AD NUMBER: AD0108273
CLASSIFICATION CHANGES
TO: Unclassified
FROM: Confidential
LIMITATION CHANGES
TO: Approved for public release; distribution is unlimited.
FROM: Distribution authorized to U.S. Government Agencies and their Contractors; Administrative/Operational Use; 1 May 1956. Other requests shall be referred to Army Chemical Center, Aberdeen Proving Ground, MD 21005
AUTHORITY
U per DPG D/A ltr 24 Aug 1981; ST-A per DPG D/A ltr 24 Aug 1981

EXCLUDED

FROM GENERAL CLASSIFICATION SCHEDULE
IN ACCORDANCE WITH
INFORMATION SECURITY PROGRAM REGULATION

DATED - JULY 1972

DOD 5000.1R & EXECUTIVE ORDER 11652
(EXECUTIVE ORDER 10501 AMENDED)

BY

Defense Documentation Center
Defense Supply Agency
Cameron Station
Alexandria, Virginia 22314

DEC 1972

CONFIDENTIAL

CRLR 555
Project 4-92-03-013-02

FORMAL REPORT

THICKENING OF DMHP WITH POLYMETHYL METHACRYLATE (U)

by

Lt. James D. Moneymaker
Sigmund R. Eckhaus

FC

REGRADING DATA CANNOT BE PREDETERMINED

CHEMICAL CORPS
CHEMICAL AND RADIOLOGICAL LABORATORIES
Army Chemical Center
Maryland

28 May 1956

CONFIDENTIAL

CONFIDENTIAL

CHEMICAL CORPS
CHEMICAL AND RADIOLOGICAL LABORATORIES
Army Chemical Center
Maryland

CRLR 555
Project 4-92-03-013-02

FORMAL REPORT
THICKENING OF DMHP WITH POLYMETHYL METHACRYLATE (U)

Submitted by:

James D. Moneymaker
1Lt. James D. Moneymaker

Sigmund R. Eckhaus
*Sigmund R. Eckhaus

*Author

Recommending approval:

Gordon N. Jarman
Gordon N. Jarman
Chief, Chemical Process Branch

M.G. Ringenberg
M.G. Ringenberg
Chief, Plants Division

APPROVED:

for William Greene
FRED J. DELMORE
Colonel, CmlC
Commanding

Notebooks: 4431
4458

Experimental work:
Started 2 February 1955
Completed: 27 June 1955

Control no.
5022-555

Typed: 13 April 1956
eew

56AA 28379

CONFIDENTIAL

ABSTRACT

Object.

The object of project 4-92-03-013-02 is to design, install maintain, and operate pilot-plant equipment and facilities used in connection with the development and manufacture of CW agents.

The object of the work summarized in this report was to develop and operate a process for thickening DMHP (dimethyl hydrogen phosphite) with polymethyl methacrylate (plexiglass) and to manufacture required amounts of thickened DMHP at specified viscosities.

Results.

The preparation of thickened DMHP in an open bench-scale 2-gal. apparatus was not successful. Plexiglass precipitated out of the product during stability and surveillance tests due to moisture pickup. It was determined that less than 0.5% water will cause the thickener to separate.

Three 2-gal. batches were produced in a closed system, and a stable and uniform product was obtained. Dissolution of the plexiglass could not be accomplished with undistilled DMHP.

The batch mixing apparatus used for thickening DMHP with nitrocellulose (1) was adapted for use in this operation. Using the equipment shown in fig. 4, DMHP was thickened with plexiglass in 2 lots of 1,000 and 400 gal. to viscosities of 240 and 54 cp. respectively. Viscosity adjustments of blended lots were made to within ±5% of the desired viscosity.

Conclusions.

1. DMHP can be thickened with polymethyl methacrylate (plexiglass) in lots up to 1,000 gal. in a batch process.

2. Using a closed system blanketed with dry air, a stable uniform product can be manufactured and viscosity adjustments made to within ±5% of the desired viscosity.

Recommendations.

None, since work is continuing on this project.

TABLE OF CONTENTS

THICKENING OF DMHP WITH POLYMETHYL METHACRYLATE (U)

I. INTRODUCTION.

A. Object.

The object of project 4-92-03-013-02 is to design, install, maintain, and operate pilot-plant equipment and facilities used in connection with the development and manufacture of CW agents.

The object of the work summarized in this report was to develop and operate a process for thickening DMHP (dimethyl hydrogen phosphite) with polymethyl methacrylate (plexiglass) and to manufacture required amounts of thickened DMHP at specified viscosities.

B. Authority.

The authority for this work was contained in the 1955 project program, Project 4-92-03-013-02 CW Agent Pilot Plants.

II. STATEMENT OF PROBLEM.

The need for thickened agents to decrease rates of evaporation in the field has been reported (2, 3, 4, 5). Thickening of DMHP with nitrocellulose has been summarized in CRLR 476 (1). As a result of this work, DMHP was thickened to viscosities of 50, 250, and 2,000 cp. with nitrocellulose. The results of subsequent field tests with this material were not satisfactory (6). Apparently at high rates of shear, as a result of airplane spray tests, the nitrocellulose-thickened material broke down, and recovery on the ground was no greater than with unthickened DMHP. A polymethyl methacrylate-DMHP system was reported to be a slightly dilatant fluid (7), that is, one whose apparent viscosity increases with increasing rates of shear. Thus, this system appeared more promising for airplane dissemination with high shear rates, and the following work was undertaken.

