

WADC TECHNICAL REPORT 55-89

PART V

ASTIA DOCUMENT No. AD 118341

PHYSICAL AND CHEMICAL LABORATORY
EVALUATION OF SILICATE BASE
HIGH TEMPERATURE HYDRAULIC FLUIDS

PART V. ROOM TEMPERATURE HYDROLYSIS STUDIES

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MATERIALS LABORATORY

JULY 1957

PROJECT No. 7331

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by the Lubricants Section, Organic Materials Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center. The work was accomplished under Project No. 7331 entitled "Hydraulic Fluids," Task No. 73313 entitled "Hydraulic Fluids." The work was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with 1st Lt. H. M. Schiefer and Mr. George Baum as project engineers. 2nd Lt. G. Buell and Dr. J. Dacons also contributed to this program. Infra-red spectra were obtained by the Analysis and Measurements Branch of this laboratory.

This report covers work conducted from June 1955 to August 1956.

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ABSTRACT

Silicate-esters are being considered for use in 400°F hydraulic systems. Previous study had established evidence of the hydrolytic instability of the silicate-ester formulations.

The behavior of four silicate-ester base formulations toward extended storage with varying quantities of water was studied. The formulations presented varying degrees of hydrolytic stability. Solids formation was encountered with all formulations. However, the disiloxane formulation (MLO 8200) produced significantly lower quantities of solids than the other three formulations. Addition of a diester to this disiloxane formulation resulted in a large increase in the amount of solids formed. The solids formed were not a linear function of water present. Instead, maximum solids occurred at intermediate water concentrations.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

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I. INTRODUCTION

Water contamination of hydraulic systems is a current problem. The presence of water in a system not only represents a rust forming condition but may also have a detrimental effect on the hydraulic fluid. Water may react with the fluid, leach additives from it, or form stable emulsions with it. Water may enter a hydraulic system in a number of ways:

1. Water may enter a system during ground servicing operations.
2. Water may enter in flight through breathing of static seals and dynamic seals of exposed actuator rods.
3. Water may be condensed in the reservoir when bleed air from the engine is used for pressurization.

The extent of the contamination varies in different parts of a system and different system designs. Major contamination usually occurs in the reservoir and accumulators. Up to 6% of water has been found in hydraulic fluid drained from the reservoir.

Previous reports in this series have reported on the overall assessment of the physical and chemical properties of several silicate-ester type hydraulic fluids for high temperature hydraulic systems. Each of the fluids reported previously has been noted as hydrolytically unstable in the presence of free water. This report will examine the hydrolytic stability of silicate-ester formulations under room temperature storage conditions. A report to be published later in this series will examine the hydrolytic stability of silicate-ester formulations at 400°F.

The formulations used for this study are those that have been reported in the previous reports in this series. These formulations utilize either a tetra alkoxy silane or a hexalkoxy disiloxane as the base stock and include additives to improve such properties as lubricity, viscosity, and oxidation stability. The formulations may contain a dibasic acid ester to increase the swell of neoprene "R" stock, which is used for high temperature "O" ring compounds.

The chemical literature has shown that the alkoxy-silicon bond may be cleaved by water under mild conditions. This cleavage is both acid and base catalyzed. The rate of cleavage of the oxygen-silicon bond may be slowed down by steric or inductive effects. Thus,

"Manuscript released by author 22 April 1957 for publication as a WADC Technical Report."

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while the hydrolysis of silicate-ester type fluids may be retarded, hydrolysis represents a potential source of difficulty in the utilization of these fluids in aircraft hydraulic fluids. The data reported in the following sections is a study of fluid deterioration at room temperature.

II. PROCEDURE

The four fluids used in this study were:

1. 72073-C - R. M. Hollingshead Corporation
2. OS-45 - Monsanto Chemical Company
3. 8515 - Oronite Chemical Company
4. 8200 - Oronite Chemical Company

A series of 50 milliliter samples containing 0.5, 1, 2, 3, and 5% water by weight were prepared for each of the test fluids. Into each sample bottle (two fluid ounce capacity) was placed a polished copper strip 5 cm by 1.5 cm. The bottles were periodically opened and the contents examined. The copper strip was rubbed with a rubber policeman to remove any adhering solids. The fluid and any solids that were formed were placed in a dry, weighed 100 ml centrifuge tube and centrifuged at 1500 rpm for 45 minutes. The fluid was decanted and its viscosity and neutralization number were determined. The residue in the centrifuge tube was washed with petroleum ether and centrifuged at 1500 rpm for 15 minutes. The ether was decanted and the washing cycle was repeated. The centrifuge tube containing the residue was dried in an oven at 210°F and then weighed.

The viscosities were determined at 210°F in an Ostwald-Cannon-Fenske pipette type viscometer. Neutralization numbers were determined by an electrometric titration with dilute aqueous KOH. The titration solvent was a 1:1 volume ratio solution of water and ethanol.

III. DISCUSSION OF RESULTS

All of the data obtained are presented in Tables I through V. Table I represents neutralization numbers obtained in this program. The numbers are all very low. Little or no stable acid formation occurred during hydrolysis reactions.

Table II represents viscosity data obtained. The Monsanto fluid maintained its viscosity at a constant value. The Hollingshead fluid gained in viscosity at higher water concentrations. Both Oronite fluids lost viscosity at all water concentrations.

Table III represents the weight change of the immersed copper strip. Only mild or slight copper effects were observed. Both Oronite fluids left small patches of black deposits on the copper. Hollingshead fluid at high water concentrations formed appreciable deposits on the copper although the weight gain was not significant. Figure 1 is a photograph of the strips after extended immersion times.

Table IV represents the data obtained on the per cent by weight of solids formed. Solids formation was the major evidence of fluid deterioration and is a convenient way of following the extent of deterioration with time.

These data were plotted to illustrate solids build-up with time and the effect of water concentration.

Figures 2 through 6 show for all test fluids the deposition of solids at each water concentration. All experimental points are shown. Some of the data had a certain amount of variance, and the curves drawn represent trends of behavior.

The solids formed varied from a gelatinous mass to a fine maroon powder. After drying in an oven at 210°F in order to obtain a dry weight of solids, the gelatinous mass condensed to rubbery resin. The maroon powder was suspended in Nujol and the infra-red absorption spectra was recorded. The absorption spectra was very similar to that of silica gel for all of the powdered residues.

