

AD-A149 935

SCALE-UP OF VANADIUM TRINEODECANOATE(U) NAVAL SURFACE
WEAPONS CENTER SILVER SPRING MD R E FARNCOMB 01 FEB 84
NSWC/RR-84-150

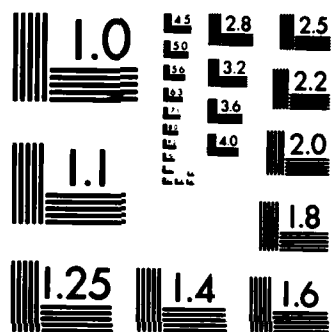
1/1

UNCLASSIFIED

F/G 11/9

NL

						END							
						FILED							
						DTIC							



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A149 935

NSWC/TR 84-150

UIC FILE COPY

SCALE-UP OF VANADIUM TRINEODECANOATE

BY ROBERT E. FARNCOMB

RESEARCH AND TECHNOLOGY DEPARTMENT

1 FEBRUARY 1984

Approved for public release, distribution unlimited

DTIC
ELECTE
S FEB 6 1985 D
A



NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

85 01 28 159

909/

UNCLASSIFIED

CLASSIFICATION OF THIS PAGE (When Data Entered)

A 149 935

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC TR 84-150	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SCALE-UP OF VANADIUM TRINEODECANOATE		5. TYPE OF REPORT & PERIOD COVERED Final Report January 1980 - January 1984
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert E. Farncomb	8. CONTRACT OR GRANT NUMBER(s) N6830579WR90217 N6830582WR20143	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center (Code R11) White Oak Silver Spring, Maryland 20910	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Army-funded	
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE 1 February 1984
		13. NUMBER OF PAGES 47
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Vanadium Trineodecanoate Solutions, Vanadium Promoter, Promoter for Polyester Resins.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Vanadium trineodecanoate (VND) is one of the promoter components of the fiberglass-reinforced plastic required for the Marine Corps' flexible membrane surfacing for soils. A synthesis procedure for VND, developed by the Naval Weapons Center, China Lake, was scaled up by a factor of 20 to produce 15-kg batches of the material. Since the VND-product solution is incompatible with the by-product hydrochloric acid, it is necessary to complete the reaction within 6 hours.		

DD FORM 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

after the addition of the neodecanoic acid. The minimum cost for VND solution prepared at the 15-kg batch level is \$25/kg. It is calculated that a process based on a continuous flow reactor with a capacity of 10 kg/hr could produce the VND solution at a cost of \$10/kg. In a much larger continuous reactor, the price for VND would drop to about \$4/kg.

Originator furnished Keywords include:

32 1473 (F10110)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

FOREWORD

This report describes the development of procedures for the scaled-up synthesis of vanadium trineodecanoate (VND). This compound is one of the promoter components for the on-site preparation of flexible membrane surfacing for soil used by the Marine Corps. Fifteen kilogram batches have been successfully prepared and a continuous flow reactor is proposed for larger scale production. This work was supported by contracts, N6830579WR90217 and N6830582WRZ0143.

The author gratefully acknowledges M. Houser and K. Mueller of NSWC and M. Hironaka of the Civil Engineering Laboratory for assistance in the preparation of this report.

H. S. Haiss

H. S. HAISS, Acting Head
Energetic Materials Division

Accession For	
NTIS GRA&I	☒
ERIC TAB	☐
Unannounced	☐
Justification	☐
Distribution/	
Availability Codes	☐
Avail and/or	☐
Dist	Special
A-1	



CONTENTS

	<u>Page</u>
INTRODUCTION.....	1
SCALE-UP TESTS.....	2
1. PREPARATION OF VND IN 3-kg BATCHES.....	2
2. PREPARATION OF VND IN 15-kg BATCHES.....	3
3. PREPARATION OF VND IN 150-kg BATCHES.....	4
4. RECOMMENDED VND SYNTHESIS PROCEDURE.....	5
MATERIAL AND STORAGE REQUIREMENTS FOR VND SOLUTIONS.....	6
ENVIRONMENTAL CONSIDERATIONS OF VND PRODUCTION.....	6
MATERIAL SOURCES AND COSTS.....	7
CONCLUSIONS.....	7
RECOMMENDATIONS.....	7
REFERENCES.....	21
APPENDIX A - COMPATIBILITY OF VND WITH HYDROCHLORIC ACID.....	A-1
APPENDIX B - DETAILED RECOMMENDED PROCEDURES FOR MAKING VND SOLUTIONS IN 15-kg BATCHES.....	B-1
APPENDIX C - DETAILED RECOMMENDED BATCH PROCEDURE FOR MAKING VND SOLUTIONS IN 15-kg BATCHES.....	C-1
APPENDIX D - MEASUREMENT OF GEL TIME AND TIME AT MAXIMUM TEMPERATURE.....	D-1
APPENDIX E - MATERIAL SAFETY DATA SHEET.....	E-1

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	APPARATUS FOR MAKING VND IN 3-kg BATCHES.....	8
2	APPARATUS FOR 15-kg VND BATCHES.....	9
3	EQUIPMENT FOR 150-kg VND BATCHES.....	10
4	CONTINUOUS VND FLOW REACTOR.....	11
5	EQUIPMENT FOR MAKING VND IN 15-kg BATCHS.....	12

TABLES

<u>Table</u>		<u>Page</u>
1	SUMMARY OF VND BATCHES.....	13
2	DISTILLATION CUTS IN 15-kg VND BATCH.....	17
3	STORAGE OF VND SOLUTIONS.....	18
4	COST OF RAW MATERIALS FOR VND.....	19
B-1	EQUIPMENT FOR MAKING VND IN 3-kg BATCHES.....	B-3
C-1	EQUIPMENT FOR MAKING VND IN 15-kg BATCHES.....	C-2
C-2	SUPPLIERS OF EQUIPMENT FOR MAKING VND.....	C-3

INTRODUCTION

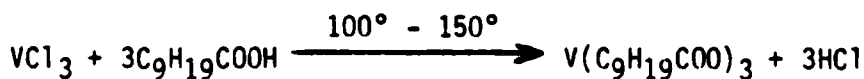
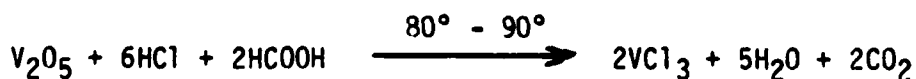
Vanadium trineodecanoate (VND) is one of the promoter components of the fiberglass-reinforced plastic composite material required for the Marine Corps flexible membrane surfacing for soils. This composite material was developed by the Naval Civil Engineering Laboratory, Port Hueneme, CA. It requires the following steps for application:

- a. soil preparation
- b. spreading of fiberglass matting
- c. spraying of polyester resin, catalyst, and promoter solution (100:1.1:0.4) on the fiberglass, using three metering pumps
- d. applying extra resin and fiberglass as needed

The catalyst for the system is cumene hydroperoxide and the promoter is a solution of N,N-dimethyl-p-toluidine and VND.

The flexible membrane surface is applied to soil surfaces to control erosion and to improve the possibilities for amphibious landings and vehicular and aircraft traffic (reference 1).

The Naval Weapons Center (NWC), China Lake, CA, developed a procedure for the preparation of VND (reference 2). The procedure has two steps, consisting of the reduction of pentavalent vanadium to trivalent vanadium and the formation of the metal salt. The chemical equations are shown below:



In the first step, the vanadium pentoxide is dissolved in concentrated hydrochloric acid and reduced by formic acid to vanadium trichloride at 80° - 90°C. During this reduction the color of the reaction mixture changes from brown to deep blue. In the second step, VND is formed by reacting neodecanoic acid (NDA) with vanadium trichloride, in the presence of

triethylphosphate. The water and the byproduct hydrochloric acid are removed by azeotropic distillation with xylene. The reactants and their molar ratios, as well as the solvents used in the NWC procedure, are listed below:

Ingredient	Amount	Moles	Moles/Mole V_2O_5
Vanadium pentoxide	54 g	0.30	1.00
Hydrochloric acid (36%)	540 ml	5.31	17.88
Formic acid (90%)	42 g	0.82	2.67
Paraformaldehyde	6 g	0.20	0.67
Xylene	250 ml	-	-
Triethylphosphate	192 g	-	-
Neodecanoic acid	330 g	1.92	6.45

The reaction yields 750 g of a deep blue solution of the following composition:

Vanadium trineodecanoate	45%
Triethylphosphate	25%
Xylene	27%
Neodecanoic acid	3%
Water and chloride ion	<0.5%

A potential problem in the scaled-up preparation of VND is the by-product hydrochloric acid, which causes decomposition of VND. See Appendix A for further information on this problem.

SCALE-UP TESTS

SCALED-UP PREPARATION OF VND SOLUTIONS

Experiments to prepare VND solutions started with a repeat of the NWC procedure. Then a series of intermediate-size scaled-up reactions were run, primarily at the 3 and 15-kg levels. Three batches were run at the 150-kg level. Optimized procedures yielding an acceptable product at the 3- and 15-kg batch levels are described below and in more detail in Appendices B and C, respectively. The 150-kg batches did not yield an acceptable product. Table 1 gives a summary of the results of all VND batches run under this program.

Preparation of VND in 3-kg Batches

The equipment used to prepare 3-kg batches of VND solution consisted of a five-liter, three-necked glass flask in an electric heating mantle, equipped with stirrer, distillation head, and distillation set-up as shown in Figure 1. The reaction and distillation in the equipment were carried out with a nitrogen purge of 500 ml/min.

The five-liter glass reaction flask was charged with 1800 ml of 37% hydrochloric acid, 168 g of 90% formic acid, and 1000 ml xylene. After

starting the agitator, 216 g vanadium pentoxide and 24 g paraformaldehyde were added. Then the heating mantle was turned on to maintain about 90°C in the reaction flask for a period of three hours, during which the color of the reaction mixture changed from brown to deep blue. After this reaction period, 768 g triethylphosphate were added to the reaction mixture and the temperature controller setting for the heating mantle increased to 125°C. This started an azeotropic distillation of aqueous hydrochloric acid and xylene. The two distillate phases were separated, the xylene returned to the distillation flask, and the aqueous phase withdrawn automatically by a liquid level controller. After the distillation had produced 1300 ml of aqueous distillate phase, the temperature controller setting for the heating mantle was increased to 155°C, and 1452 g neodecanoic acid added to the reaction flask with a tubing pump. The azeotropic distillation was then continued until the temperature in the reaction flask reached 155°C, which yielded an additional 560 ml aqueous distillate phase. After the distillation residue (VND solution) had cooled to 20°C, 25 g Celite were added and the entire mixture poured through a coarse, 600 ml fritted glass Buchner funnel containing a bed of 20 g Celite. The resulting 3.09 kg of clear VND solution had a vanadium content of 3.79% (3.88% theoretical). The gel-time of this solution was 6.3 minutes and 12 minutes with a maximum reaction temperature of 210°C after the addition of 0.4 g promoter solution. See Appendix D for further information on measurement of gel-time and maximum temperature.

