hr). The crystalline crop had a bulk density of 0.51 g/cc.

On the second run, the slope-sensing light fixture failed after 6 hours; thus, the flask contents experienced a temperature drop of 73 C over a 10 hour period. The vessel contents were cooled to ambient (~ 2 hr) and the product collected. The bulk density of this crop was 0.35 g/cc.

The HNS solutions were subjected to cyclic crystallization techniques which involved (1) the reduplication of the heating and cooling over a narrow temperature range (100 - 75 C), or (2) over a broader range

(106 - 61 C), where the high and low limits of each successive cycle were decreased by 5 C. The HNS bulk density realized from these techniques were 0.445 g/cc and 0.451 g/cc, respectively.

During the first cooling period a mixture of moderately large and minute crystals was deposited. As the temperature was elevated, the small particles were redissolved but the larger crystals, because of their greater volume, were not totally dissolved before inception of the following cooling period. With each recurrent cycle the process was repeated resulting in a product of higher mass per unit volume.

Additional runs involving cyclic recrystallization techniques produced HNS particles of similar densities; however, all of these yields continued to display a poor length to width ratio. Compensation was attempted prior to sample collection through rapid agitation (400 to 700 rpm) of the flask contents. A pronounced vortex developed as the whirling mass sped along the vessel walls. No fragmentation of the needle-shaped crystals as a result of this stirring was detected.

Adjustment of the length to width ratio was implemented by crumbling of the long needle-shaped crystals while suspended in water. The HNS was treated in a Waring blender containing just sufficient water to cover the cutter and keep the solid suspended. It was established that activation of the blender at fast speed for 5 seconds was as effective as treatment over a longer period. Not only were the ratios improved, but the products also manifested an increase in bulk density (see Table II).

Experimental runs 8 HNS/DMF and 9 HNS/DMF evaluated the use of a 2-phase (DMF with 15% dioxane) solvent system. Clear, well-defined crystals were obtained from this solvent pair; however, on drying (100 C) these crystals assumed a permanent milky-white turbidity. Further evaluation of the crystals revealed excessive dioxane occlusions.

Experimental runs 10 HNS/DMF, 11 HNS/DMF and 19 HNS/DMF employed acetonitrile as a diluent. Addition of acetonitrile, as a diluent, to an HNS/DMF solution promotes the precipitation of well-defined HNS crystals. The diluent must be added in small quantities to avoid pronounced temperature changes. As the dilution continues, the solution concentration drops below the saturation point and crystallization is induced.

Introduction of 35 ml acetonitrile was made at 107 C, with stirring (325 rpm) into a solution consisting of 10 g HNS and 125 ml DMF. The solution temperature was maintained above 105 C throughout the addition, which required about 8 minutes. The first HNS crystals were observed after a total of 18 ml diluent had been introduced; thereafter the crystalline crop increased. Upon completion of the diluent introduction, heating was discontinued. Stirring was continued throughout the cooling (uncontrolled) period. The product, collected at 41C, was given one methanol wash followed by 3 water washes. After a final acetone rinse, the product was collected and dried. An 81% yield was realized with a bulk density of 0.51 g/cc.

Figs. 3 through 11 are photomicrographs of the crystals formed in some of the test runs.

Bulk density determinations were made on all products, while melting points via DTA were determined for most batches. Additionally, 3 samples were evaluated for surface moisture and volatiles, water-soluble material, and insoluble material. This testing was conducted per the procedure outlined in HNS specification WS-5003F (Naval Ordnance Systems Command, Naval Ordnance Laboratory) to check for product compliance with established and proposed specifications. The results are listed in Table III. A complete evaluation of other samples was not available for tabulation in this report period.

Recrystallization of HNS in quantities ranging from 0.5 to 5 kg has been successfully induced through procedures fashioned after the cyclic techniques cited here. Details of these efforts are listed in another report. The products obtained have been subjected to extensive evaluation. Some of the analytical values are listed in Table III under 51 xx -137 series.

FUTURE WORK, COMMENTS, CONCLUSIONS

This study had a two-fold objective; the primary aim was to establish parameters which would repeatedly induce the crystallization of a product with a bulk density = 0.45 g/cc. The second aim was to obtain a product with a low, to moderately low, length to width ratio.

Recrystallization techniques were developed which produced HNS with a bulk density exceeding the specified value.

The typical HNS crystallization product from DMF solution consists of long, needle-shaped particles whose length to width ratio makes them unsuitable for some applications. Efforts at effecting a change in the crystal habit proved unsuccessful. An adjustment on the length to width ratio was achieved through longitudinal fracturing of the crystal by introducing the aggregate into a Waring blender (or similar equipment) and crumbling the water suspended particles.

Upon evaluation of the products realized from the different experimental environments, a few observations can be made, tempered with an awareness that they were generated from very limited data.

1. Control of the physical crystallization factors involved in this study did not alter the HNS crystal habit.
2. Heating of an HNS/DMF solution should not exceed 115 C since DMF begins to decompose above this temperature.

3. At a dissolution temperature of 115 C, the solution composition (by weight) should consist of 7 to 10 parts HNS per 100 parts DMF.
4. Crystal bulk density was enhanced by cooling from the dissolution temperature to ambient at a slow rate (~ 2 C/hr).
5. High crystal bulk density can be induced by cyclic precipitation techniques. This may involve (1) reduplication of heating and cooling limits, or (2) incremental temperature decrease per cycle.
6. Crystal length to width ratios can be adjusted through hydraulic attrition of the HNS aggregates.