Table V indicates the nature of the residue at each water concentration for each fluid at a particular time interval. At shorter intervals, it was difficult to assess the nature of the residue due to the small quantities of solids formed.

The relationship between water concentration and the quantity of solids formed can be better illustrated if these two variables are plotted against each other with storage time as the parameter. Figures 7 through 10 were prepared in this manner.

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The quantity of solids deposition reaches a maximum at 1% water concentration for both the Hollingshead and 8515 fluids. The solids were resinous at the water concentration where the very high quantities of solids were formed and accounts for their bulk. Fluid 8200 deposited very little solids throughout the test duration. The only difference between the 8515 and 8200 formulations is the presence of di(2-ethylhexyl)sebacate in 8515 to act as a rubber swell additive.

In order to obtain some information as to the source of the resins, the resins were ignited on a spatula. Table V summarizes the observations made. The resins from Hollingshead fluid ignited readily leaving a mixture of ash and white powder. Resins from the other fluids ignited to a clean fine white powder. In all cases, the residue constituted about as much bulk as the original resin. Several of the resins were ignited to quantitatively determine the silicon content. Two such ignitions were carried out on resins from 8515. The silicon content was calculated to be 33 and 37%. The data obtained are tabulated in Table VI.

The weight of silicon present in hexabutoxy disiloxane is about 8.5%. the resins formed are therefore highly hydrolyzed silaceous material. That the solids originated from the base stock rather than the silicone thickener can be deduced from the very little viscosity change of the fluid even when very large amounts of solids were formed. The exact role of diester in affecting solids formation is not clear from the data presented. The addition of a diester to fluid 8200 was very deleterious to the hydrolytic stability of the base stock. Solids formed was greatly increased especially at low concentrations of water. A very sharp maximum in solids formation occurred at 1% water concentration.

V. CONCLUSIONS

1. Extended storage at room temperatures of silicate-ester base fluids contaminated with water resulted in formation of significant quantities of solids. The disiloxane formulation (MLO 8200) produced significantly lower quantities of solids than the other three formulations.

2. The presence of dibasic acid ester in a disiloxane base formulation was very deleterious to the hydrolytic stability of the formulation. Fluid 8515 precipitated large quantities of solids in contrast to MLO 8200 fluid.

3. In the presence of dibasic acid ester maximum hydrolysis of the silicate-ester occurs at low water concentrations of about 1%.

TABLE I

ACID FORMATION DURING STORAGE

Sample Designation	% Water	Neutralization Number mg KOH/gm sample		
72073-C		<u>13 weeks</u>		<u>62 weeks</u>
	0.5	0.00		0.08
	1.0	0.05		0.08
	2.0	0.03		0.12
	3.0	0.08		0.00
	5.0	0.10		0.26
OS-45		<u>13 weeks</u>	<u>37 weeks</u>	<u>61 weeks</u>
	0.5	0.00	0.00	0.28
	1.0	0.00	0.00	0.00
	2.0	0.00	0.00	0.26
	3.0	0.00	0.00	0.30
	5.0	0.00	0.00	0.00
8515			<u>35 weeks</u>	<u>59 weeks</u>
	0.5		0.11	0.00
	1.0		0.11	0.00
	2.0		0.08	0.04
	3.0		0.24	0.04
	5.0		0.01	0.08
8200			<u>34 weeks</u>	<u>58 weeks</u>
	0.5		---	0.00
	1.0		0.03	0.00
	2.0		0.03	0.00
	3.0		0.02	0.00
	5.0		0.00	0.00

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TABLE II

VISCOSITY DURING STORAGE

Sample Designation	% Water	Viscosity at 210°F in cs.						
72073-C		<u>1 week</u>	<u>2 weeks</u>	<u>5 weeks</u>	<u>38 weeks</u>	<u>51 weeks</u>	<u>62 weeks</u>	<u>62 weeks</u>
	0.5	7.4	7.2	7.4	----	6.9	6.83	
	1.0	7.0	7.2	7.2	6.7	7.2	7.01	
	2.0	7.2	7.1	7.2	6.8	6.91	8.81	8.34
	3.0	7.1	7.3	7.2	6.7	5.23	8.23	8.47
	5.0	7.2	7.1	7.7	----	6.76	8.55	7.90
05-45		<u>1 week</u>	<u>2 weeks</u>	<u>5 weeks</u>	<u>37 weeks</u>	<u>50 weeks</u>	<u>61 weeks</u>	
	0.5	4.0	3.8	3.9	3.82	2.87	3.93	
	1.0	4.0	4.0	4.0	4.00	3.85	3.90	
	2.0	4.0	4.0	4.0	----	5.41	3.91	
	3.0	4.0	4.0	4.0	3.89	4.01	3.97	
	5.0	4.0	4.0	4.0	3.91	3.89	3.86	
8515		<u>1 week</u>	<u>2 weeks</u>	<u>5 weeks</u>	<u>35 weeks</u>	<u>48 weeks</u>	<u>59 weeks</u>	<u>59 weeks</u>
	0.5	8.9	8.8	8.8	8.82	7.87	8.32	
	1.0	8.9	9.0	8.9	8.78	8.05	8.10	8.14
	2.0	9.0	8.9	8.8	8.86	9.40	8.07	8.32
	3.0	8.9	8.9	9.0	8.43	8.09	8.36	
	5.0	8.9	8.9	8.8	9.03	8.78	8.74	
8200		<u>1 week</u>	<u>2 weeks</u>	<u>5 weeks</u>	<u>34 weeks</u>	<u>47 weeks</u>	<u>58 weeks</u>	
	0.5	9.5	9.8	9.7	----	8.82	9.42	
	1.0	9.9	10.0	10.1	9.76	9.32	9.51	
	2.0	9.9	10.0	10.1	9.52	9.51	9.47	
	3.0	10.0	10.1	9.9	----	9.49	9.44	
	5.0	10.1	10.1	9.9	----	9.56	9.45	