The ploymethyl methacrylate-DMHP system did offer several operational problems which required certain modifications of the equipment used previously (1). The rate of dissolution was reported to be extremely long (20 and therefore, heating was added to the equipment to accelerate dissolution of the polymethyl methacrylate (see fig. 4). Also moisture pickup by the system was found to be excessive and could not be tolerated (see section IV, Discussion). Therefore, the equipment had to be covered with tight fitting lids and blanketed with dry air.

These were the only changes made in the equipment that was used with nitrocellulose and DMHP. The addition of 0.002% Dow-Corning Antifoam A to reduce the surface tension of the DMHP was the same as previously reported, and the addition of 0.1% food coloring to identify the dispersed thickened agent in the air and on the ground was continued.

The selection of Rohm and Haas' polymethyl methacrylate, plexiglass, 5406 XP-100, was based on the reproducibility of various viscosities with agents of interest to the Chemical Corps. Curves showing the relationship between the plexiglass concentration and the viscosity of thickened DMHP at various temperatures are plotted in figs. 1 and 2. A sample calculation indicating how fig. 1 was use in determining the amounts of material required per batch is included in the appendix.

III. EXPERIMENTAL.

A. Materials and Equipment.

1. Materials.

a. D. C. Antifoam A, semisolid silicone compound, Dow-Corning Corporation.

b. DMHP (dimethyl hydrogen phosphite). $(CH_3O)_2POH$, as supplied from Site A.

c. Dye, FD&C Red No. 32, Oil Red XO, certified food color, National Dyes.

d. Polymethyl methacrylate, Plexiglass, 5406XP-100, manufactured by Rohm and Haas Co.

2. Equipment.

a. Balance, solution, 20 -kg. capacity.

b. Dehumidifier, electrodrier, equipped with 1/4-h.p. blower.

c. Mixer, Lightnin, Mixer Equipment Co., model D-1, shaft r.p.m. 393, with 1/8-h.p., 1,725-r.p.m. explosion-proof motor.

d. Mixer, Lightnin, Mixing Equipment Co., model F.

e. Tank, stainless steel, 2 gal.

f. Tank, stainless steel, 1,000 gal.

g. Tank, stainless steel, 36-in. diam., 39-in. height, cylindrical, open top, approximately 160-gal. capacity.

h. Pump, Bump, size 16, Bump Pump Co., with 1-h.p. master motor, 1,140 r.p.m., procured from Louis M. Borish and Co.

i. Stopwatch, Elgin timer.

FIGURE 1

VISCOSITY OF THICKENED DMHP AT 25°C.