Preparation of VND in 15-kg Batches

The equipment used was a 22-liter flask in an electric heating mantle set up as shown in Figure 2. The flask was charged with 9000 ml of 35% hydrochloric acid, 840 g of 90% formic acid, 5000 ml xylene, and the agitator and nitrogen purge started; 1080 g vanadium pentoxide and 120 g paraformaldehyde were then added. The mixture was agitated for 3 hours at 81° - 92°C. During this time, the color changed from brown to deep blue, after which 3840 g triethylphosphate were added. The water and hydrochloric acid were removed by azeotropic distillation with xylene, the xylene returned to the flask, and the aqueous phase removed via a solenoid valve. The solenoid valve was controlled by an electronic conductance liquid level controller*. (See Table 2 for distillation cuts, temperatures of flask and vapors, etc.) A tubing pump was used to add 7200 g neodecanoic acid to the flask and the azeotropic distillation then continued until the flask temperature reached 155°C.

After the VND solution cooled to 20°C, 100 g Celite were added to the flask; the VND solution was then transferred, via a tubing pump, to a 3-liter coarse-fritted glass Buchner funnel which had a 100-gram bed of Celite. Using a second tubing pump, the VND solution was pumped to a 22-liter storage flask. The filtration was completed in less than an hour. The reaction flask, tubing, filter, and pumps were washed with one liter of xylene.

*DynaSense C-7186-00, Electronic Liquid Level Controller, Cole-Parmer Instrument Co., Chicago, Illinois 60648.

The 11.95 kg VND solution was sampled and analyzed as containing 3.80% vanadium, 0.35% chloride, and 0.04% water. The gel-time of this solution was 9.1 minutes, and 11 minutes for maximum temperature of 236°C after addition of 0.4 g promoter solution. The analysis of the 1.8 kg wash solution showed 2.52% vanadium. The gel-time of this solution was 19.5 minutes, and 24 minutes for the maximum temperature of 203°C. These solutions account for 82% of the starting vanadium; the remainder of the vanadium was in the precipitate - a mixture of coarse blue-black solids and blue slime.

A fire occurred in VND batch 67-27 while preparing anhydrous vanadium trichloride. Present in the 22-liter flask at the time of the incident were 5.5 liters xylene, 4224 g triethylphosphate, 2054 g vanadium trichloride, and up to 5 kg water, under nitrogen purge. At the time of the incident, all the excess hydrochloric acid had been removed and about half the water. The most probable cause of the incident is that the agitator stopped, allowing solid and liquid phases to separate. The unstirred material 'bumped'*, ejecting xylene and triethylphosphate out of the flask onto the hot heating mantle. The resulting fire ejected the rest of the flammable material.

Future VND batches will be made using equipment with beaded glass pipe fittings which are rated for 15 psig (Figure 5), thus preventing ejection of reactants if bumping occurs.

Preparation of VND in 150-kg Batches

Details of the 50-gallon glass-lined reactor with 2-inch glass heat exchanger used in this phase of the experiment can be seen in Figure 3. A nitrogen purge of one liter per minute was used during additions and 0.1 liter per minute during reaction and distillation.

Using a 3/8-inch ID Viton tubing pump, 8.4 kg of 90% formic acid, 102.6 kg of 35% hydrochloric acid, and a slurry of 10.8 kg vanadium pentoxide and 1.2 kg paraformaldehyde in 43.0 kg xylene were added to the reactor. The reactor was heated for 3 hours at 80° - 90°C while being agitated, then 38.4 kg triethylphosphate added. In 36 hours of xylene distillation, 108 kg of dilute hydrochloric acid were collected, and the xylene returned to the reactor. During the distillation, the reactor temperature was 100° - 110°C and vapor temperature was 97° - 106°C. The distillation was limited by condenser flooding. This flooding was controlled by a steam controller monitoring the vapor temperature.

The batch was left for 3 weeks** at room temperature. With the reactor temperature at 102°C; 66 kg neodecanoic acid and one liter xylene wash were

*'bumping' is localized superheating leading to unstable distillation.

**Interruption caused by circumstances beyond operator control - jury duty.

then pumped into the reactor. The reactor was heated from 102°C to 149°C with 40 psig steam; the vapor temperature increased from 98° to 100°C. A total of 2.6 kg of 7.6% hydrochloric acid was collected. The remainder of the hydrochloric acid from the reaction of vanadium trichloride with neodecanoic acid was absorbed in the sodium hydroxide scrubber.

The VND solution was cooled to 25°C and filtered in a perforated bowl centrifuge in one hour. The centrifuge bowl was 12 inches in diameter, 6 inches high, and spun at 4000 rpm. The solids were collected in a 30-micron polypropylene filter bag with a 1-cm bed of Celite. The analysis of the VND solution showed values of 2.62% vanadium, 0.24% chloride, and 1.15% water. The gel-time using 0.4 g promoter from this solution was 27 minutes.

Three 150-kg batches were run in this 50-gallon reactor. The incompatibility of the by-product hydrochloric acid resulted in low vanadium concentrations in all three. The analyses of these VND solutions yielded values of 2.6%, 0.1%, and 0.1% vanadium, instead of the expected 4% vanadium.

Large quantities of blue solids remained in the reactor, which were soluble in 50°C hydrochloric acid.

Recommended VND Synthesis Procedure

Vanadium trineodecanoate (VND) is degraded when heated with hydrochloric acid at 90°C for 6 hours.

In a continuous reactor, the VND will be heated with the hydrochloric acid for less than 4 hours. The continuous flow reactor shown in Figure 4 has a capacity of 10 kg of VND solution per hour. The main components of this flow reactor are:

Three metering pumps to add:

1. Xylene
2. 85% vanadium trichloride in hydrochloric acid
3. Solution of neodecanoic acid, triethylphosphate, xylene

A 4-inch glass boiler at 100°C with 0.5 m² heat transfer area, with agitator

A 2-inch glass heat exchanger at 100°C.

A 2-inch glass heat exchanger at 150°C.

Three 2-inch glass heat exchangers to condense vapors

A 2-inch glass heat exchanger to cool product to room temperature.

For each kilogram of VND solution prepared, 22,000 calories of heat need to be transferred and about 60 to 100 liters of vapor condensed.

MATERIAL AND STORAGE REQUIREMENTS FOR VND SOLUTIONS

Construction materials for equipment used in the preparation of trineodecanoate solutions are limited by the nature of boiling xylene and hydrochloric acid. Glass, Teflon^R, and platinum are compatible with this mixture. Neoprene stoppers exposed to the hot vapors swelled and had surface discoloration, but were usable after more than 100 hours exposure. Viton^R tubing exposed to the hot vapors had surface scaling but was useable after 100 hours exposure.

Polyethylene and Viton^R tubing are compatible with the cold solutions encountered in making VND solutions.

VND solutions can be stored in glass and polypropylene bottles under a nitrogen atmosphere. The storage results are listed in Table 3. After one year storage, the gel-time increased 4% and 17% in glass and polypropylene, respectively.

VND solutions should not be in contact with 316 stainless steel or aluminum for more than a month.

Gel-time promoter solutions (50% VND, 50% DMT) stored in a nitrogen atmosphere in full glass bottles changed from 6.4 minutes to 8.3 minutes after one year storage. This is a 30% increase in gel-time. Promoter solutions stored under air in almost-empty bottles were decomposed to a brown solution which had no gelling properties.

VND solutions can be stored in glass and polyethylene bottles under a nitrogen atmosphere; a gallon bottle holds 3.8 kg (8.4 pounds) of VND solution.

ENVIRONMENTAL CONSIDERATIONS OF VND PRODUCTION

During the distillation, a scrubber is needed to remove uncondensed hydrochloric acid. An efficient scrubber was 20% sodium hydroxide solution pumped through a plastic aspirator. In the larger batches, about 20% of the hydrochloric acid was absorbed in the scrubber. A more efficient heat exchanger will reduce the caustic consumption.

The vanadium concentration in the unusable product can be lowered to 0.1% by adding acid. Dilute hydrochloric or sulfuric acid decomposed the VND within 16 hours at room temperature. The vanadium concentration can be lowered by extraction with a liquid ion exchange system. Alamine 336, a (trademark) product of General Mills, is a liquid ion exchanger developed for vanadium extraction. It is a water insoluble tertiary amine dissolved in kerosene. Alamine^R extracts vanadium at pH 1.2-2 and releases it at pH 11-12 (reference 3); the vanadium can then be recovered using standard metallurgical techniques.

The vanadium concentration can also be lowered to 1 ppm (part per million) by treatment with sodium borohydride at pH 9-10 (reference 4).

Appendix E is the Material Safety Data Sheet for the polyester promoter, (OSHA standard form OMB No. 44-R1387).

VND MATERIAL SOURCES AND COSTS

Neodecanoic acid and triethylphosphate are made by one United States manufacturer (reference 5). Both compounds are used in large quantities and will be available for VND manufacture. The other raw materials have at least 5 United States manufacturers (reference 5).

The raw materials cost for VND solutions is \$3.20 per kilogram. See Table 4 for an itemized list with suppliers. VND solutions will cost about \$25 per pound when made in 15-kg batches. This cost is valid using the procedure in Appendix D and already-installed equipment.

CONCLUSIONS

1. VND solutions can be made in 15 to 30-kg batches.
2. VND solutions can be stored over a year in glass or polypropylene bottles under a nitrogen atmosphere.

RECOMMENDATIONS

The continuous reactor outlined in Figure 4 should be investigated because it has the potential of increasing production of VND and reducing the cost of the product.