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TABLE III

WEIGHT CHANGE OF COPPER IN STORAGE

Fluid	Water	%	Weight Change of Copper (mg/cm ²)									
			1 wk	2 wks	5 wks	9 wks	13 wks	17 wks	25 wks	38 wks	51 wks	62 wks
72073-C		0.5	-0.02	0.00	-0.03	-0.01	-0.44	+0.10	-0.02	-0.01	+0.11	-0.65
		1.0	-0.02	-0.04	-0.04	+0.03	-0.20	-0.05	-0.25	-0.08	+0.09	-0.08
		2.0	-0.02	-0.07	-0.01	-0.14	-0.29	-0.17	-0.26	-0.01	+0.09	-0.11
		3.0	-0.03	-0.11	-0.14	-0.12	-0.32	-0.31	-----	+2.46	-0.08	-0.29
		5.0	-0.15	-0.18	-0.29	-0.27	-0.58	-0.51	-0.26	+2.43	-0.20	-0.15
OS-45		0.5	-0.01	-0.01	-0.02	-0.01	+0.02	+0.01	-0.01	+0.73	-1.00	+0.03
		1.0	-0.01	-0.02	-0.03	-0.02	-0.06	+0.02	-0.02	+0.05	+0.34	-0.01
		2.0	-0.01	-0.03	-0.05	-0.06	-0.07	-0.05	-0.07	-0.03	+3.89	+0.03
		3.0	-0.03	-0.02	-0.04	-0.03	-0.05	-0.03	-0.07	+0.35	-5.74	-0.10
		5.0	-0.03	-0.04	-0.05	0.00	-0.06	-0.13	-0.12	-0.03	+2.73	-0.13
8515		0.5	-0.02	0.00	-0.01	-0.04	+0.01	+0.01	+0.01	+0.73	+0.19	
		1.0	-0.02	-0.02	-0.02	-0.02	-0.01	+0.02	+0.03	+0.13	+0.15	
		2.0	-0.01	0.00	-0.01	-0.01	-0.01	+0.03	+0.03	+0.05	+0.19	
		3.0	-0.01	0.00	-0.01	-0.02	0.00	+0.01	+0.03	+0.06	+0.14	
		5.0	0.00	0.00	0.00	-0.01	-----	-0.02	+0.03	-----	+0.17	
8200		0.5	0.00	-0.01	0.00	-0.01	+0.01	+0.02	+0.02	+0.07	+0.34	
		1.0	0.00	-0.02	0.00	-----	-0.01	+0.02	+0.02	+0.07	+0.15	
		2.0	0.00	0.00	-0.02	-0.02	+0.03	0.00	+0.03	+0.08	+0.27	
		3.0	0.00	0.00	-0.01	-----	+0.01	+0.01	+0.02	+0.06	+0.13	
		5.0	0.00	0.00	-0.01	-0.02	+0.06	+0.02	+0.04	+0.06	+0.17	

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TABLE IV

SOLIDS FORMATION DURING STORAGE

Fluid	% Water	Weight % of Solids Formed						
72073-C		<u>1 wk</u>	<u>2 wks</u>	<u>5 wks</u>	<u>9 wks</u>	<u>13 wks</u>	<u>17 wks</u>	<u>25 wks</u>
	0.5	0.0000	0.0038	0.0062	0.1284	0.1348	0.4390	0.4294
	1.0	0.0210	0.0164	0.0934	2.6982	0.1818	0.4382	0.6778
	2.0	0.0024	0.0060	0.0596	0.1784	0.2014	0.3014	0.4728
	3.0	0.0044	0.0244	0.0620	0.1706	0.1772	0.3040	0.4568
	5.0	-----	0.0194	0.0378	0.0820	0.1612	0.3832	0.4617
OS-45		<u>1 wk</u>	<u>2 wks</u>	<u>5 wks</u>	<u>9 wks</u>	<u>13 wks</u>	<u>19 wks</u>	<u>25 wks</u>
	0.5	0.0114	0.0060	0.0042	0.1718	0.2114	-----	0.2608
	1.0	0.0052	0.0006	0.0000	0.0172	0.2172	0.1442	-----
	2.0	0.0024	0.0012	0.0014	0.0122	0.0392	0.1574	0.1854
	3.0	0.0462	0.0092	0.0462	0.0304	0.1290	0.1590	0.1564
	5.0	0.0916	0.0024	0.0008	0.0448	0.2110	0.1306	0.1638
8515		<u>1 wk</u>	<u>2 wks</u>		<u>9 wks</u>	<u>13 wks</u>	<u>20 wks</u>	<u>27 wks</u>
	0.5	0.0184	0.0116		0.0072	0.0310	0.0116	0.2254
	1.0	0.0176	0.0052		0.0058	0.1888	0.0452	0.2856
	2.0	0.0200	0.0044		0.0244	0.0158	0.1280	0.2500
	3.0	0.0204	0.0188		0.0108	0.0136	0.0772	0.0102
	5.0	0.0308	0.0058		0.0062	0.1248	0.0598	0.0034
8200		<u>1 wk</u>	<u>2 wks</u>	<u>5 wks</u>	<u>9 wks</u>	<u>13 wks</u>	<u>20 wks</u>	<u>27 wks</u>
	0.5	0.0126	0.0132	0.0032	0.0108	-----	0.0208	0.0240
	1.0	0.0174	0.0162	0.0040	0.0084	0.1166	0.0402	0.0200
	2.0	0.0172	0.0108	0.0042	0.0164	0.1498	0.0558	0.0268
	3.0	0.0714	0.0282	0.0040	0.0254	0.1044	0.0282	0.0298
	5.0	0.0120	0.0176	0.0028	0.0210	0.0262	0.0282	0.0322

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TABLE IV (Cont'd)