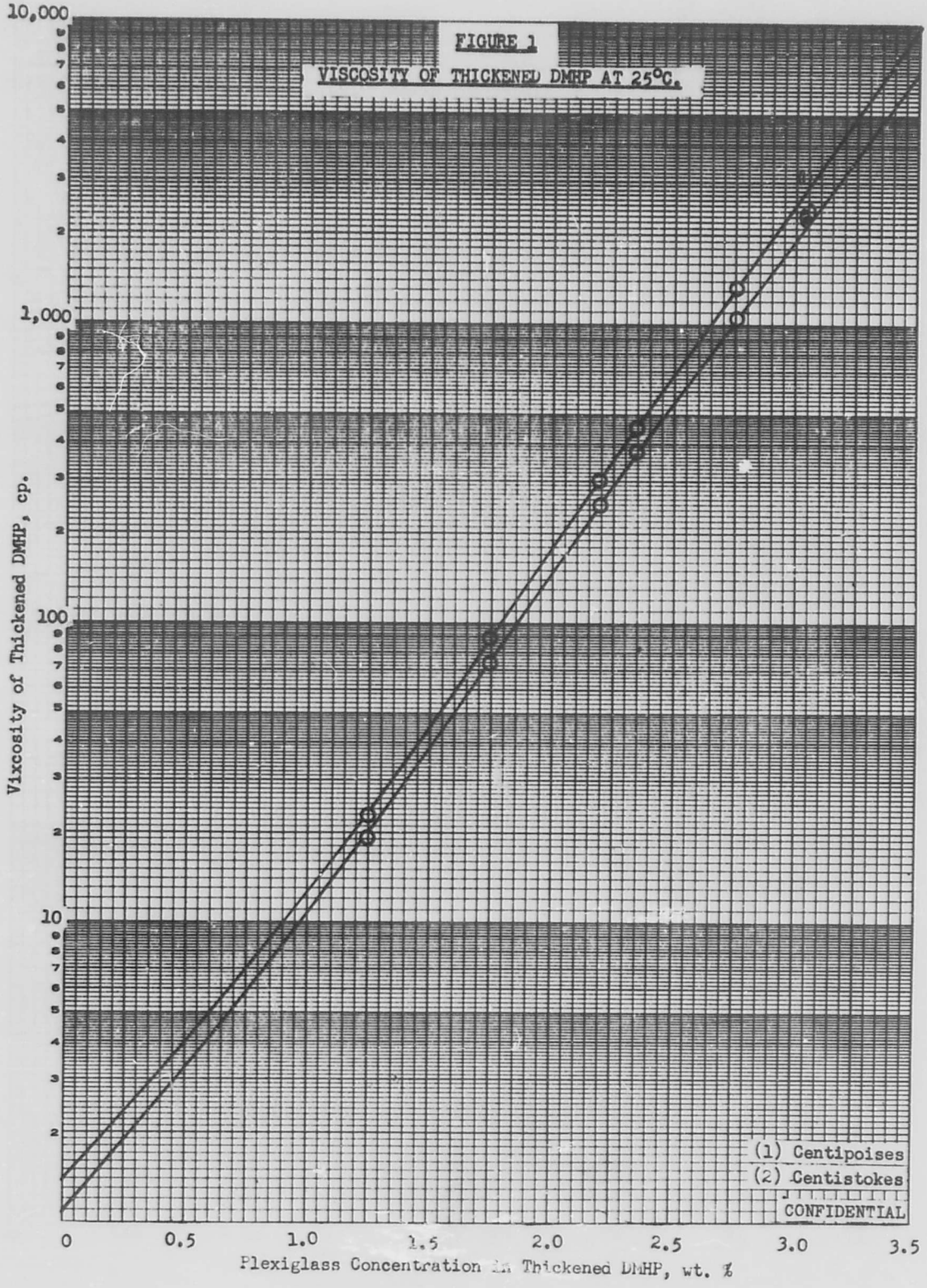
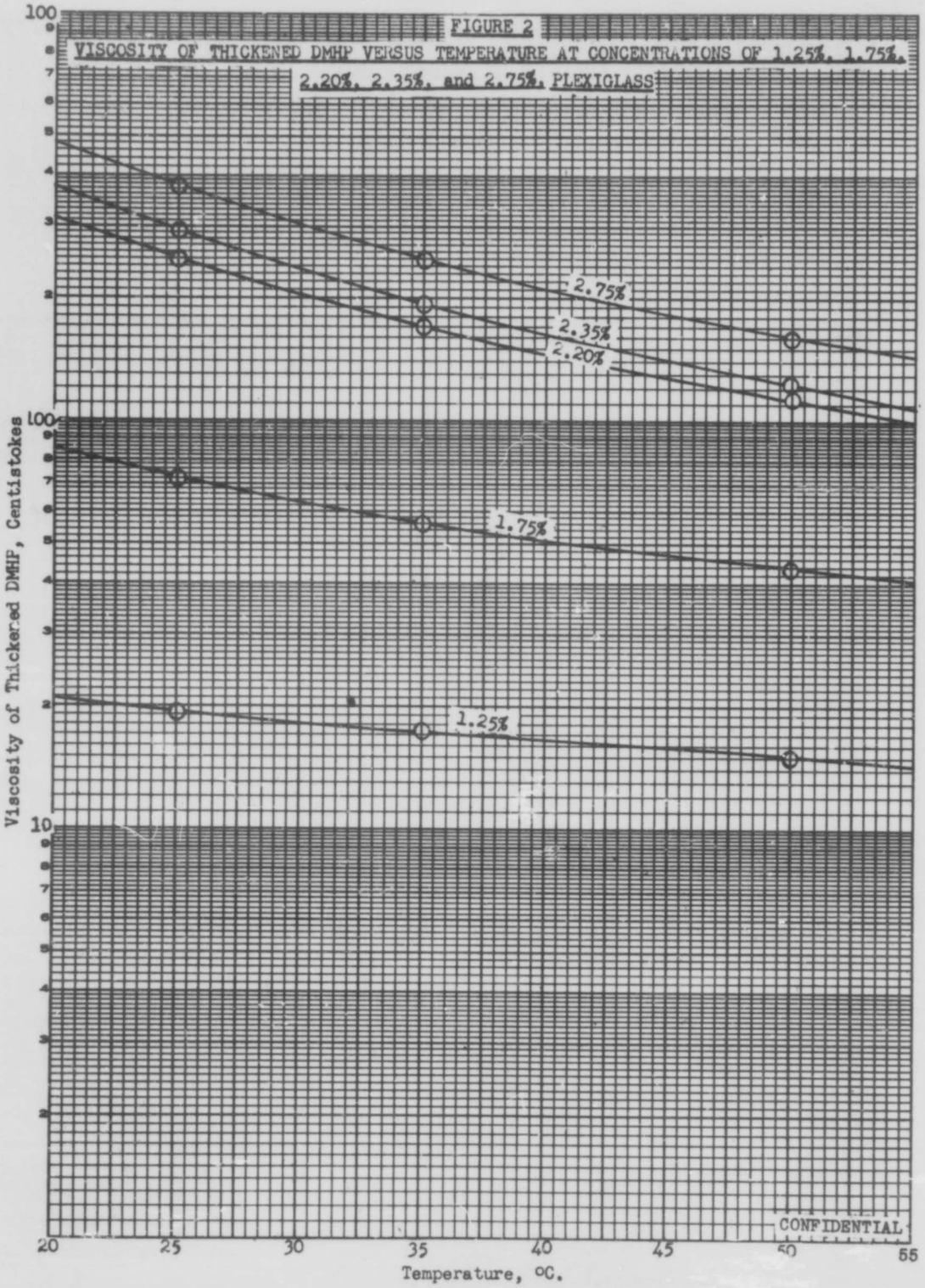


FIGURE 2

VISCOSITY OF THICKENED DMHP VERSUS TEMPERATURE AT CONCENTRATIONS OF 1.25%, 1.75%, 2.20%, 2.35%, and 2.75%, PLEXIGLASS



j. Scale, platform, 1,000-lb. capacity.

k. Scale, platform, 100-lb. capacity.

l. Viscometer, pyrex glass, Ostwald-Cannon-Fenske.

m. Viscometer, Brookfield, multispeed model LVF, Brookfield Engineering Laboratories, Inc.

