MHSMP-76-5P

The Content Effect of Water in N,N-Dimethylformamide on the Recrystallization of HNS

G. L. Clink

DEVELOPMENT DIVISION

OCTOBER - DECEMBER 1975

Normal Process Development
Endeavor No. 107

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 647
AMARILLO, TEXAS 79177
806-335-1581

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

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ABSTRACT

The water content of technical grade DMF, above which the total dissolution of HNS for recrystallization purposes cannot be effected, has been determined at 104 C. A rapid, acceptably accurate NMR method for the analysis (certification) of the water content of technical grade DMF has been developed.

DISCUSSION

The presence of water in N,N-dimethylformamide (DMF) above relatively low, yet previously undetermined compositional levels, is known to be retardant toward the dissolution of hexanitrostilbene (HNS) in the solvent during the recrystallization/purification process.

Duplicating actual process recrystallization practice, the weight percent content of water in DMF(*1*) was varied from less than 0.007 up to 2.53%, and the appropriate amounts of HNS (6.5 g/100 mℓ) were mixed in the various DMF/HOH solutions. The several mixtures were heated from ambient (21 C) to 104 C (220 F) and held at the upper temperature for 25 minutes. During the heating cycle, the mixtures were kept agitated by means of Teflon coated stirring bars. The use of transparent conical vials (Pyrex) allowed the determination of total solubility to be made visually. The results are presented in Table I.

From the solubility data obtained in this study, it appears that under process conditions of 104 C and 6.5 g/100 mℓ, a maximum water content of 0.50% is allowable.

NMR analysis of DMF has shown itself to be a rapid and acceptable method to certify the technical grade DMF for use in its recrystallization and purification. The DMF sample is run neat (no added solvent) and with no need for adding an internal lock material, as the formyl proton which appears at 800 Hz (TMS) is well down field of the N,N-dimethyl doublet ($\sim$ 280 Hz), and is used as the internal lock. The HOH peak, depending upon its concentration (and degree of hydrogen bonding), appears between 335 - 310 Hz (TMS). Water content data are obtained through HOH and N,N-dimethyl peak integration, with HOH content determined by normalizing the HOH/DMF content. Sampling time for one sample is 20 to 30 minutes, with time/sample decreased appreciably with an increase in the number of samples.

For process control purposes, the accuracy-sample turnaround time is quite acceptable. NMR analysis results for various DMF/HOH samples, most of which were used in the first part of this study, are presented in Table II.

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(1) Burdick and Jackson, Water Content < 0.007%.

Table I. HNS Solubility in Various DMF/HOH Solutions

104 C

DMF (mℓ, ± 0.05)	HOH (Wt. %)	HNS Added (mg)	HNS Added (g/100 mℓ)	Complete Solubility*
3.0	0.007	195	6.5	Yes
3.0	0.36	193	6.5	Yes
3.0	0.44	193	6.5	Yes
3.0	0.56	196	6.5	No (∿ 95% dissolved)
3.0	0.91	195	6.5	No
3.0	1.01	197	6.5	No
3.0	1.18	196	6.5	No
3.0	1.40	194	6.5	No
3.0	2.53	196	6.5	No

**25 minute digestion, with stirring, at 104 C.*

Table II. NMR Analysis of DMF/HOH Solutions

Water Content				
Actual (Wt. %)	NMR Analysis (Wt. %)			Method
2.53	2.4	2.4	2.5	Peak Integration
1.40	1.3	1.4	1.4	Peak Integration
1.18	1.2	1.2	1.2	Peak Integration
1.01	1.0	1.0	0.9	Peak Integration
0.91	0.9	0.9	0.9	Peak Integration
0.56	0.6	0.6	0.5	Peak Integration
0.44	0.4	0.5	0.4	Peak Integration
0.36	0.3	0.4	0.4	Peak Integration
0.26	0.3	0.2	0.2	Peak Height Comparison*
0.18	0.2	0.1	0.2	Peak Height Comparison*

**Due to the higher than normal NMR sample viscosity of DMF by not adding a solvent to the system, the spinning side bands interfere with peak integration in the range of 0.02 - 0.3% and below.*

COMMENTS

In the past several weeks, three recrystallization processes failed to dissolve HNS completely. NMR analysis of the DMF or the DMF/HNS reaction mixtures showed water contents in the range 1 to 5%. As this has been shown to be a process retardant, and the method of analysis is acceptably accurate and rapid, it would seem feasible and advisable to certify each lot (barrel) of DMF for water content prior to use in processing.