SOLIDS FORMATION DURING STORAGE

Fluid	% Water	Weight % of Solids Formed					
72073-C		<u>38 wks</u>	<u>51 wks</u>	<u>62 wks</u>	<u>64 wks</u>	<u>64 wks</u>	
	0.5	0.5438	0.0436	0.8810	-----	-----	
	1.0	0.3134	0.2226	3.1856	1.9344	-----	
	2.0	0.5392	0.6416	0.7342	-----	-----	
	3.0	0.5744	5.7436	0.5356	0.9636	0.7820	
	5.0	0.0904	0.7424	0.6058	-----	0.6922	
OS-45		<u>37 wks</u>	<u>50 wks</u>	<u>61 wks</u>	<u>63 wks</u>	<u>63 wks</u>	
	0.5	0.3746	0.1730	0.4976	-----	-----	
	1.0	-----	2.1952	0.2284	0.1992	-----	
	2.0	-----	0.4322	0.8862	-----	0.3666	
	3.0	1.1622	0.3170	1.1600	0.1624	0.2872	
	5.0	0.2764	0.3604	1.0340	-----	0.7606	
8515		<u>35 wks</u>	<u>48 wks</u>	<u>59 wks</u>	<u>61 wks</u>	<u>61 wks</u>	
	0.5	0.6268	1.0998	3.2374	-----	0.9250	
	1.0	1.8348	3.2162	3.8450	-----	-----	
	2.0	1.0040	2.2482	2.2880	-----	-----	
	3.0	10.1388	0.1046	0.6634	0.0642	0.1200	
	5.0	-----	0.0844	0.6644	0.2122	0.2130	
8200		<u>34 wks</u>	<u>47 wks</u>	<u>58 wks</u>	<u>60 wks</u>	<u>60 wks</u>	<u>61 wks</u>
	0.5	-----	0.0654	0.0540	-----	-----	-----
	1.0	0.2546	0.3294	0.0602	0.0430	-----	0.0822
	2.0	0.2950	0.3272	0.4336	-----	0.0516	0.1042
	3.0	0.2340	0.2876	0.6944	-----	0.1028	0.0934
	5.0	0.4498	0.2116	0.0460	0.0642	-----	0.0664

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TABLE V

NATURE OF THE SOLIDS FORMED

Fluid	% Water		Combustible	Residue From Combustion
72073-C - 62 weeks	0.5	Resin	Yes	Ash-white powder
	1.0	Resin	Yes	Ash-white powder
	2.0	Hard maroon powder	No	No change
	3.0	Hard maroon powder	Slightly	Fine white powder
	5.0	Hard maroon powder	Slightly	Fine white powder
8515-59 weeks	0.5	Resin	Yes	Fine white powder
	1.0	Resin	Yes	Fine white powder
	2.0	Resin	Yes	Fine white powder
	3.0	Maroon powder	No	Fine white powder
	5.0	Maroon powder	No	Fine white powder
OS-45-61 weeks	0.5	Resin	Yes	Fine white powder
	1.0	White powder	No	No change
	2.0	White powder	No	No change
	3.0	White powder	No	No change
	5.0	White powder	No	No change
MLO 8200-58 weeks	0.5	Maroon powder	No	No change
	1.0	Maroon powder	No	No change
	2.0	Maroon powder	No	No change
	3.0	Maroon powder	No	No change
	5.0	Maroon powder	No	No change

SILICON CONTENT OF RESINS FROM 8515

	I	II
Weight resin	1.2993	0.8820
Weight SiO ₂	1.0356	0.6255
Weight % SiO ₂	79	71
Weight % Si (calc.)	37	33