B. Procedure.

1. Bench-Scale Method.

a. Open System.

To a 2-gal. stainless-steel tank equipped with a variable-speed mixer set at 380 r.p.m. and a heating coil were added 7,306 g. of DMHP and 2.3% by wt. or 172 g. of plexiglass. The reactants were heated to 45°C. and agitated for 12 hr., at which time dissolution was complete. The viscosity of the batch was then determined with an Oswald-Fenske-Cannon viscometer and with a Brookfield viscometer. The thickened DMHP was allowed to stand open to the atomsphere for 2 wk. with viscosity determinations being made periodically.

To determine the evaporation rate DMHP, 3,285 g. was heated to 45°C. with agitation in an open top 2-gal. stainless-steel tank. The DMHP was weighed at 24-hr. intervals, and the approximate rate for evaporation of an agitated liquid at 45°C. into still air at room temperature was determined.

b. Closed System.

The apparatus described for the open system was modified by the addition of a tight fitting lid and the use of a dry-air purge supplied just above the liquid level in the tank (fig. 3). The dry air was obtained by forcing compressed air through a 24-in. by 1-in. glass tube filled with calcium chloride. A bubbler was used to indicate the flow rate of dry air into the system. To minimize evaporation, a very small throughput of air was maintained.

A charge of 10,321 g. of DMHP, 0.2 g. (0.002%) of Antifoam A, and 224.6 g. (2.13%) of plexiglass was made. The reactants were agitated for 12 hr. at 45°C., and then 0.1% of red dye was added. The thickened DMHP was sampled for viscosity determinations and bottled.

2. Batch Mixing Process.

To thicken DMHP with plexiglass in batches of 100 to 1,000 gal., the batch mixing apparatus used for nitrocellulose thickening (1) was adapted for use (fig. 4). A 3/4-in. stainless-steel coil 12 ft. long was installed in

the mix tank and connected to 20 lb. of steam. A 1/2-in. plywood lid was fabricated to cover the tank, and a dry-air purge supplied by an electrodrier filled with alumina was provided for the mix tank and the blend tank. A heat exchanger 4 ft. by 2 in. jacketing the 1-in. recycle line on the blend tank was also installed. Steam at 20 lb./sq. in. was circulated through the jacket.

DMHP was charged to the mix tank using an overhead chain hoist. The liquid level in the tank was used to determine the volume and weight of DMHP. The required amount of plexiglass (determined from fig. 2) and 0.002% of Antifoam was charged to the DMHP heated to 45°C. With a slight flow of dry air supplied to the surface of the liquid, the reactants were agitated for 12 hr. at 383 r.p.m. One hour prior to the end of the mixing cycle 0.1% of red dye was added. This batch was then sampled and transferred to the 1,000-gal. blend tank. Depending upon production requirements, subsequent mix-tank batches were prepared and blended in the 1,000-gal. tank to a desired uniform viscosity. Blending was accomplished by continuous recirculation through a bump pump for 8 to 16 hr. The final viscosity was adjusted when necessary by adding required volumes of thickened or unthickened DMHP to the large lot. The product was transferred to 55-gal. stainless-steel drums (40 gal. per drum) for delivery.

C. Results.

The results of thickening DMHP with plexiglass are summarized in tables 1 through 4. Table 1 shows the results of one batch prepared in the bench-scale open-system apparatus. The data from four batches manufactured in the closed apparatus are given in table 2. The results of two lots produced by the batch mixing process are shown in tables 3 and 4.

IV. DISCUSSION.

A. Bench-Scale Open System.

Preliminary work on thickening DMHP with plexiglass was done in bench-scale equipment attempting to simulate conditions of the 1,000-gal. capacity batch mixing apparatus.

One batch was prepared with 2.3% plexiglass in the open top 2-gal. tank. At various intervals following the mixing cycle the viscosity was measured with a Brookfield viscometer. The viscosities measured 12 hr. after mixing by both the Brookfield and the Ostwald-Cannon-Fenske viscometers did not agree, and it was concluded that the viscosity of thickened DMHP changes with rate of shear. The use of the mechanical Brookfield viscometer was not possible, and all other viscosities were measured with the Ostwald-Cannon-Fenske viscometer.