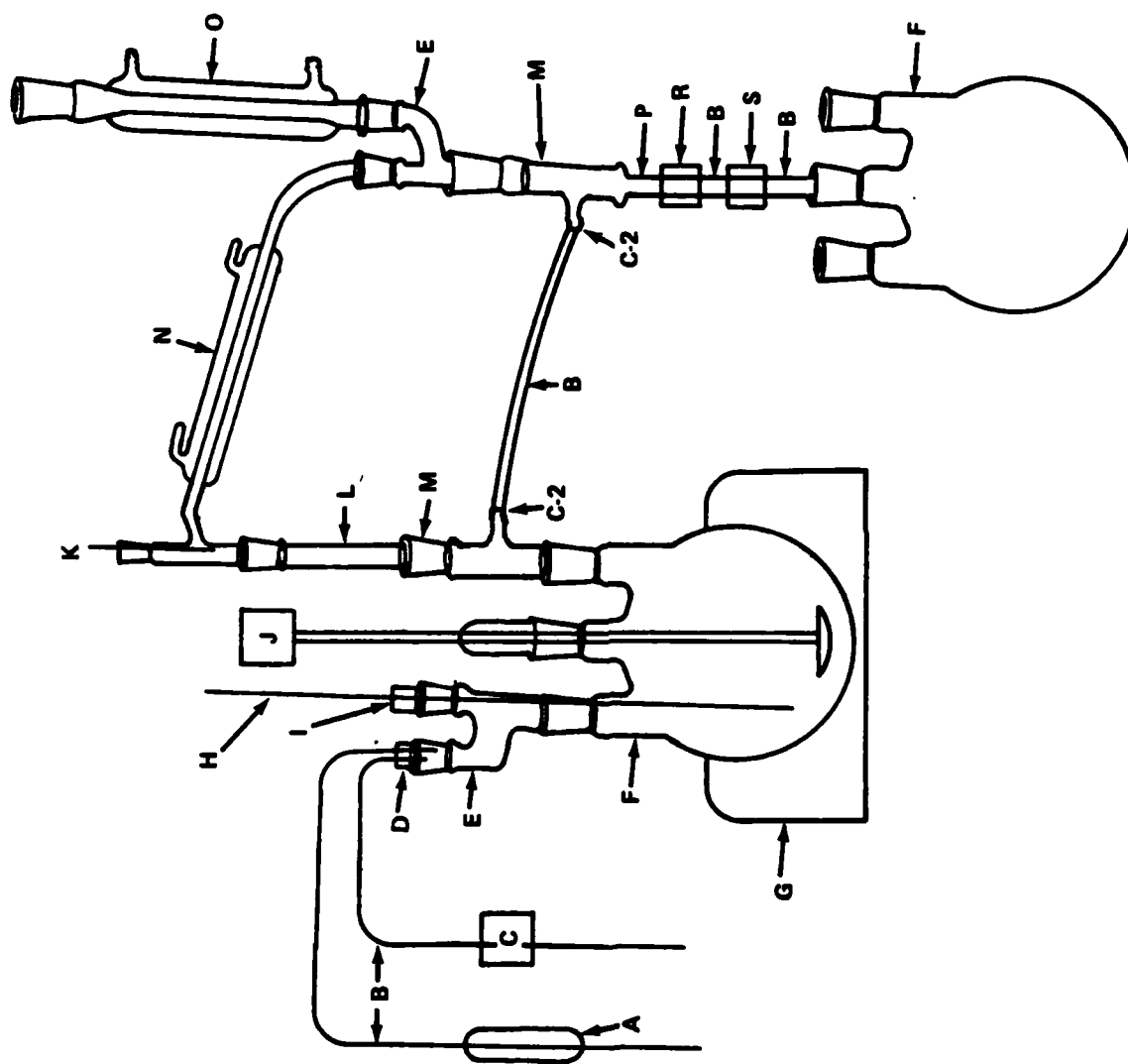


FIGURE 1. APPARATUS FOR MAKING VND IN 3 KG BATCHES
SEE TABLE 5 FOR LISTING

1. THERMOMETER VAPOR
2. AIR POWERED STIRRER
3. FLASK THERMOMETER EQUIPPED WITH THERMO-WATCH TEMPERATURE CONTROLLER
4. 22-LITER FLASK
5. HEATING MANTLE
6. XYLENE-WATER INTERFACE (WATER BOTTOM LAYER)
7. VITON TUBING
8. LEVEL CONTROLLER PROBES
9. TEFLON SOLENOID VALV
10. WATER COLLECTION FLASK