FIGURE 1
APPEARANCE OF COPPER STRIPS AFTER EXTENDED STORAGE

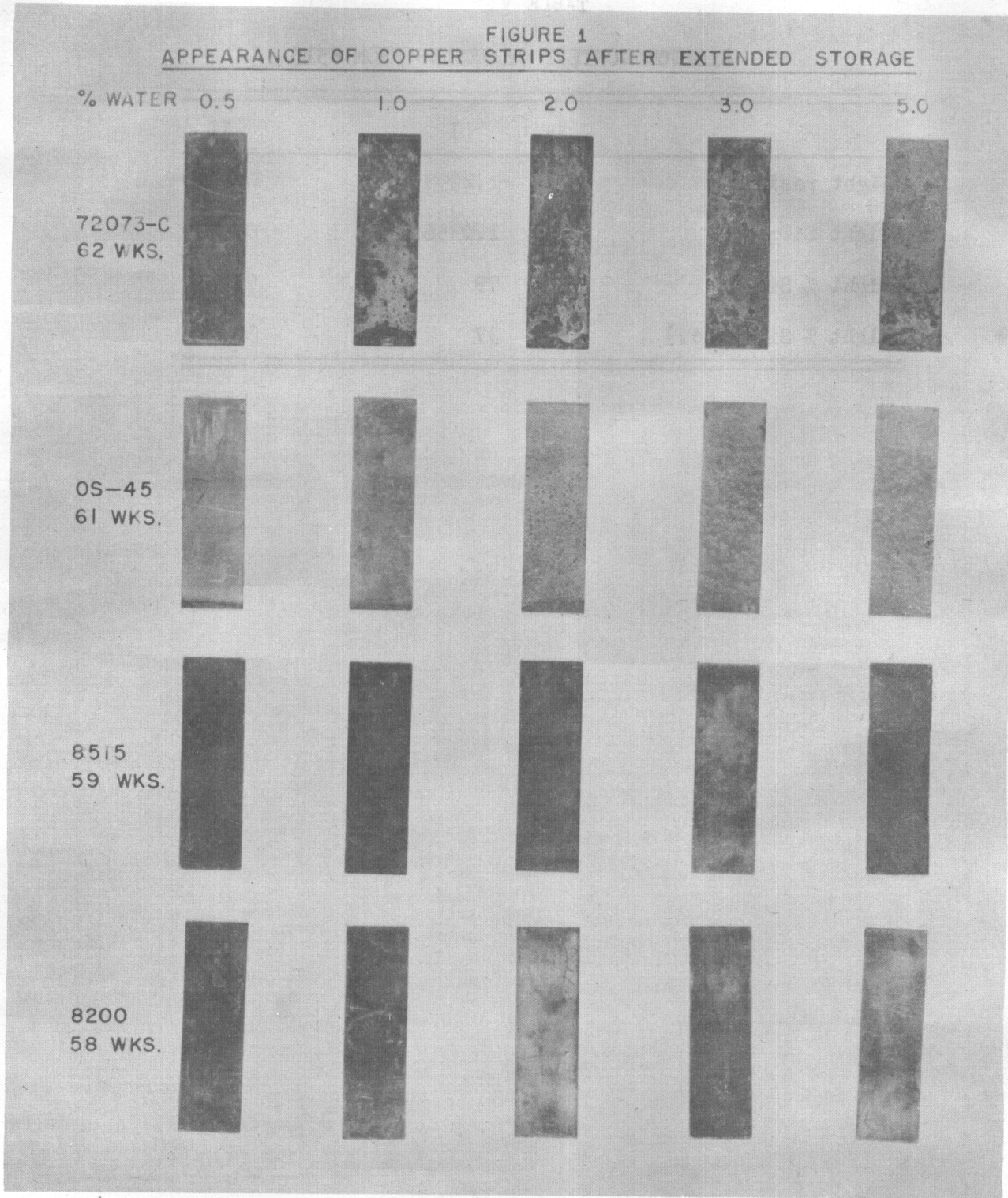


Figure 1

Appearance of Copper Strips After Extended Storage

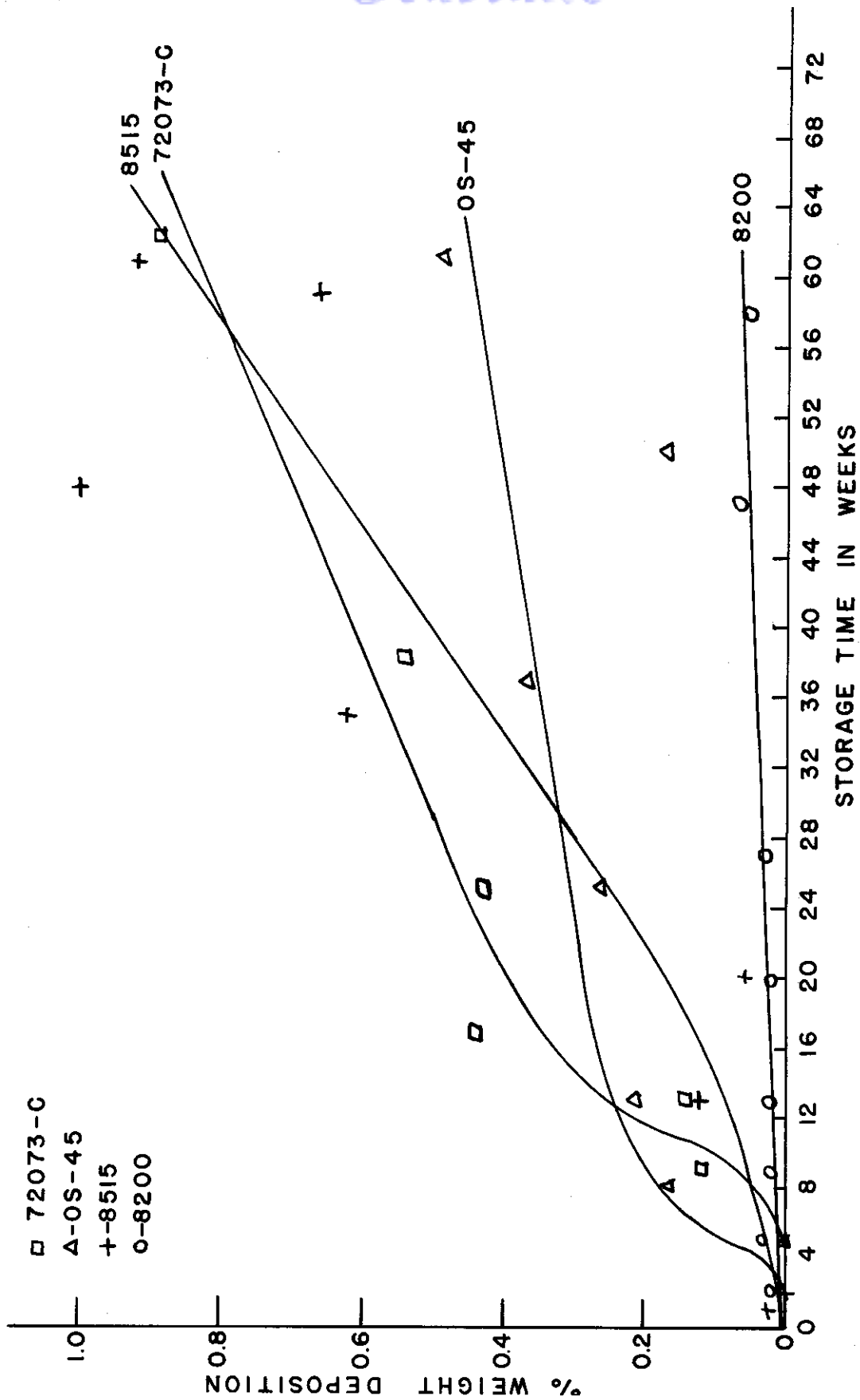