The product was allowed to stand in the reactor open to the atmosphere for 2 wk. the plexiglass began to precipitate after 2 da., and after 2 wk. the viscosity of the remaining liquid was 3 cp. The proposed reasons for the precipitation were that the DMHP was hygroscopic and/or some DMHP had evaporated. To determine the amount of water necessary

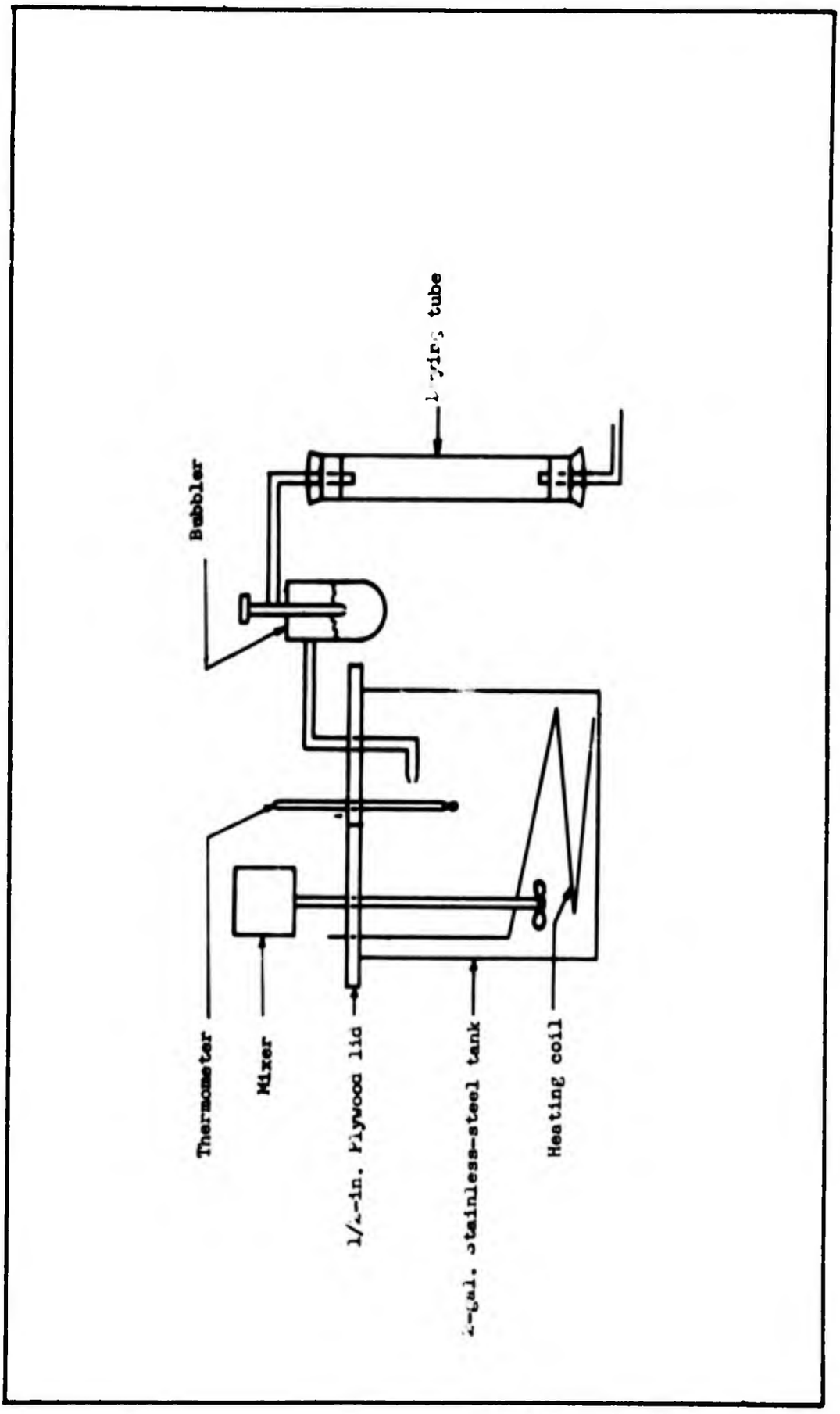


FIGURE 3

BENCH-SCALE APPARATUS, CLOSED SYSTEM

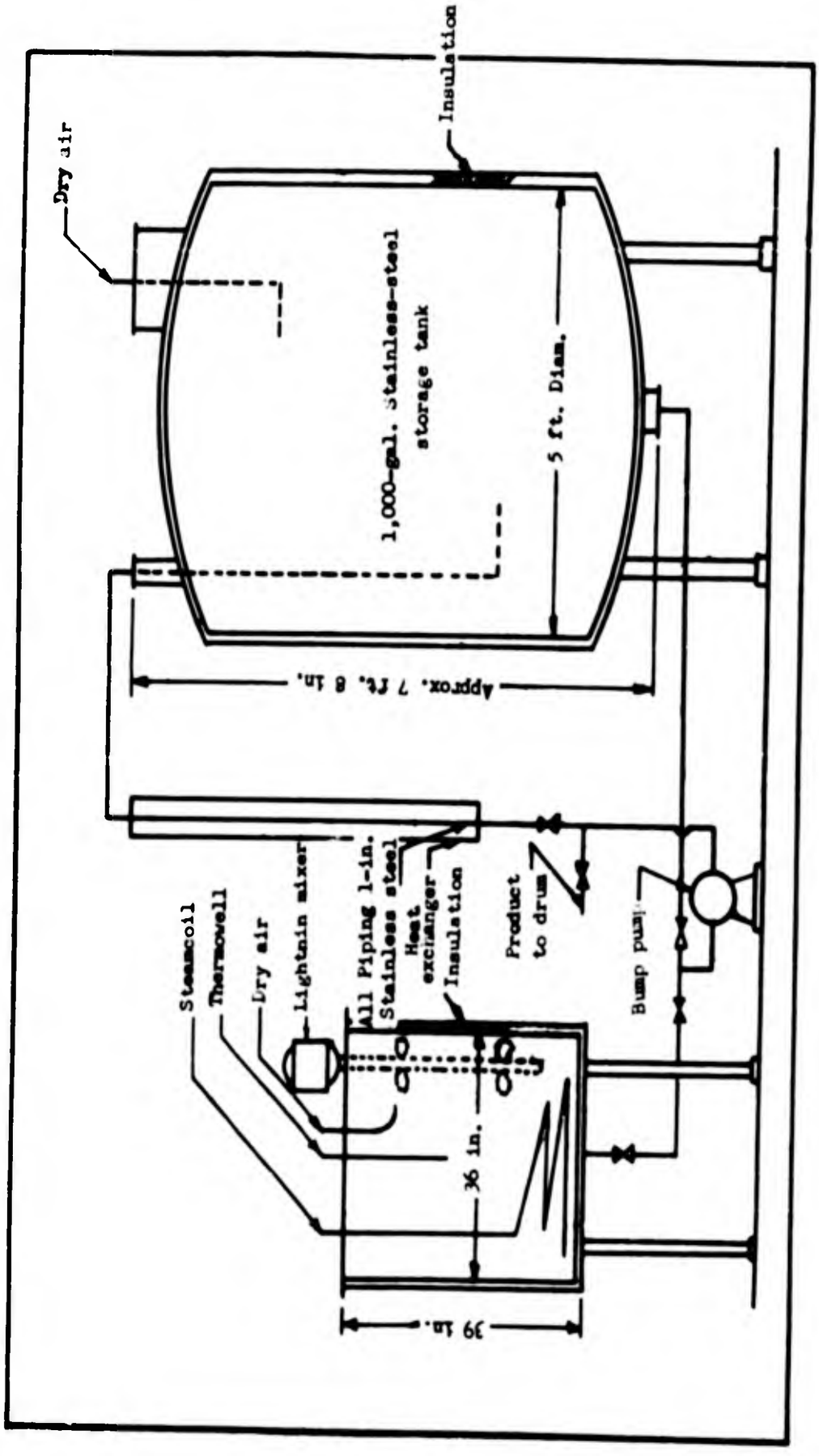


FIGURE 4

BATCH MIXING PROCESS

Table 1

Bench-Scale System - Batch 1*

Brookfield viscometer				Cannon-Oswald-Fenske viscometer		
Time after mixing cycle	Temp.	Spindle	viscosity	Time after mixing cycle	Temp.	Viscosity
hr.	°C.	r.p.m.	cp.		°C.	cp.
0	45	6	266	-	-	-
12	20	6	969	12 hr.	19.5	1,151
56	39	6	490	-	-	-
-	-	-	-**	2 wks.	26.0	3.1

* Desired viscosity, 400 cp.

**Large amount of plexiglass precipitated; viscosity of remaining decanted liquid, believed to be hydrolyzed DMPH.

CONFIDENTIAL

Table 2

Bench-Scale Closed System

Batch	DOHP	Plexiglass		Mix time	Desired viscosity	Hold time (a)	temp.	Viscosity
	g.	%	g.	hr.	cp.	hr.	°C.	cp.
2	10,321	2.15	224.6	12	250	12	25	225
3	10,125	1.55	157.5	12	50	12	25	51
4	10,505	2.92	316.0	12	2,000	12	25	1,651 (c)
5	10,390 (b)	2.15	226.1	12	250	-	-	

(a) Time after mixing cycle completed.

(b) Undistilled DOHP used.

(c) Plexiglass did not dissolve.

Table 3

Batch Mixing Process, Lot 1