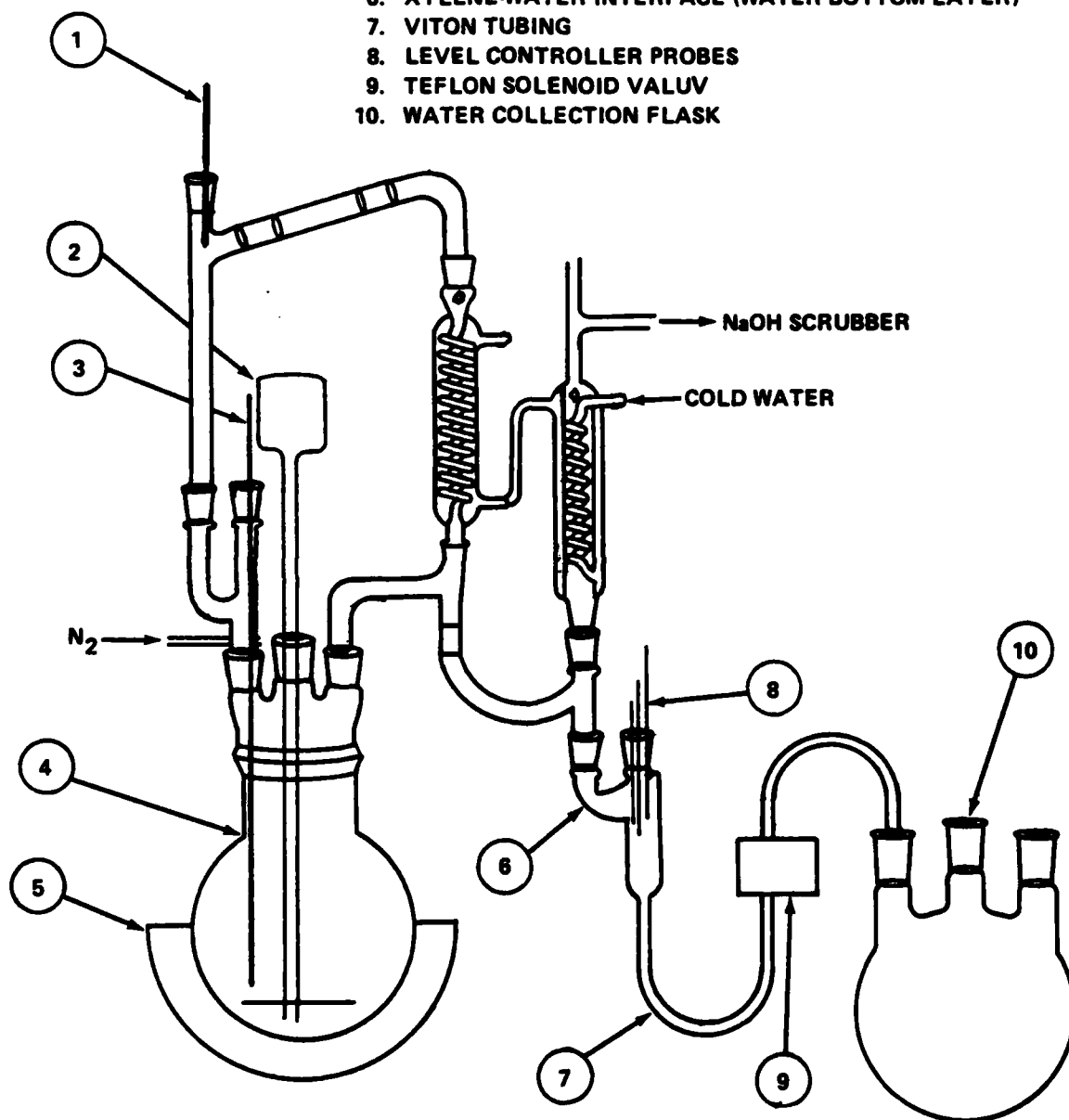


FIGURE 2. APPARATUS FOR 15-KG VND BATCHES

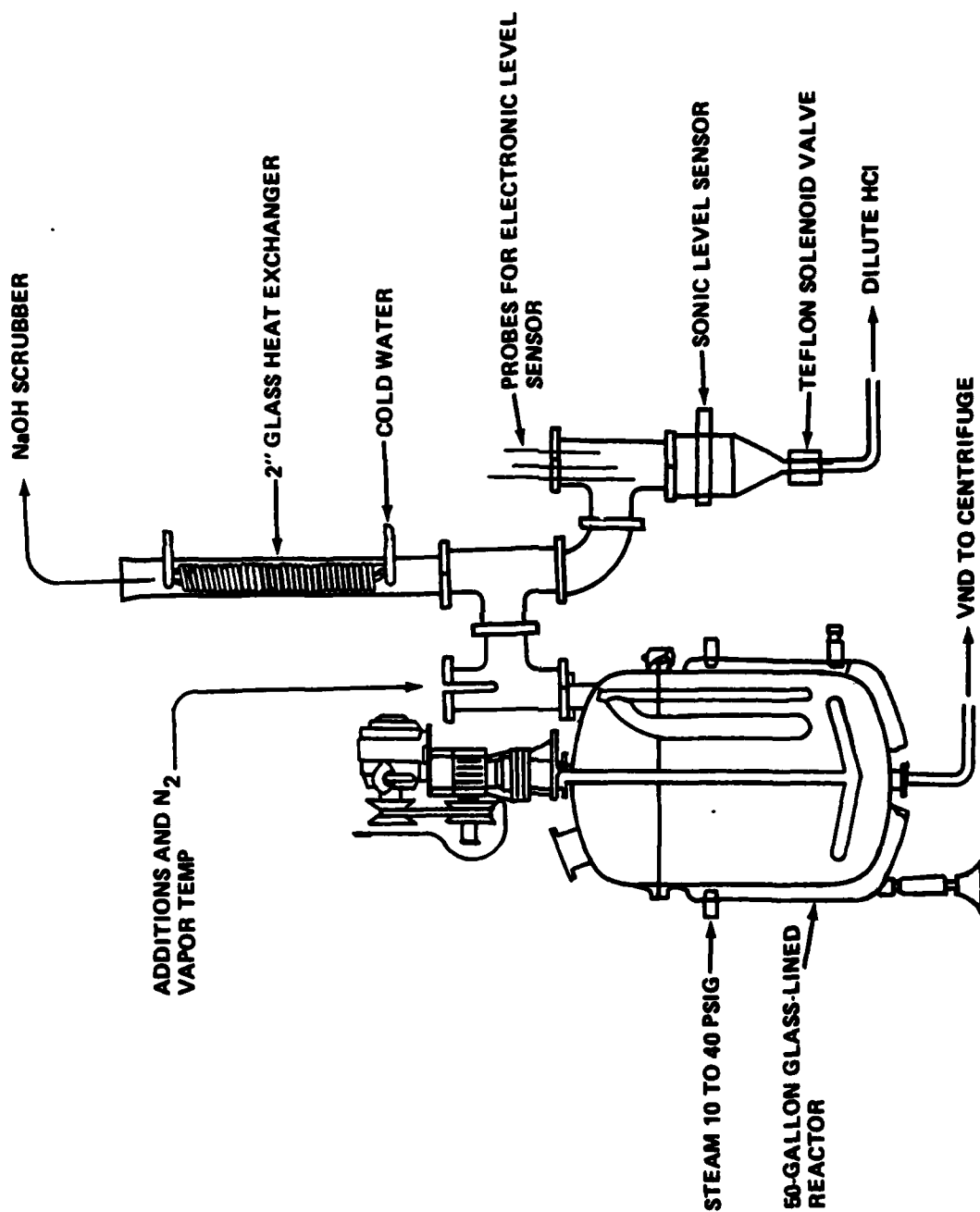


FIGURE 3. EQUIPMENT FOR 150-KG VND BATCHES

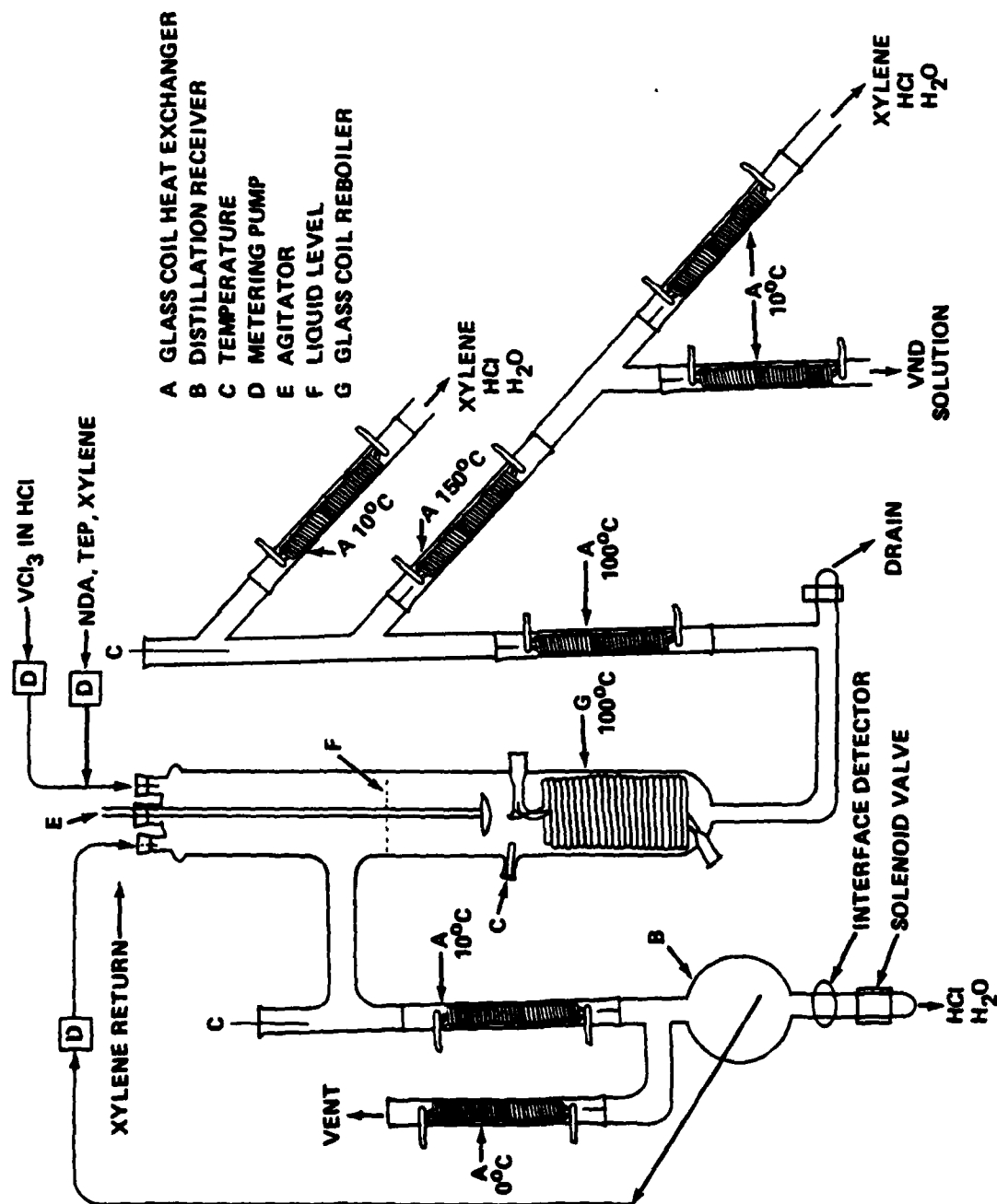


FIGURE 4. CONTINUOUS VND FLOW REACTOR

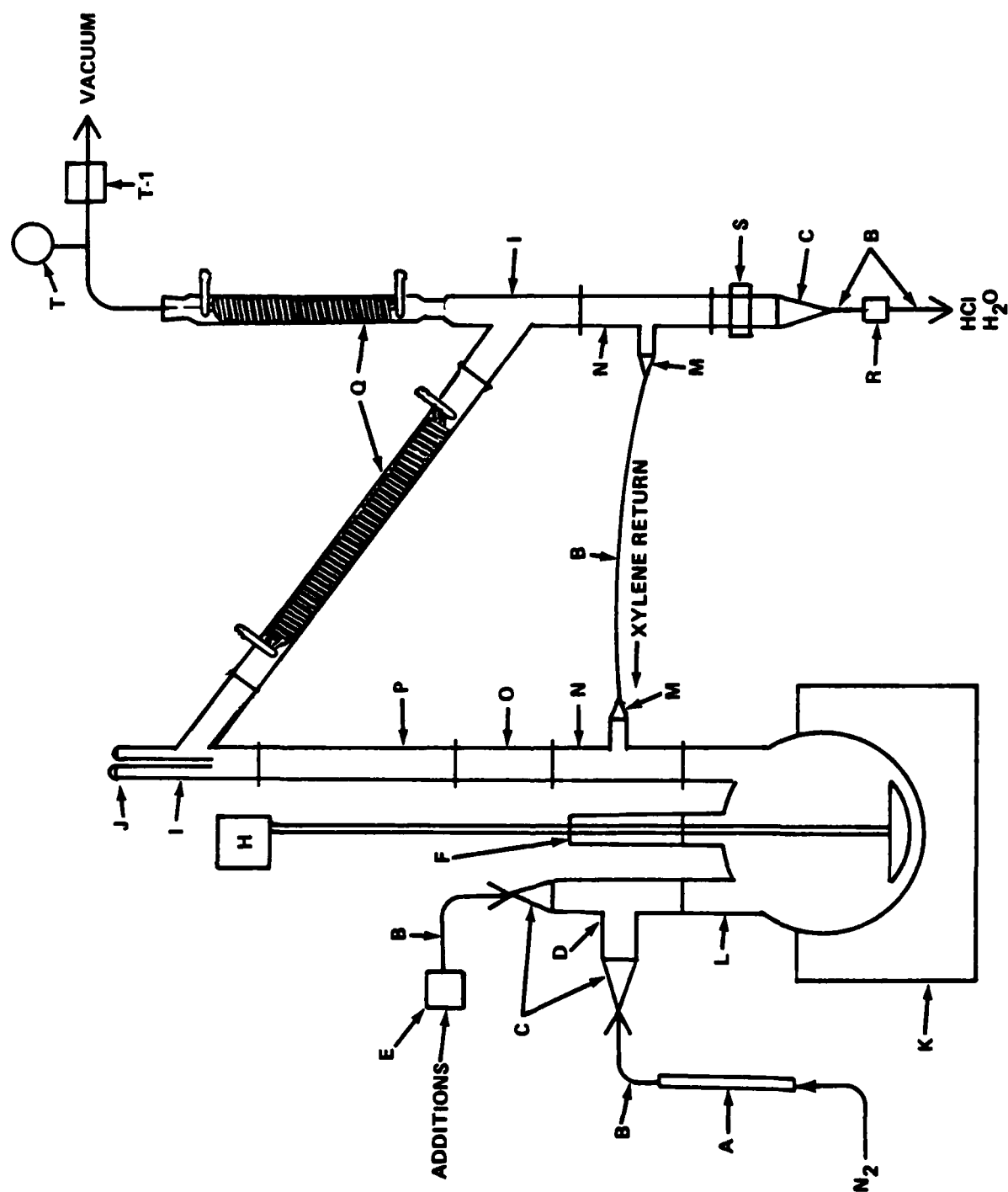


FIGURE 5. EQUIPMENT FOR MAKING VND SOLUTIONS IN 15-KG BATCH
(22-LITER FLASK WITH 1/2-INCH BEADED GLASS FITTINGS)

USE TABLE 6 FOR LISTING

TABLE 1. SUMMARY OF VND BATCHES

Batch	Batch Size ¹	% v2	Theor. % v3	Hours VND Sol'n Heated After Addition of NDA	H ₂ O HCl Removal ¹⁴	Gel Time With 0.4 g promoter min.	Maximum Temp. of Gel °C	Time of Maximum Temp. Min.	Comments
66-1	1	0.2	3	18	A	-	-	-	Large amounts of blue solids
90-2	1	1.9	3	15	A	10.5	190	13	Black brown foam after temperature reached 185°C
90-3	1	-	3	-					Pentrolite W-4088 Water-oil emulsion added - foamed
95-4	1	0.5	3	12	A	40+	-		
1-5	1	2.88	3	6	B	13.8	190	17	
2-6	1	2.6	3	6	B	15.4	145	20	
9-7	3	0.1	4.3	15	B	-	-	-	Brown solution
12-8	3	0.1	4.0	19	B	-	-	-	Brown solution
14-9	3	0.1	4.1	21	B	-	-	-	Brown solution - blue solid
16-10	3	0.1	4.0	-	B	-	-	-	High speed agitation, large N ₂ purge used, black foam
17-11	3	0.27	4.0	24	B	-	-	-	Hot oil bath at 150°C used for heating
20-12	2	0.1	3.4	28	B	-	-	-	Brown solution, blue solids
28-13	2	1.1	5.0	20	B	-	-	-	Heated with hot oil bath, brown solution, coarse black solid

TABLE 1. SUMMARY OF VND BATCHES (CONT)

Batch	Batch Size	% V2	Theor. % V3	Hours VND Soln Heated After Addition of NDA	H ₂ O HCl Removal ⁴	Gel Time With 0.4 g promoter min.	Maximum Temp. of Gel °C	Time of Maximum Temp. Min.	Comments
29-14	2	-	4.0	12	B	-	-	-	Light yellow sol.
30-15	1.5	2.57	3.3	5	B	-	210	21	160°C oil bath, fast agitation, fast N ₂ purge
34-16	3	2.45	2.9	5	B	16.2	201	24	
34-17	3	1.1	2.9	7	B	-	-	-	Large amounts of solids
35-18	3	2.44	2.9	4	B	-	-	-	Add NDA after most of HCl removed
36-19	3	3.05	3.5	5	B	6.3	202	9	No solids in flask
38-20	3	2.28	3.1	3	B	30.3	175	52	
41-21	3	3.85	4.2	6	C	7.1	201	12	
48-22	4	3.50	3.7	3	C	10.0	205	13.4	
49-23	4	3.79	4.0	4	C	6.3	210	12.0	
51-24	20	3.84	4.3	6	C	8.1	210	9.7	22-liter flask
54-25	20	3.79	4.3	6	C	10.5	206	13.5	
64-26	20	3.80	4	4	D	9.1	236	11	0.35% Cl 0.04% H ₂ O
67-27	22	-	-	-	D	-	-	-	Fire occurred during batch
2-28	200	2.62	4	8	D and E	27	188	52	50 gallon reactor left 3 weeks, after about 50% HCl removed.