FIGURE 2
SOLIDS BUILD-UP AT 0.5% WATER CONCENTRATION

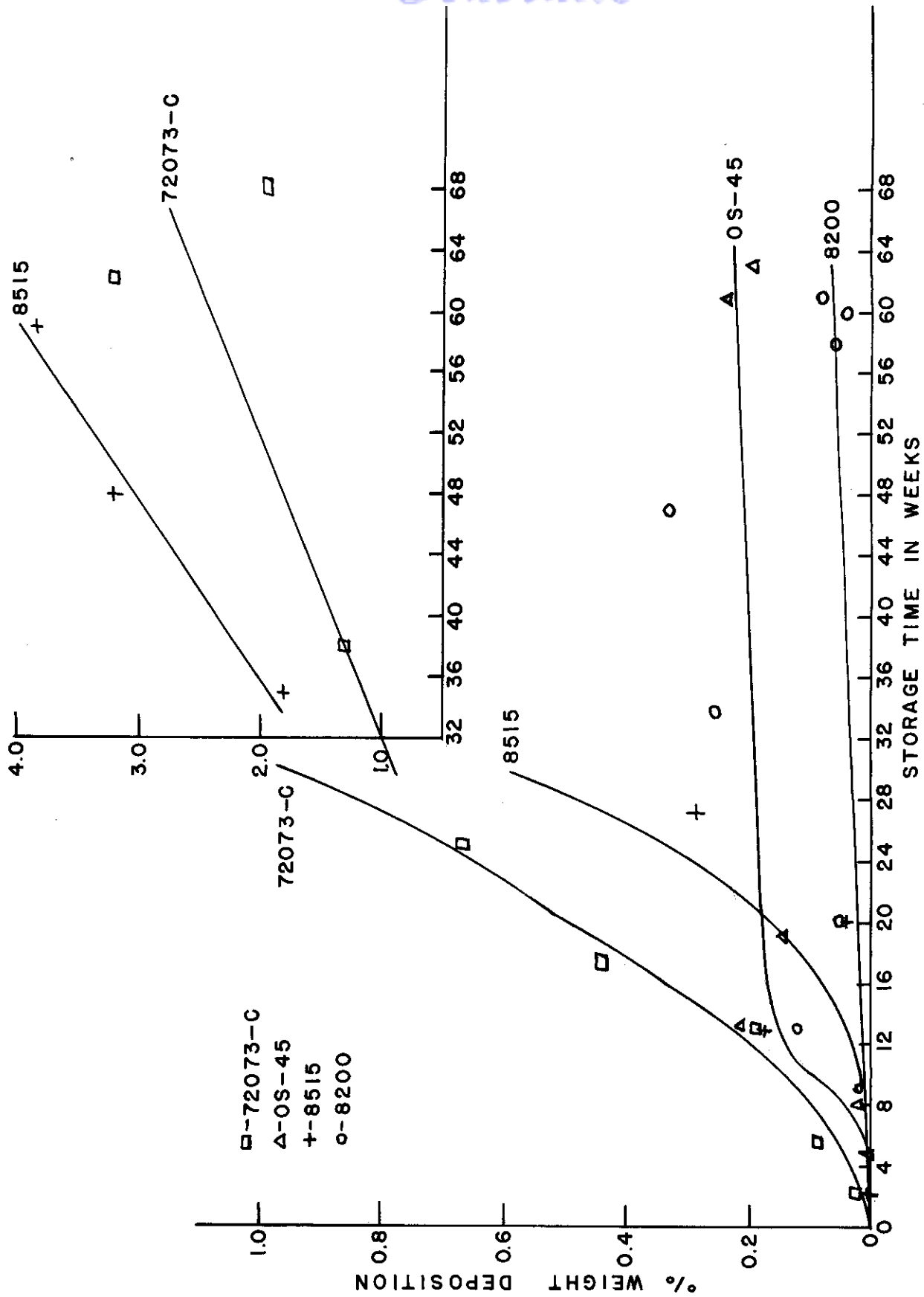


FIGURE 3
SOLIDS BUILD-UP AT 1% WATER CONCENTRATION