Mix-tank batch	DOP	Plexiglass	Viscosity at 25°C.	Blend-tank sample	Mix-tank batch components	Blended Viscosity at 25°C.
	lb.	P.	cp.			cp. (a)
1	1,252	12,320	259	-	-	-
2	1,250	12,320	259	1	1	250
3	1,250	12,320	268	2	1-2	229
4	1,250	12,320	268	3	1-3	225
5	1,250	12.320	254	4	1-4	250
6	1,250	12,320	289	5	1-5	256
7 (c)	1,480	15,000	246	6	1-6	242
-	-	-	-	7 (b)	1-6	240

(a) Desired viscosity. 250 cp.

(b) Final viscosity.

(c) Mix-tank batch 7 not dyed and not blended with dyed batches.

Table 4

Batch Mixing Process, Lot 2

Desired viscosity	Previously thickened DMHP			DMHP	Plexiglass	Lot size	Final viscosity
	40 cp.	200 cp.	250 cp.				
cp.	lb.	lb.	lb.	lb.	lb.	gal.	cp.
50 to 60	-	745	402	2,855	38.2	400	40
50 to 60	1,200	-	-	-	5.5	400	54

to precipitate the plexiglass from the thickened DMHP, water was added dropwise to a 10-ml. sample prepared in a moisture-free system. Less than 1 drop or 0.5% of water was required to precipitate the thickener confirming the orginal supposition.

B. Bench-Scale Closed System.

To reduce the moisture pick up, dry air was supplied to blanket the tank fitted with a close-fitting lid. Three 2-gal. batches were made at viscosities of 223, 51 and 1,615 cp. A 12-hr. mixing cycle at 45°C. was sufficient for complete dissolution, except for a final batch prepared with crude DMHP and 2.13% plexiglass, in which the plexiglass would not completely dissolve. It was therefore concluded that crude DMHP (approx. 80% pure) could not be thickened with the existing process.