TABLE 1. SUMMARY OF VND BATCHES (CONT)

Batch	Batch Size	% V2	Theor. % V3	Hours VND Soln Heated After Addition of NDA	H ₂ O HCl Removal ⁴	Gel Time With 0.4 g promoter min.	Maximum Temp. of Gel °C	Time of Maximum Temp. Min.	Comments
4-29	200	0.1	4	8	D and E	-	-	-	The distillation cut before the NDA addition was 13% HCl; 1 hour after the addition of NDA, the precipitated solids stopped the agitator until the temp reached 120°C.
4-30	200	0.1	4	7	D and E	40.1	-	-	Agitator stopped 3 hours after addition of NDA because of solids.
11-31	1	3.75	4.1	-	D	10.1	210	12	VC13 in HCl added to NDA TFP, xylene at 140-150°C
13-32	4	3.80	4.0	-	D	9.2	212	12	Same comments as batch 11-31.
16-33	20	0.1	4.0	-	D	-	-	-	Same comments as batch 11-31.
29-34	25	3.57	4.0	3.5	D	13.8	196	18	Used procedure in Appendix C
30-35	25	2.37	4.0	7.5	D	-	-	-	Black foam, NDA added at 105.
34-36	20	0.1	4.0	4.0	D	-	-	-	Sodium salt of NDA added at 95°C
37-37	20	0.1	-	6	D	-	-	-	Brown foam, NDA add 115°C

TABLE 1. SUMMARY OF VND BATCHES (CONT)

Batch	Batch Size ¹	% V ²	Theor. % V ³	Hours VND Sol'n Heated After Addition of NDA	H ₂ O HCl Removal ⁴	Gel Time With 0.4 g promoter min.	Maximum Temp. of Gel °C	Time of Maximum Temp. Min.	Comments
41-38	20	-	-	-	D	-	-	-	Heating mantle burn-out.
43-39	20	0.1	-	4	D	-	-	13	Blue solids NDA added 115-120°C
46-40	20	3.62	4	3	D	8	208	13	Operated under 10 inches of vacuum
48-41	20	1.06	4	6	D	12.6	218	18	
53-42	20	2.02	4	4	D	-	-	-	

¹Batch size multiples of NMC procedure: 42 g 90% formic acid, 450 ml of hydrochloric acid, 54 g of vanadium pentoxide, 192 g triethylphosphate, 6 g of paraformaldehyde, 250 ml of xylene.

²Vanadium analysis by Galbraith Laboratories Inc., Knoxville, Tennessee 37921.

³Theoretical % vanadium calculated from total weight of solution and the amount of vanadium pentoxide added.

⁴Method for determining the dilute hydrochloric acid xylene interface:

- Visual with manual valve
- Reservoir filled with xylene and replaced with dilute hydrochloric acid.
- Capacitance with Teflon solenoid valve, Thermo-o-Watch made by Instruments for Research and Industry, Cheltenham, PA 19012.
- Electronic with Teflon solenoid valve, Dyna-Sense Electronic Liquid Level Controller, Cat. No. C-7186-00 Cole-Parmer, Chicago, Illinois 60648.
- Ultrasonic with Teflon solenoid valve, Envirotech Sensall Ultrasonic Non-Penetration Liquid Level Sensor, Model 621S with 400C Controller, ordered from Briggs and Cooper Controls, Wilmington, Delaware 19803.

TABLE 2. DISTILLATION CUTS IN 15-KG VND BATCH

Cut No.	Time for Cut hr	Temperature in		H ₂ O, HCl Distillate Grams	HCl in Distillate %
		Flask °C	Vapors °C		
1	12	91	87-88	6335	17.9
2	1/4	91	87	120	0.01
Added Neodecanoic Acid					
3	1 1/4	91-115	87-97	520	20.3
4	1	115	98	340	21.1
5	1 1/2	115-122	98	900	24.6
6	1	122-138	98	500	16.8
7	1 1/4	138-151	98	130	13.9
8	1 1/2	151-155	98	250	11.0

TABLE 3. STORAGE OF VND SOLUTIONS^a

	Polypropylene Bottle	Glass Bottle	316SS in Glass	Aluminum in Glass Bottle
Start of test				
VND gel-time (min) ^b	9.1	9.1	9.1	9.1
Maximum temp of gel (°C)	236	236	236	236
Time of maximum temp (min)	11	11	11	11
Wt. of metal sample (grams)	-	-	8.216	0.9009
Area of metal sample (cm ²)	-	-	8.718	6.397
After 30 days at 20-35°C				
VND gel-time (min) ^b	9.5	9.5	10.1	10.0
Maximum temp. (°C) during gelling	210	210	209	208
Time of maximum temp (min) during gelling	12	11	14	15
% increase in gel-time	4	4	11	10
After 400 days at 20-35°C				
VND gel-time (min) ^b	10.7	9.5	13	15
Maximum temp. (°C)	210	210	210	212
Time of maximum temp. (min)	13	12	18	21
% increase in gel-time	17	4	42	64
Change in weight of metal sample (grams)	c		+0.0043 ^d	-0.0025 ^d
Corrosion rate cm/400 days	-	-	-	0.00014

^aVND solutions with 3.80% vanadium, 0.35% chloride, and 0.04% water. Stored in a nitrogen atmosphere..

^b0.4 grams of promoter solution. The promoter solution is a 50% by weight mixture of vanadium trineodecanoate solution and 50% N,N-dimethyl-p-toluidine (DMT).

^cThe polypropylene bottle was deformed by xylene attack.

^dAfter 400 days at room temperature, both metal samples were coated with a blue slime and had a tarnished surface even after cleaning.

TABLE 4. COST OF RAW MATERIALS FOR VND

Material	\$/kg ^a	Unit of Issue	Kg/100-kg Batch	\$/100-kg Batch
Nitrogen	-	Cylinder	-	10.00
Formic Acid	1.20 ^b	500 lb drum	5.6	6.72
Hydrochloric acid	0.22 ^b	30 gallon drum	68	14.96
Paraformaldehyde	1.40 ^b	12 Kg drum	0.8	1.12
Vanadium Pentoxide	10.50 ^c	100 lb drum	7.2	75.60
Xylene	0.60 ^b	55 gallon drum	28	17.20
Triethyl- phosphate	3.00 ^d	55 gallon drum	25.6	76.80
Neodecanoic Acid	1.99 ^e	55 gallon drum	44.0	87.56
Celite	0.70 ^b	100 lb bag	3	2.10
Other	-	-	-	27.94
				<u>320.00</u>

or \$3.20/kg

^aPrice December 1983^bTilley Chemical Company

Baltimore, MD 21220 (301)574-4500

^cUnion Carbide Metals Division

Pittsburgh, PA 15205 (800)248-6272

^dEastman Kodak Company

Rochester, NY 14650 (716)254-1300

^eExxon Chemical Company

P.O. Box 3272

Houston, TX 77001 (800)231-6633

REFERENCES

1. M. C. Hironaka, "Improved Chemicals for Fiberglass-Reinforced Plastic Soil Surfacing--Field Evaluation," TN-1527, Civil Engineering Laboratory, Port Hueneme, California, September 1978.
2. A. L. Woodman, R. A. Henry, A. Adicoff, D. Fine, "Vanadium Trineodecanoate Promoter for Fiberglass-Polyester Soil Surfacing," NWC/TP 6184, Naval Weapons Center, California, June 1980.
3. D. W. Agers, J. L. Drobnick, C. J. Lweis, "The Recovery of Vanadium from Acidic Solutions by Liquid Ion Exchanger," General Mills Chemicals Inc., Minneapolis, Minnesota 55435.
4. M. M. Cook, J. A. Lander, "Sodium Borohydride Controls Heavy Metal Discharge," Pollution Engineering, December 1981.
5. R. G. Muller (Director), "1979 Directory of Chemical Producers in United States of America," SRI International, Menlo Park, California 94025, 1979.

APPENDIX A

COMPATIBILITY OF VND WITH HYDROCHLORIC ACID

When VND solutions decompose, the deep blue color changes to brown, solids form, and the gel-time changes from 7-10 min to over 40 min. VND solutions were heated at 90°C to 100°C with various amounts of 5 to 30% hydrochloric acid. In all tests, the solution decomposed in 6 to 8 hours of heating. Thus it is necessary to complete the removal of hydrochloric acid within 6 hours after the addition of NDA.

REMOVAL OF HYDROCHLORIC ACID

The excess and by-product hydrochloric acid is removed from vanadium trichloride and VND solutions by azeotropic distillation with xylene. Less than 20% of the distillate is the aqueous phase. At the start of this distillation there are two phases, the blue aqueous vanadium trichloride phase and the top xylene triethylphosphate phase. Thus, good agitation is required to avoid bumping*. If agitation stops, restarting causes overpressurization of system and flooding of the condenser. At start of the distillation the VND solution is at 90°C. The distillation is continued until the aqueous phase of the distillate is about 3-5% hydrochloric acid. The neodecanoic acid is added, and the distillation is complete when the VND solution is heated to 150°C. If NDA is added when too much hydrochloric acid is present, black foamy solids form by acid attacking VND. If added when too little hydrochloric acid is present, the NDA precipitates the vanadium trichloride, forming blue solids. See Table 2 for typical distillation cut details. The addition of acid-stable emulsifying agents caused excessive foaming and is not recommended.

The removal of the dilute hydrochloric acid with the xylene azeotropic distillation was automated. The condensed xylene was returned to the reactor and the lower insoluble aqueous phase was removed through a Teflon® solenoid valve. Three types of xylene-water interface sensors were tested for controlling the solenoid valve. See Table 1 for batch tested.

*bumping is localized superheating leading to unstable distillation.

The Thermo-O-Watch capacitance level sensor controlled the interface in a 10mm glass tube. This unit works by detection of the difference in electrical capacitance in the xylene and the aqueous phase. This sensor worked well with 36 to 5% hydrochloric acid. It required frequent adjustments with lower concentrations.

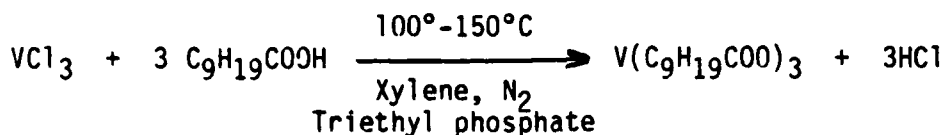
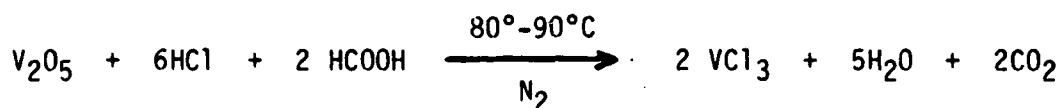
The Dyna-sense electronic liquid level controller works by measurements of the conductance between platinum tipped glass probes. This sensor worked very well with all concentrations of hydrochloric acid. The probes were mounted in a glass tee with a neoprene stopper.

The Sensall ultrasonic liquid level sensor worked very well. This sensor was clamped on the outside of the 2 inch glass pipe. This unit works by detecting different transmittance of an ultrasonic signal in xylene and in the aqueous phase.