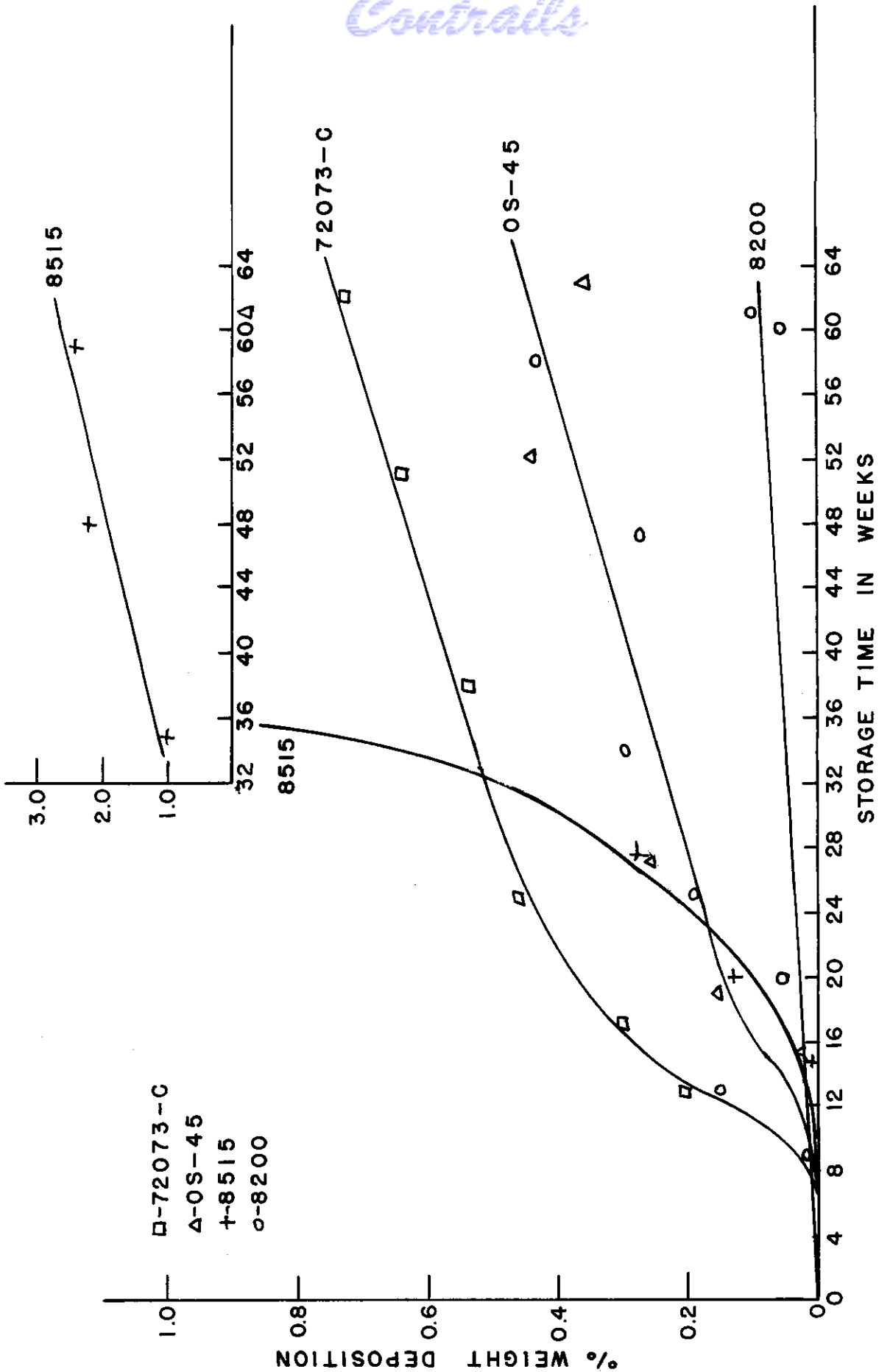


FIGURE 4
SOLIDS BUILD-UP AT 2% WATER CONCENTRATION

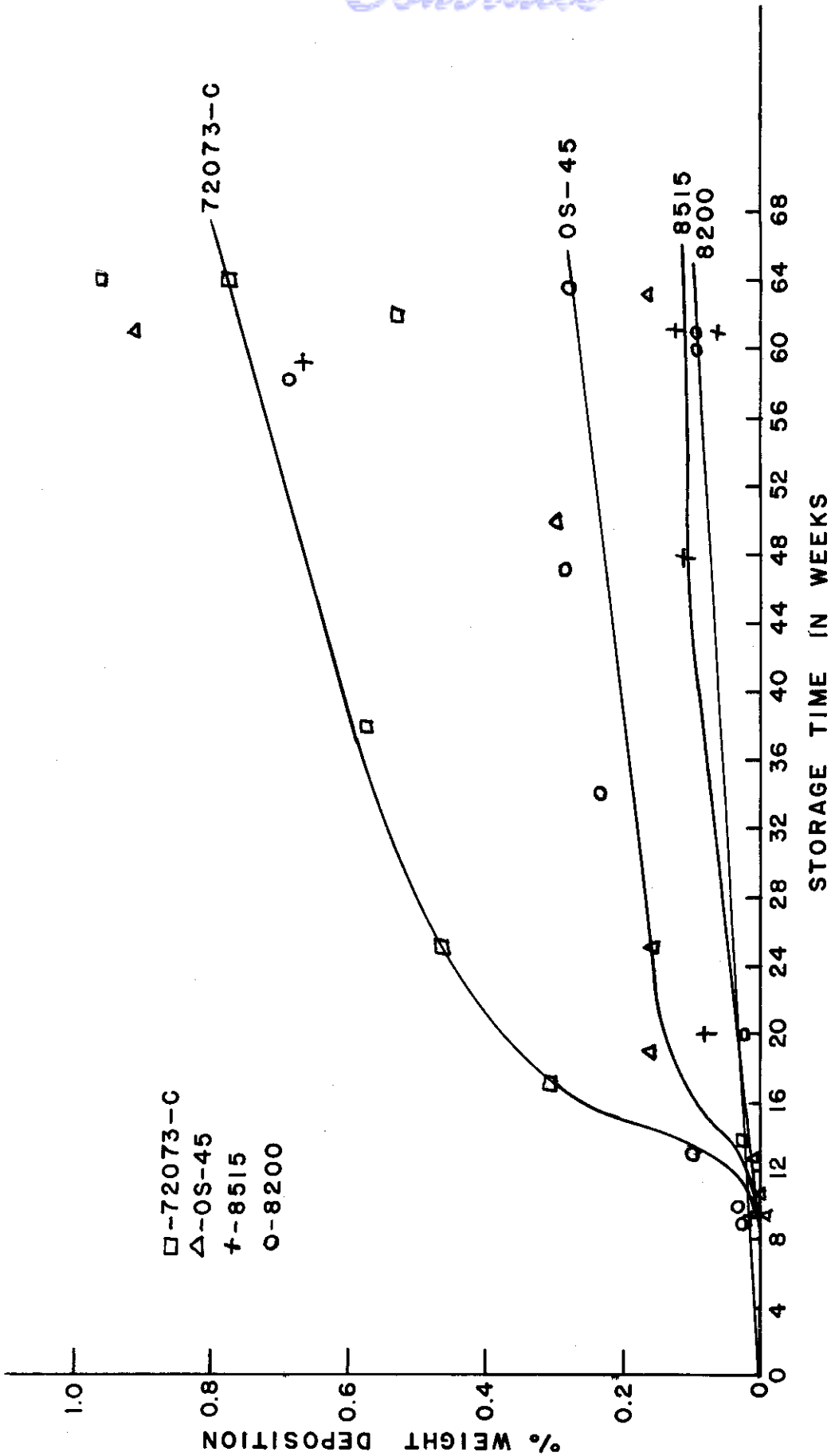


FIGURE 5
SOLIDS BUILD-UP AT 3% WATER CONCENTRATION