The final viscosities of the three batches were 15% to 20% lower than the theoretical viscosities determined from the concentration-viscosity curve (fig. 1). An error in the curve or variations in the raw materials would cause this difference. Since viscosity adjustments could be easily accomplished in the batch mixing process, no further work was required to study the relationship between the plexiglass concentration and the viscosity of thickened DMHP.

Samples of material produced in the closed system were observed during storage for 2 wk. The plexiglass did not precipitate, and the product seemed stable at a uniform viscosity during the surveillance period.

C. Batch Mixing Process.

The batch mixing process used for thickening DMHP with nitrocellulose was modified by installing a dry-air supply to the mix and blend tanks. Steam heating coils and a steam-jacket heat exchanger were also added to the system.

Using the procedure described earlier in the report, two lots of thickened DMHP were prepared. A 750-gal. lot at 240 cp. was the result of blending six mix-tank batches produced from distilled DMHP and 2.13% plexiglass.

A second lot of 400 gal. at 50 cp. was prepared from 120 gal. of previously thickened material by diluting with 130 gal. of DMHP. One 150-gal. mix-tank batch was thickened to 500 cp., and the entire lot of 400 gal. was then blended for 12 hr. The final viscosity was not within the desired limits (50 to 60 cp.), and it was necessary to add 5.5 lb. of plexiglass to the batch, increasing the viscosity to 54 cp. While drumming the product, four viscosity determinations were run. The viscosity of each sample was 54 cp., showing that dissolution was complete and that the lot was uniform.

V. CONCLUSIONS.

1. DMHP can be thickened with polymethyl methacrylate (plexiglass) in lots up to 1,000 gal. in a batch process.

2. Using a closed system blanketed with dry air, a stable uniform product can be manufactured and viscosity adjustments made to within ± 5% of the desired viscosity.

VI. RECOMMENDATIONS.

None, since work is continuing on the project.

VII. BIBLIOGRAPHY.

1. Moneymaker and Eckhaus, CRLR 476, Thickening of DMHP With Nitrocellulose, 2 May 1955.

2. B.M. Zeffert, et al., CRLR 129, Thickening Plant GB With Polymethyl Methacrylate, February 1953.

3. Zeffert and Macy, CRLR 182, The Volatility of Thickened Toxic Agents, 26 May 1953.

4. Military Intelligence Division ETF 550-936, Summary of U. S. Progress in Toxic Chemical Agents Since the Seventh Tripartite Conference, II Toxic Chemical Agents, 1 October 1953.

5. Author, Summary Technical Report, ETF 550-994, Toxic CW Agents, Ninth Tripartite Conference, 21 July 1954.

6. Verbal conversation with R. Wheeler, Munitions Division, Chemical and Radiological Laboratories, 11 July 1955.

7. Verbal communication from F. Coulter, Physical Branch, Chemical Division, Chemical and Radiological Laboratories, 31 January 1955.

APPENDIX

SAMPLE CALCULATIONS FOR DETERMINATION OF BATCH SPECIFICATIONS (LOT 2)

Basis: 400 gal. of thickened DMHP at 50 cp.

Plexiglass Required:

400 gal. at 10 lb./gal. = 4,000 lb.

50 cp. = 1.55% plexiglass (fig. 1)

4,000 lb./0.0155 = 62.0 lb.

Plexiglass available in 120 gal. of thickened DMHP:

743 lb. at 200 cp. = 2.05% (fig. 1)

402 lb. at 250 cp. = 2.13%

743 lb./0.0205 = 15.23 lb.

402 lb./0.0213 = 8.56 lb.

total plexiglass = 23.79 lb.

Mix-Tank Batch Specifications:

Basis: 150 gal. of DMHP with 37 lb. of plexiglass

Weight and Per Cent Plexiglass:

62.0 lb. - 23.79 = 38.21 lb.

37 lb. used to remain on low side

% Plexiglass

$$\frac{37}{1537}(100) = 2.41\%$$

Theoretical viscosity of mix tank batch

2.41% = 520 cp. (fig. 1)

Final Product:

114 gal. of previously thickened DMHP

136 gal. of DMHP = 30.6 in. (fig. 6)

150 gal. of DMHP thickened with 2.41% plexiglass

Final viscosity = 40 cp.

Adjustment of Blended Lot to 55 cp.:

Basis: 400 gal. of thickened DMHP at 50 to 60 cp.

Plexiglass required: 60 cp. = 1.61%

4,000 lb. (0.0161) = 64.4 lb.

Plexiglass available:

40 cp. = 1.46%

4,000 lb. (0.0146) = 58.4 lb.

Plexiglass to be added:

64.4 - 58.4 = 6 lb.

5.5 lb. plexiglass added

per cent plexiglass and viscosity

$$\frac{63.9}{4,063.9}(100) = 1.575\%$$

1.575% = 55 cp.