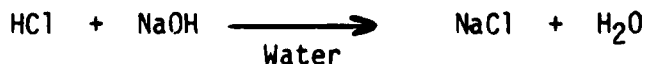
The ultrasonic sensor is the recommended controller. It works with all concentrations of hydrochloric acid and does not require entry into the piping.

APPENDIX B

DETAILED RECOMMENDED PROCEDURE FOR MAKING VND SOLUTIONS IN 3-KG BATCHES



By-product HCl not condensed



Vanadium trineodecanoate (VND) solution with 4% vanadium can be made in 3-kg batches with this procedure. The equipment illustrated in Figure 3 and listed in Table 5 consists of a 5-liter, three-neck flask with 29/42 standard taper joints. A spring clamp and copper wire keep each joint together.

ASSEMBLY OF EQUIPMENT

Reasonable substitution of equipment is acceptable.

- A-1 Put 5-liter flask in heating mantle and clamp in place.
- A-2 Assemble equipment as in Figure 1.
- A-3 Install thermocouple in the flask's thermowell and connect to the Love controller - digital thermometer.
- A-4 Plug the variable transformers into the controller. Plug heating mantle into the transformers.
- A-5 Connect sonic level sensor and connect to controller. Plug solenoid valve into the controller.

- 4-6 Add the three sink-float standards to measure specific gravity (spgr) of the hydrochloric acid distillate. When the spgr is below the value the standard will sink.

<u>SpGr</u>	<u>% HCl to Float Standard</u>
1.02	3
1.03	6
1.05	10

Preparation of VND in 3-Kg Batches

- B-1 Remove addition tee from 5-liter reaction flask and add:
 252 grams of formic acid (90%)
 2700 ml of hydrochloric acid (36%)
 36 grams of paraformaldehyde
- B-2 Turn on water to agitator bearing and turn on agitator
- B-3 Slowly add 325 grams of vanadium pentoxide (V_2O_5) to the 5-liter flask.
- B-4 Add 1200 ml xylene to the 5-liter flask.
- B-5 Clamp addition-tee on the flask.
- B-6 Turn on nitrogen purge at setting #35 (500 ml/min).
- B-7 Turn on condenser water.
- B-8 Turn on temperature controller and set for 85°C. Turn on and set transformer for 70 volts.
- B-9 Agitate 5-liter flask for at least 3 hours at 80°-90°C.
- B-10 Change temperature controller's set point to 110°C. (NOTE: agitation rate and set point should be changed to maintain rapid distillation without foaming. Reduce nitrogen purge to 100 ml/min (setting #10)).
- B-11 Turn on liquid level sensor controller and collect dilute hydrochloric acid distillate.
- B-12 Add 1152 grams triethylphosphate (TEP) to the 2-liter addition flask.
- B-13 As dilute hydrochloric acid is distilled, slowly pump the TEP into the 5-liter reaction flask. Keep total volume under the original 4.5 liters.
- B-14 Add 1992 grams prime-grade neodecanoic acid to a 5-liter addition flask.
- B-15 When distillate is less than 3% hydrochloric acid:
 -Add the neodecanoate acid with the tubing pump,
 -Set temperature controller for 150°C,
 -Set transformers to 100-110 volts.
- B-16 Continue distillation until the temperature of the distillation flask is 150°C and the distillate contains no water.
- B-17 Turn off transformers and cool product to room temperature.
- B-18 Remove addition-tee and add 100 grams celite.

- B-19 Assemble VND filtration system. The components are:
1. Three liter coarse glass Buchner funnel.
 2. #12 Neoprene stopper.
 3. Four liter filtering flask.
 4. Connect and turn on water aspirator.
- B-20 Mix 100 grams of celite with 100 ml of xylene and add to the 3-liter coarse-fritted glass Buchner funnel.
- B-21 Filter by pouring the VND solution into the 3-liter Buchner funnel.
- B-22 Add 200 ml xylene to the reaction flask, agitate and filter wash solution as in B-21 into a 3-liter bottle.
- B-23 Weigh filtrates and send samples of VND solution and xylene wash for vanadium, water, and chloride analysis to:
- Galbraith Laboratory
PO Box 4187
Knoxville, TN 37921
(615)546-1335
- B-24 Calculate and add the amount of xylene wash and xylene needed to make a 4.0% vanadium solution.
- B-25 Run gel time and time to maximum temperature.
- B-26 Reaction flask can be cleaned with warm dilute hydrochloric acid collected in step B-11.

Table B-1. EQUIPMENT FOR MAKING VND IN 3-KG BATCHES

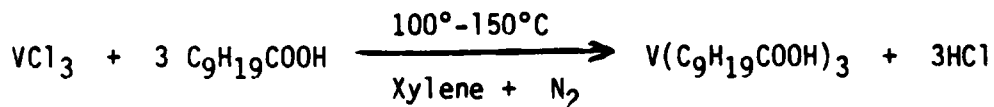
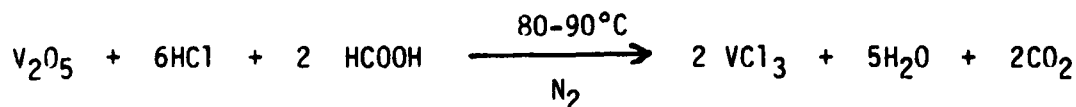
Item (See Figure 1)	Supplier (See Table 7)	Catalog #	Item Name
A	1	C-3202-20	Shielded flow meter size #2
B	1	C-6406-74	Teflon 3/8 inch FEP tubing
C	1	K-7553-10	Tubing pump 1 to 100 RPM
C-1	1	K-7018-20	Pump head
C-2	1	K-6412-48	Viton tubing
D	11	14-141H	Neoprene stopper size 6 1/2
E	2	5055-15	Claisen adapter
F	2	6947-64	5000-ml, three 29/42 T neck flask
G	2	12053-25	Electric heating mantle
G-1	2	12081	Powerstat variable electric transformer
H	24	6500-05	Thermometer well
H-1	11	13-280	Thermometer 308 mm immersion
H-2	7	1518-52-9	Type K thermocouple
H-3	7	149-786	Love controller
I	4	K150750-343	Adapter
J	1	K-4685-00	Heavy duty air driven stirrer
J-1	11	14-513-65B	Glass stirrer with Teflon paddle
J-2	11	14-513-60A	Jacketed bearing

Table B-1. EQUIPMENT FOR MAKING VND IN 3-KG BATCHES (CONT)

Item (See Figure 1)	Supplier (See Table 7)	Catalog #	Item Name
K	11	15-002C	Thermometer
L	2	5035-15	Straight adapter
M	2	5265-15	Gas inlet adapter
N		6608-22	Distilling head
O	2	5998-64	Condenser
P	2	7565-23	Full length joint size 14/35
P-1	2	5005-20	Reducing adapter
R	12	L6-1000	Thermo-O-Watch or sonic sensor
S	8	DV2-146NCA1	Teflon ^R solenoid valve
Not Shown			
T	4	K-955000-3032	3-liter coarse fritted glass Buchner funnel
T-1	5	56388-280	#12 neoprene stopper
T-2	2	6982-25	4-liter filtering flask

APPENDIX C

DETAILED RECOMMENDED BATCH PROCEDURE FOR MAKING VND SOLUTIONS IN 15-KG BATCHES



Vanadium trineodecanoate (VND) solution with 4% vanadium can be made in 15-Kg batches with this procedure. The equipment illustrated in Figure 4 and listed in Table 6 consists of the 22-liter flask, 2-inch beaded glass pipe fittings, and heat exchangers. Each joint of the beaded glass pipe has 3° of deflection and can withstand 15 psig.

ASSEMBLE THE EQUIPMENT

Reasonable substitution of equipment is acceptable. The 22-liter flask and heating mantle can be replaced with a 10-gallon steam heated glass lined agitated reactor.

- A-1 Put 22-liter flask in the heating mantle and clamp in place.
- A-2 Assemble equipment as in Figure 5 using beaded pipe couplings.
- A-3 Install thermocouple in the flask's thermowell and connect to the Love controller - digital thermometer.
- A-4 Plug the two variable transformers into the controller. Plug heating mantle into the transformers.
- A-5 Connect sonic level sensor and connect to controller. Plug solenoid valve into the controller.
- A-6 Add the three sink-float standards to measure specific gravity (spgr) of the hydrochloric acid distillate. When the spgr is below the value, the standard will sink.

<u>SpGr</u>	<u>% HCl to Float Standard</u>
1.02	3
1.03	6
1.05	10

Table C-1. EQUIPMENT SUPPLIERS FOR MAKING VND IN 15-KG BATCHES

Item From Figure 5	Supplier See Table 7	Catalog Item
A	1	C-3202, 20, Shielded flowmeter, size #2
B	1	C-6406-74, Teflon FEP 3/8-inch OD tubing
C	2	Adapter, 2-inch beaded glass pipe to Ace #11 threads, Teflon bushing and FETFE o-ring.
D	3	72-2287, 2-inch glass beaded tee
E	1	K-6833-10 tubing clamp
F	4	K-784000, Modified heavy duty stirrer bearing modified with 2-inch beaded pipe
G	4	K-784010-0005, Heavy duty (19mm OD, glass shaft) with K-784030-0005 Teflon stirrer blade.
H	1	C-4685-00, Heavy duty air-driven stirrer.
H-1	5	56433-104, Vacuum tubing 3/4-inch ID, 4 inches long
H-2	1	C-6403-05, Hose clamp
I	3	72-6422, Sanitary Y-branch, 2-inch beaded pipe
J	2	8852-09, Thermowell with beaded pipe and 6 inches long.
J-1	6	870 Keithley digital thermometer with type K thermocouple.
K	4	K-726000-2200 Heating mantle for 22-liter flask.
K-2	5	62546-455 Variable transformer
L	4	K-606200 Modified 22-liter flask with three 2-inch beaded pipe fittings and thermowell.
L-1	7	150-876, Love controller for type K thermocouple-digital read out.
L-2	7	F4-250-600 KA33-B15, Type K thermocouple
M	2	Adapter, 1-inch beaded glass pipe to Ace #11 threads
N	3	72-2086, Beaded glass tee 2 x 1-inch
O	3	72-2062, Beaded glass pipe 2 inches, 6 inches long.
P	3	72-20122, Beaded glass pipe, 12 inches long.
Q	3	HE-2 QVF glass Coil condenser
Q-1	3	Flange system to connect QVF condenser to beaded glass pipe
R	8	DV2-146NCA1 Teflon solenoid valve.