This study was limited to the crystallization of HNS from its DMF solution. The evaluation of other solvents or the utilization of a diluent was a secondary part of this investigation. Further investigation is warranted to evaluate other solvents.

Crystallization of HNS in quantities as high as 5 kg has been successfully promoted. The procedures through which crystallization was induced from solution permit reduplication of the process. The only limiting consideration which may have to be resolved is related to facility and instrument availability and adaptation.

HNS-I, Lot 66-48
Mag. ~ 50X

HNS-I, Lot 66-48
Mag. ~ 125X

HNS-II, Lot 66-47
Mag. ~ 50X

HNS-II, Lot 66 47
Mag. ~ 125X

Fig. 3. Chemtronics HNS I, HNS II

HNS (5 hour run)
Mag. $\sim 50X$

HNS (5 hour run)
Mag. $\sim 125X$

HNS (6.5 hour run)
Mag. $\sim 50X$

HNS (6.5 hour run)
Mag. $\sim 125X$

Fig. 4. Photomicrographs of Two HNS Crystallization Crops

Before Blending ($\rho = 0.37$)
Mag. $\sim 50X$

Before Blending ($\rho = 0.37$)
Mag. $\sim 125X$

After Blending ($\rho = 0.51$)
Mag. $\sim 50X$

After Blending ($\rho = 0.51$)
Mag. $\sim 125X$

Fig. 5. HNS 24-2 Before and After Crumbling in Blender

Before Blending ($\rho = 0.38$)
Mag. $\sim 50X$

Before Blending ($\rho = 0.38$)
Mag. $\sim 125X$

After Blending ($\rho = 0.50$)
Mag. $\sim 50X$

After Blending ($\rho = 0.50$)
Mag. $\sim 125X$

Fig. 6. HNS (7-HNS/DMF) Before and After Blender Treatment

3 HNS/DMF, 6% Seed
($\rho = 0.22$) Mag. $\sim 50X$

3 HNS/DMF, 6% Seed
($\rho = 0.22$) Mag. $\sim 125X$

4 HNS/DMF, Unseeded
($\rho = 0.15$) Mag. $\sim 50X$

4 HNS/DMF, Unseeded
($\rho = 0.15$) Mag. $\sim 125X$

Fig. 7. Photomicrograph of HNS Crops from Seeded and Unseeded Solutions

Before Blending ($\rho = 0.51$)
Mag. $\sim 50X$

Before Blending ($\rho = 0.51$)
Mag. $\sim 125X$

After Blending ($\rho = 0.71$)
Mag. $\sim 50X$

After Blending ($\rho = 0.71$)
Mag. $\sim 125X$

Fig. 8. 20 HNS/DMF Crop without Agitation (20 hour cooling period, before and after blending)

13 HNS/DMF, Unseeded
($\rho = 0.45$) Mag. $\sim 50X$

13 HNS/DMF, Unseeded
($\rho = 0.45$) Mag. $\sim 125X$

14 HNS/DMF, 6% Seed
($\rho = 0.46$) Mag. $\sim 50X$

14 HNS/DMF, 6% Seed
($\rho = 0.46$) Mag. $\sim 125X$

Fig. 9. Seeded and Unseeded HNS Crop (Cyclic Technique)

Before Blending ($\rho = 0.48$)
Mag. $\sim 50X$

Before Blending ($\rho = 0.48$)
Mag. $\sim 125X$

After Blending ($\rho = 0.71$)
Mag. $\sim 50X$

After Blending ($\rho = 0.71$)
Mag. $\sim 125X$

Fig. 10. 21 HNS/DMF Crop (Cyclic Technique) Before and After Blending

Before Blending ($\rho = 0.51$)
Mag. $\sim 50X$

Before Blending ($\rho = 0.51$)
Mag. $\sim 125X$

After Blending ($\rho = 0.65$)
Mag. $\sim 50X$

After Blending ($\rho = 0.65$)
Mag. $\sim 125X$

Fig. 11. 19 HNS/DMF Crop from Acetonitrile Treated Solution (Before and After Blending)

Table III. Sample Analysis of HNS-II

Physical/Chemical Requirements (HNS Specification WS-5003F)				16 HNS/DMF	7 HNS/DMF	HNS 24-2	5156-137-01	5157-137-01	5163-137-01	5163-137-02	5171-137-01	5175-137-01	5178-137-01
Requirement	Procedure	Value											
Melting Point	4.5.1.1			318	319	319	318	320	319	318	317	320	320
Melting Range	4.5.1.1												
Vac. Stab.	4.5.1.2												
(a)	mz/g	20 min	0.6 max										
(b)	mz/g	140 min	0.6 max										
Surface Moisture	4.5.1.3		0.05 max	0.006	0.02	0.02	0.001	0.001		0.008	0.008	0.013	0.02
Water Soluble	4.5.1.4		0.05 max	0.02	0.03	0.02	0.098	0.006				0.01	0.003
Insoluble Material	4.5.1.5.2		0.03 max	0.06	0.03	0.02	0.035	0.006		0.02	0.008	0.009	0.02
Bulk Density	4.5.1.6		0.45 min	0.20	0.38	0.37	0.20	0.23	0.35				0.40
Bulk Density*				0.46	0.50	0.51				0.66	0.39	0.66	0.60

*These numbers designate bulk densities after blender treatment.