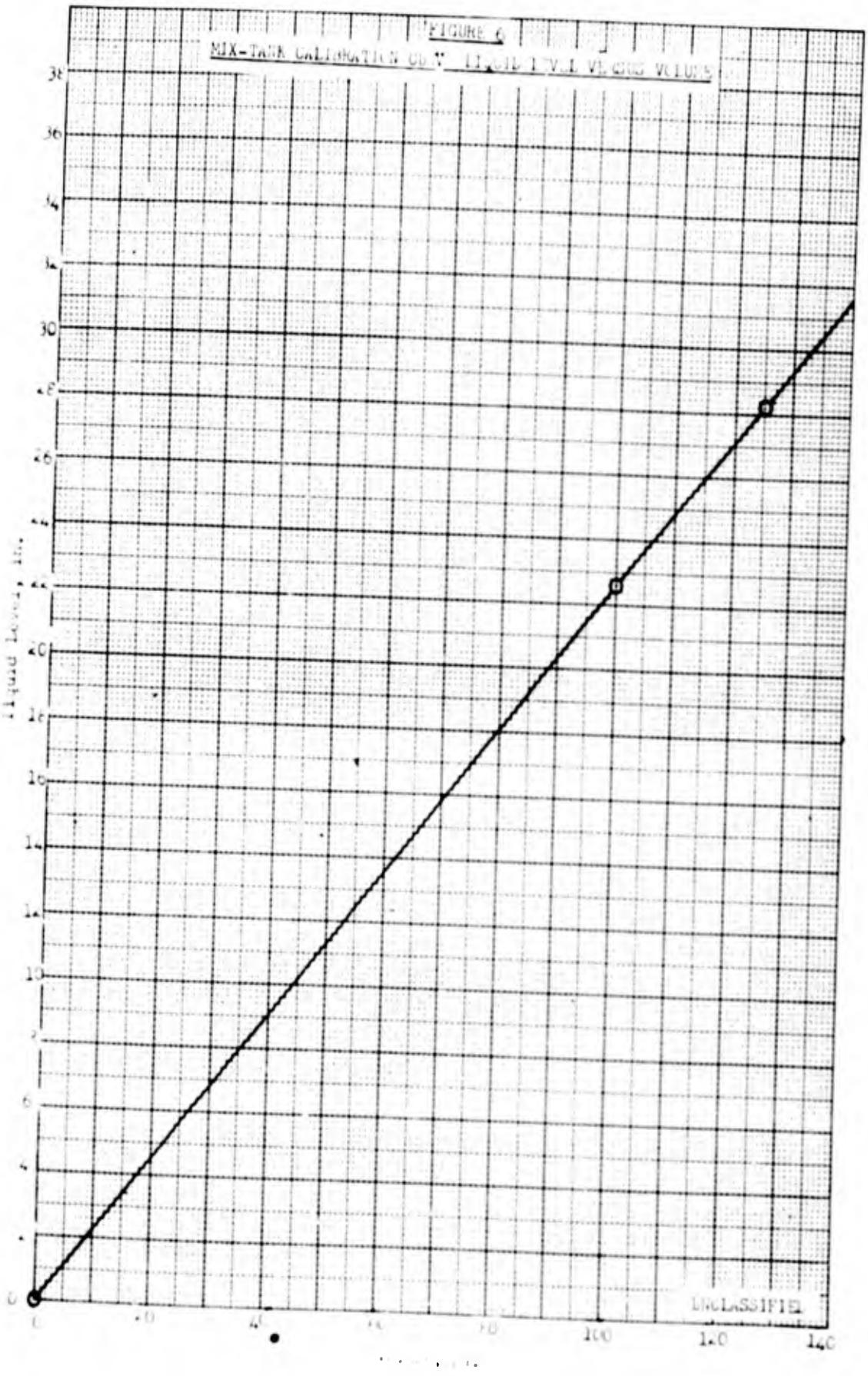


FIGURE 6
MIX-TANK CALIBRATION CURVE USING VARIOUS VOLUMES
UNCLASSIFIED

DISTRIBUTION LIST

Copies made: 43

Copies 1 - 10 Technical Library, CW Labs
11 - 13 Chief Chemical Officer, Washington 25, D. C.
14 Commanding Officer, CmlC Research and Development Command, Washington 25, D. C., Attn: Research Division
15 - 17 Commanding Officer, CmlC Intelligence Agency, Building T-7, Dept. of the Army, Gravelly Point, Washington 25, D. C.
18 - 19 Commanding General, CmlC Materiel Command, Building 1, Army Chemical Center, Md.
20 - 21 Commanding General, CmlC Training Command, Ft. McClellan, Ala.
22 President, CmlC Board, Army Chemical Center, Md.
23 Commanding Officer, CmlC Engineering Command, Building 250, Army Chemical Center, Md.
24 Executive Director, CmlC Advisory Council, Army Chemical Center, Md.
25 Operations Research Group, Bldg. 483, Army Chemical Center, Md.
26 Secretary, CmlC Technical Committee, Army Chemical Center, Md.
27 - 31 Director, Armed Services Technical Information Agency, UB Bldg., Dayton 2, Ohio, Attn: DSC-SD
32 Office of the Assistant Secretary for Defense for Research and Development, CW Committee, Pentagon, Washington 25, D. C.
33 - 38 British Liaison Officer, Building 330, Army Chemical Center, Md.
39 - 42 Canadian Army Technical Representative, Building 330, Army Chemical Center, Md.
43 U. S. Army Standardization Group, UK, Box 65, USN 100, FPO, New York, N.Y., Attn: Lt. Col. L.C. Miller, Representative for Chemical Corps

UNCLASSIFIED