TABLE C-1. EQUIPMENT SUPPLIERS FOR MAKING VND IN 15-KG BATCHES (CONT)

Item From Figure 5	Supplier See Table 7	Catalog Item
S	9	621S Sonic liquid level sensor for 2-inch glass pipe (OD 2-5/8 inches)
S-1	9	400 C Liquid controller unit
T	1	K-7380-62 vacuum gauge
T-1	1	K-6469-86 vacuum control needle valve
T-2	1	K-6378-00 water-powdered vacuum pump
<u>Not Shown</u>		
U	3	72-1521, Coupling for 2-inch beaded pipe
V	3	72-1519, Coupling for 1-inch beaded pipe
W	5	21572-104, Column clamp
X	4	K-955000-3023, 3-liter coarse fritted glass Buchner funnel
X-1	4	K-15001000-026 Adapter
X-2	5	56388-247 #10 Neoprene stopper
Y	10	Sink-Float standards, 1.02 SpGr 1.03 SpGr, 1.05 SpGr
Z	1	K-7589-19 Air powered tubing pump with K-6412-73 Viton tubing

Table C-2. SUPPLIERS OF EQUIPMENT FOR MAKING VND

1. Cole Parmer, 7425 North Oak Park Avenue, Chicago, Illinois (800)323-4343
2. Ace Glass, P.O. Box 688, Vineland, New Jersey 08360 (609)692-3333
3. Sentinel Process Systems (Corning), P.O. Box 67, Hatboro, Pennsylvania 19040 (215)675-5700
4. Kontes Glass, P.O. Box 739, Vineland, New Jersey 08360 (609)692-8500
5. VWR Scientific, 6601 Amberton Drive, Baltimore, Maryland 21227 (301)796-8500
6. Scientific Associates, 9512 Lee Highway, Fairfax, Virginia 22031 (703)385-0600
7. W. H. Cook and Co., P.O. Box 263, Finksburg, Maryland 21048 (301)833-8200

TABLE C-2. SUPPLIERS OF EQUIPMENT FOR MAKING VND (CONT)

8. Fluorocarbon, P.O. Box 3640, Anaheim, California 92803
(714)956-7330
9. Briggs and Cooper Controls, P.O. Box 7229, Wilmington, Delaware 19803
(302)478-3548
10. Cargille Laboratory, Inc., Cedar Grove, New Jersey 07009
(201)239-6633
11. Fisher Scientific, 7722 Fenton Street, Silver Spring, Maryland
(301)587-7000
12. Instrument for Research and Industry, 108 Franklin Avenue, Cheltenham,
Pennsylvania 19012
(215)745-4440

A-7 Assemble VND filtration system (not shown in Figure 5). Starting with direction of flow the components are:

1. 3/8-inch OD feeling tubing
2. Viton tubing pump
3. 3-liter coarse Buchner funnel
4. #10 neoprene stopper
5. Adapter
6. 2nd Viton tubing pump
7. 3/8-inch OD tubing
8. Clean 22-liter flask for storing VND solution

Preparation of VND in 15-Kg Batches

- B-1 Remove addition-tee from 22-liter flask and add:
 - 840 grams formic acid (90%)
 - 10,600 grams hydrochloric acid (36%)
 - 120 grams paraformaldehyde
- B-2 Turn on water to agitator bearing and turn on agitator
- B-3 Slowly add 1080 grams of vanadium pentoxide to 22-liter flask.
(Should take 30 to 45 minutes)
- B-4 Clamp addition-tee on the flask
- B-5 Turn on nitrogen purge at setting #50 (1000 ml/min)
- B-6 Turn on condenser water
- B-7 Turn on water-powered vacuum pump
- B-8 Keep system at 10 inches of vacuum by adjusting vacuum control
needle valve.
- B-9 Turn on temperature controller and set for 85°C. Turn on and set
transformer for 70 volts.
- B-10 Agitate 22-liter flask for at least 3 hours at 80°-90°C.
- B-11 Add 4 liters of xylene.

- B-12 Change temperature controller's set point to 110°C. (NOTE: agitation rate and set point should be changed to maintain rapid distillation without foaming. Reduce nitrogen purge to 200 ml/min (setting #20).
- B-13 Turn on liquid level sensor controller and collect dilute hydrochloric acid distillate.
- B-14 Add 3800 grams triethylphosphate (TEP) to the 5-liter addition flask.
- B-15 As dilute hydrochloric acid is distilled, slowly add the TEP into the 22-liter reaction flask, by opening tubing clamp. Keep total volume under the original 16 liters.
- B-16 Add 6640 grams prime-grade neodecanoic acid to a 12-liter addition flask.
- B-17 When distillate is less than 3% hydrochloric acid:
-Add the neodecanoate acid by opening tubing clamp.
-Set temperature controller for 150°C.
-Set transformers to 100-110 volts.
- B-18 Continue distillation until the temperature of the distillation flask is 150°C and the distillate contains no water.
- B-19 Turn off transformers and cool product to room temperature.
- B-20 Remove addition-tee and add 100 grams of celite.
- B-21 Mix 100 grams celite with 100 ml xylene and add to the 3-liter coarse fritted glass Buchner funnel.
- B-22 The VND solution is filtered using apparatus assembled in step A-7 by:
-Inserting 3/8-inch tube into the VND flask
-Turning on 2nd tubing pump
-Turning on other tubing pump
-Continuing filtration until all VND has been filtered. Do NOT allow the filter to overflow!
-Turn off pumps.
- B-23 Add 1000 ml xylene to the 22-liter reaction flask, agitate and filter wash solution as in B-22 into a bottle.
- B-24 Weight filtrates and send samples of VND solution and xylene wash for vanadium, water, and chloride analysis to:
Galbraith Laboratories
P.O. Box 4187
Knoxville, TN 37921
(615)546-1335
- B-25 Calculate and add the amount of xylene wash and xylene needed to make a 4.0% vanadium solution.
- B-26 Send sample for vanadium analysis, and run gel time and time to maximum temperature.
- B-27 Reaction flask can be cleaned with warm dilute hydrochloric acid collected in step B-13.

APPENDIX D

MEASUREMENT OF GEL-TIME AND TIME AT MAXIMUM TEMPERATURE:

Gel-time was measured by a Sunshine gel-time meter*, model #22, which measures gel-times to 0.1 minutes. This meter operates by a glass rod suspended from a torsion spring rotating in the sample. The glass rod is connected to the torsion spring by magnet coupling. When gel-point is reached, the torsion spring twists, making contacts that stop the timer and ring a buzzer. The temperature was measured using a 870 Keithley digital thermometer.

A promoter solution of 50% VND and 50% N,N-dimethyl-p-toluidine (DMT) was mixed in a glass sample bottle.

The gel-time measurement procedure follows:

1. Add 100 grams polyester resin** to a 150 ml disposable polypropylene beaker.
2. Add 0.4 grams VND-DMT promoter solution. Start timer on gel-meter and auxiliary timer and mix for 0.5 minutes with the glass rod (other quantities of promoter solution may be used).
3. Add 1.1 grams cumene hydroperoxide catalyst and mix for 0.5 minutes.
4. Clamp the sample under gel-meter and magnetically couple the glass rod to the torsion spring.
5. When gel-point is reached, the buzzer sounds and the time is noted.
6. A silicone grease-coated immersion thermocouple probe is inserted in the gel and the time noted at maximum temperature on the auxiliary timer.

*Sunshine Scientific Instrument, 1810 Grant Ave., Philadelphia, PA 19115

**Polyester Resin CRS 503381

APPENDIX E

U.S. DEPARTMENT OF LABOR Occupational Safety and Health Administration	Form Approved OMB No. 44-R1387
MATERIAL SAFETY DATA SHEET	
Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)	

SECTION I	
MANUFACTURER'S NAME Naval Surface Weapons Center	EMERGENCY TELEPHONE NO.
ADDRESS (Number, Street, City, State, and ZIP Code) White Oak, Maryland 20910	
CHEMICAL NAME AND SYNONYMS	TRADE NAME AND SYNONYMS
CHEMICAL FAMILY Polyester promoter	FORMULA

SECTION II - HAZARDOUS INGREDIENTS					
PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					
HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES				%	TLV (Units)
Vanadium trineodecanoate				45	
Triethyl phosphate				25	
Xylene				27	100 ppm
Neodecanoic acid				3	

SECTION III - PHYSICAL DATA			
BOILING POINT (°K) 150°C (302°F)		SPECIFIC GRAVITY (H ₂ O=1)	1.1
VAPOR PRESSURE (mm Hg.)		PERCENT VOLATILE BY VOLUME (%)	30
VAPOR DENSITY (AIR=1) 4		EVAPORATION RATE (_____ =1)	
SOLUBILITY IN WATER Negligible			
APPEARANCE AND ODOR Blue solution			

SECTION IV - FIRE AND EXPLOSION HAZARD DATA			
FLASH POINT (°K) 400°F greater than 400°F	FLAMMABLE LIMITS Not available	Lel	Uel
EXTINGUISHING MEDIA Use National Fire Protection Association (NFPA) Class B extinguishers (carbon dioxide, dry chemical or foam) designed to extinguish NFPA Class IC flammable liquid fires. If water is used, fog nozzles are preferable.			
SPECIAL FIRE FIGHTING PROCEDURES Keep containers tightly closed. Isolate from heat, electrical equipment, sparks and open flame. Closed containers may explode when exposed to extreme heat. Do not apply to hot surfaces.			

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE

~~EFFECTS OF OVEREXPOSURE~~ xylene...Toxic vapors in high concentration are anesthetic. Irritant to skin and upper respiratory system. Wear self-contained breathing apparatus. Vanadium causes skin irritation after prolonged or repeated contact and is poisonous if swallowed.

~~EMERGENCY AND FIRST AID PROCEDURES~~ Fumes: Remove from exposure. Restore breathing. Keep warm and quiet. Notify a physician. Splash (eyes): Flush immediately with copious quantities of running water for at least 15 minutes. Take to a physician for definitive medical treatment if necessary. Splash (skin): Was affected areas with water. Remove contaminated clothing.

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	
INCOMPATIBILITY (Materials to avoid)			
Peroxides			
HAZARDOUS DECOMPOSITION PRODUCTS			
Vanadium compounds, and CO			
HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

Remove all sources of ignition (flames, hot surfaces, and electrical, static or frictional sparks). Avoid breathing vapor. Ventilate area. Absorb with filter aid or dry powder and shovel up.

WASTE DISPOSAL METHOD

Dispose in accordance with local, state, and federal regulations. Incinerate in approved facility. Do not incinerate closed containers.

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)

Not normally needed

VENTILATION	LOCAL EXHAUST	SPECIAL
	Sufficient to avoid accumulation of fumes	
	MECHANICAL (General)	OTHER
PROTECTIVE GLOVES		EYE PROTECTION
Impervious to oil		Chemical goggle
OTHER PROTECTIVE EQUIPMENT		
Sufficient to avoid skin contact		

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

Product is flammable. Do not store in high-temperature areas or in areas of fire or open flame.

OTHER PRECAUTIONS

Do not take internally. Avoid prolonged contact with the skin. Keep containers closed when not in use.

DISTRIBUTION

	<u>Copies</u>		<u>Copies</u>
Commander		Office of Naval Research	
Naval Sea Systems Command		Attn: 412	1
Attn: 098311	1	210	1
62R2	1	800 North Quincy St.	
62Z31B	1	Arlington, VA 22217	
62R22	3		
Washington, DC 20362		Naval Strategic Systems Proj. Ofc.	
Commander		Attn: Tech. Library	1
Naval Weapons Center		Washington, DC 20376	
Attn: 343	1	Commander	
3205	3	Naval Air Systems Command	
3272	1	Attn: 30212	1
3265	1	4115	1
China Lake, CA 93555		541A	1
		Washington, DC 20361	
Naval Underwater Systems Ctr		Army Ballistics Res. Labs	
Attn: Tech. Lib 021312	1	Attn: DRDAR-BLA-S,	
Newport, RI 02840		R. Paul Ryan	1
Naval Intelligence Support Ctr		Aberdeen Proving Ground, MD 21005	
Attn: NISC, Doc. Library	1	Army Ballistic Res. Labs	
4301 Suitland Road		Attn: DRDAR-BLI, John M. Hurban	1
Washington, DC 20390		Aberdeen Proving Ground, MD 21005	
Commander		Army Ballistic Res. Labs	
Naval Ordnance Station		Attn: DRDAR-BLV, Richard Vitali	1
Attn: 4243C	1	Aberdeen Proving Ground, MD 21005	
Indian Head, MD 20640		Acurex Corp.	
Office of Dir. of Defense		Attn: Tech Lib, Ms. Cindy Hill	1
Res. Engineering		485 Clyde Ave.	
Pentagon Room 3D-1089		Mountain View, CA 94042	
Attn: Mr. Jerome Persh	1	Commander	
Washington, DC 20301		AD (XRC)	
Naval Postgraduate School		Attn: T. O'Grady	1
Attn: 1424-Bibs Dir.	1	Eglin AFB, FL 32542	
Monterey, CA 93940		Aerojet General Corp. Sacramento	
Director Naval RSCH-West Pasadena		Aerojet Liquid Rocket Co Div.	
Attn: R. J. Marcus	1	Attn: Tech Inf. Ctr.	1
1030 East Green St.		PO Box 13222	
Pasadena, CA 91106		Sacramento, CA 95813	

DISTRIBUTION (CONT)

	<u>Copies</u>		<u>Copies</u>
Aerojet Tactical Systems Attn: R. Mironenko PO Box 13400 Sacramento, CA 95813	1	Commander AFRPL (XRX) Attn: Norman J. Vanderhyde Edwards AFB, CA 93523	1
Aerospace Corp. Los Angeles Attn: Lib Acq GP PO Box 92957 Los Angeles, CA 90009	1	Commander AFSC (DLWA) Attn: Mr. Richard E. Smith Andrews AFB Washington, DC 20334	1
Commander AFATL Attn: Capt. Darla M. Roberts Eglin AFB, FL 32542	1	Commander AFWAL (MLTN) Attn: Charles S. Anderson Wright-Patterson AFB, OH 45433	1
Commander AFRPL (DYP) Attn: David P. Weaver Edwards AFB, CA 93523	1	Commander Armament Rsch & Dev Comd Attn: Ludwig Stiefel BG 455 Dover, NJ 07801	1
Commander AFRPL (LK) Liquid Rocket Division Attn: LK, Stop 24 Edwards AFB, CA 93523	1	Commander Armament Rsch & Dev Comd Attn: DRDAR-RCA-G, Dr. Anthony J. Beardell Dover, NJ 07801	1
Commander AFRPL (Tech Lib) Attn: Tech Lib Edwards AFB, CA 93523	1	Commander Armament Rsch & Dev Comd Attn: DRDAR-BC, Dr. Jean-Paul Picard Dover, NJ 07801	1
Commander AFRPL (TSPR) Attn: TSPR Stop 24 Edwards AFB, CA 93523	1		

DISTRIBUTION (CONT)

	<u>Copies</u>		<u>Copies</u>
Commander Armament Rsch & Dev Comd Scientific & Tech Div Attn: DRDAR-TSS BG 59 Dover, NJ 07801	1	BDM Corp Monterey Attn: SCTY Supv (W. F. Sutherland) Dr. Terry Goodard 2600 Garden Road, North Bldg Monterey, CA 93940	1
Commander Army MAT DEV-Readiness Comd Attn: DRCDE-BW 5001 Eisenhower Ave. Alexandria, VA 22333	1	California Inst Technology Jet Propulsion LAB-BIB OP GP Attn: LIB ACQS/Standing Orders Floyd A. Anderson 4800 Oak Grove Drive Pasadena, CA 91103	1
Commander Army MAT SYS Analysis ACTV Attn: DRXS-PS-SCTY SPEC Aberdeen Proving Ground, MD 21005	1	California Inst Technology Jet Propulsion Lab-BIB OP GP Attn: LIB ACQS/Standing Orders 4800 Oak Grove Drive Pasadena, CA 91103	1
Commander Army MSL COMD-Redstone Sci Info Ctr Attn: DOS SEC BG 4484 Redstone Arsenal, AL 35898	1	Defense Technical Information Center Cameron Station Alexandria, VA 22314	2
Chief Army RSCH OFC RSCH Triangle PK Information PROC OFC Attn: DRXRO-TP-L PO Box 12211 Research Triangle Park, NC 27709	1	Commander ESCM (PM/STINFO) Attn: L. M. Adams Patrick AFB, FL 32925	1
Atlantic Research Corp. Attn: Technical Inf Ctr 7511 Wellington Road Gainesville, VA 22165	1	Ford Aerospace & Comm Newport Beach Aeronutronic Div Attn: Tech Inf SVC-DDC ACQS Ford & Jambore RDS Newport Beach, CA 92663	1

DISTRIBUTION (CONT)

<u>Copies</u>	<u>Copies</u>
Commander FTD Attn: Arnold Crowder 1 Wright-Patterson AFB, OH 45433	Huges Aircraft Co., El Segundo Technical DOC CTR Attn: El-E110 (B. W. Campbell) 1 PO Box 902 El Segundo, CA 90245
Commander FTD (SDRP) Attn: SDRP 1 Wright-Patterson AFB, OH 45433	Lockheed Missile & Space Co., Palo Alto Technical INF CTR Attn: ORG 83-10, Bldg. 154, Mr. Chuck Havlik 1 3251 Hanover St. Palo Alto, CA 94304
Gould Inc. Cleveland Ocean Systems Div. Attn: Info CTR, Dept. 749 PLT 2 1 For: R. J. Rittenhouse 18901 Euclid Ave. Cleveland, OH 44117	Marquardt Co. Attn: LIB 1 PO Box 2013 Van Nuys, CA 91409
Hercules Inc. Cumberland AEROSP DIV-Allegany Ballistics Lab Attn: LIB 1 PO Box 210 Cumberland, MD 21502	Martin-Marietta Corp Orlando Aerospace Attn: MP-30 TIC 1 PO Box 5837 Orlando, FL 32855
Hercules Inc. Magna Bacchus Works Attn: L00-H-2-RIB) (W. G. Young) 1 PO Box 98 Magna, UT 84044	Martin Marietta Denver Aerospace Attn: RSCH LIB 2655 1 PO Box 179 Denver, CO 80201
Hercules Inc. McGregor Attn: Tech Inf Ctr (D. A. Browne) 1 PO Box 548 McGregor, TX 76657	McDonnell Douglas, Huntington Beach Attn: LIB SVCS-A3-135 (E. G. Reed) 1 5301 Bolsa Ave. Huntington Beach, CA 92647

DISTRIBUTION (CONT)

<u>Copies</u>	<u>Copies</u>
Natl Aeronautics & Space Admin George C. Marshall Space Flt Ctr Attn: EP-25, Mr. John Q. Miller 1 Marshall Space Flt Ctr, AL 35812	Commander AFWAL/POSF Attn: Dr. H. Lander 1 Wright Patterson AFB, OH 45433
Commander OGDN ALC (MANPA) Attn: Mr. Anthony J. Inverso 1 Hill AFB, UT 84056	SRI International Document CTR Attn: Classified Doc SVS, 1 Dr. D. L. Ross 333 Ravenswood Ave. Menlo Park, CA 94025
Commander Radford Army Ammo Plant Attn: SARRA-QA 1 Radford, VA 24141	Sundstrand Corp. Attn: SCTY OFF (C. A. Hull) 1 4751 Harrison Ave. Rockford, IL 61101
Rockwell International, Canoga Park Rocketdyne Div Attn: TIC AB29 1 6633 Canoga Ave. Canoga Park, CA 91304	Talley Industries Attn: LIB 1 N. Diane Lee PO Box 849 Mesa, AZ 85205
Rohm & Haas Co. Attn: SCTY OFF, Dr. H. M. Shuey 1 723-A Arcadia Circle Huntsville, AL 35801	Teledyne Ryan Aeronautical Attn: Tech Info SVCS (W. E. Ebner) 1 2701 Harbon Dr. San Diego, CA 92101
Commander SAALC (SFTT) Attn: W. E. Vandeventer 1 Kelly AFB, TX 78241	Thiokol Chem Corp., Brigham City Wasatch Div. Attn: Tech Lib (J. E. Hansen) 1 Brigham City, UT 84302
AFRPL Attn: MKPA H. Stacer 1 Edwards AF Base, CA 93523	Thiokol Corp. Huntsville Div. Attn: Tech Lib (H. H. Sellers) 1 Huntsville, AL 35807

DISTRIBUTION (CONT)

	<u>Copies</u>		<u>Copies</u>
Thiokol Corp Elkton		Commander	
Attn: SCTY Off	1	White Sands Missile Range	
PO Box 241		Attn: Tech Lib (A. Sutton)	1
Elkton, MD 21921		White Sands Missile Range, NM	
		88002	
TRW Inc. Redondo Beach		The Johns Hopkins University	
TRW Electronics & Defense Sector		Applied Physics Lab	
Attn: Tech Inf Ctr-Dov SVCS,		Attn: CPIA-R. D. Brown (ML)	1
S/1930	1	Johns Hopkins Road	
One Space Park		Laurel, MD 20707	
Redondo Beach, CA 90278			
TRW Inc Redondo Beach		Naval Civil Engineering Laboratory	
TRW Electronics & Defense Sector		Attn: Melvin Hironaka	10
Attn: Tech Inf Ctr-Doc SVCS,		Port Hueneme, CA 93043	
R. C. Reeve, San Bernardino	1		
One Space Park		Internal Distribution:	
Redondo Beach, CA 90278		E432	3
United Technologies Corp		R11	1
Chemical Systems Div		R11 (Farncomb)	10
Attn: Library	1	R11 (Fauth)	1
PO Box 358		R11 (Houser)	1
Sunnyvale, CA 94086		E431	9
		E35	1
		R16	1
United Technologies Corp.			
Research CTR			
Attn: ACQ Lib			
(M. E. Donnelly)	1		
400 Main St.			
East Hartford, CT 06108			
Vought Corp Dallas			
Attn: LIB 2-58010	1		
PO Box 225907			
Dallas, TX 75265			

END

FILMED

3-85

DTIC