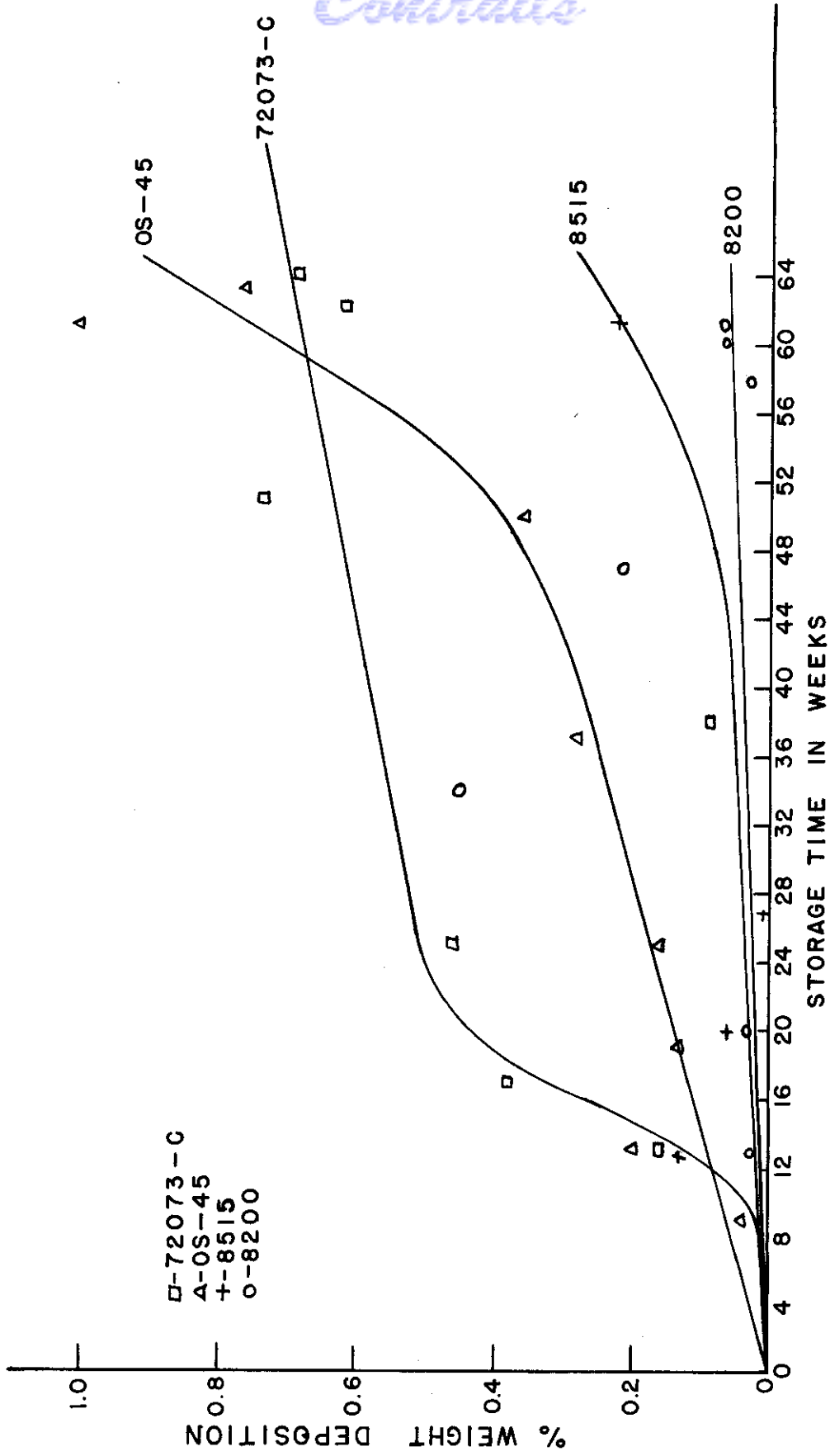


FIGURE 6
SOLIDS BUILD-UP AT 5% WATER CONCENTRATION

Contrails

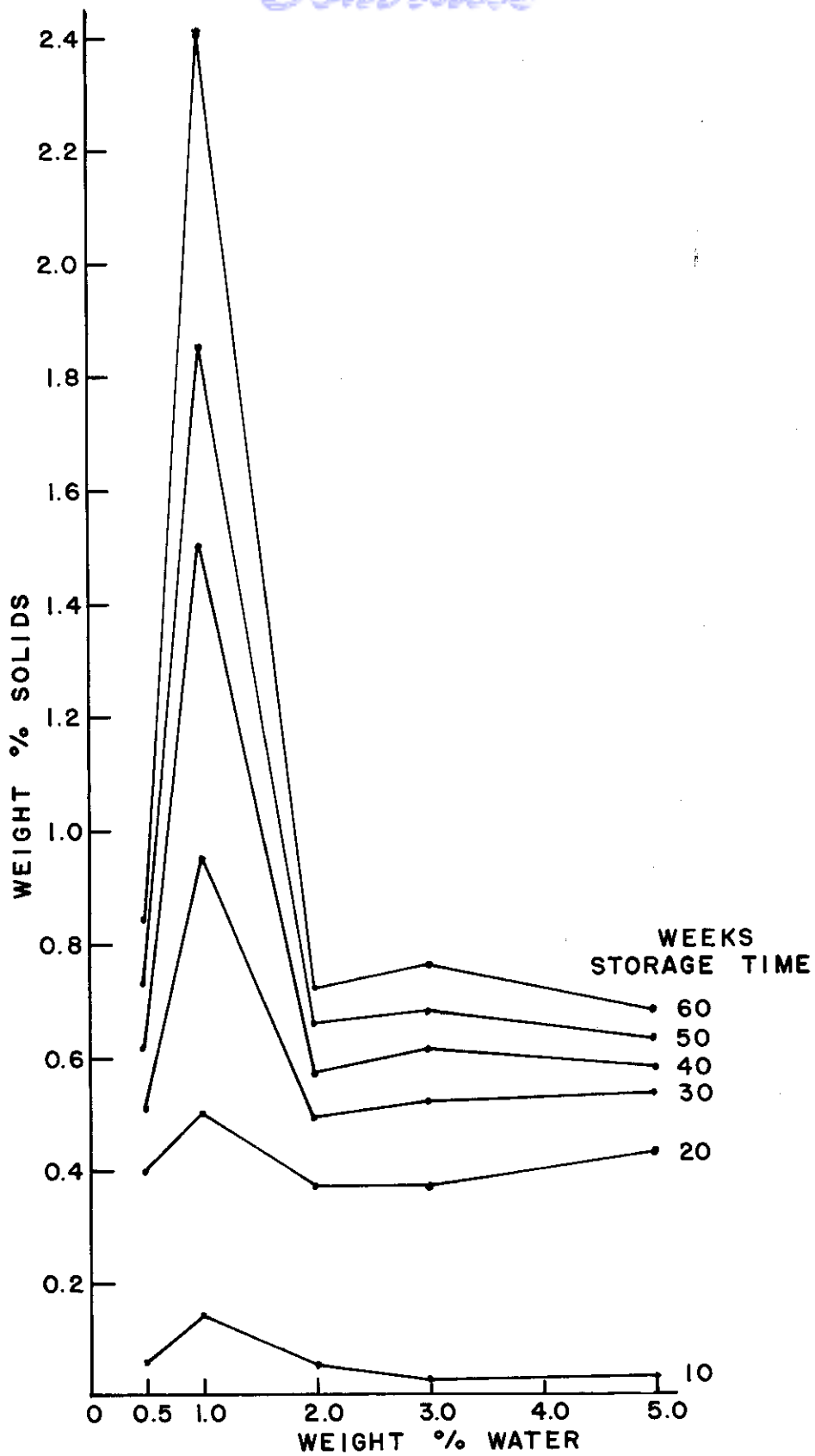


Figure 7

Effect of Water on Storage of 72073-C Fluid

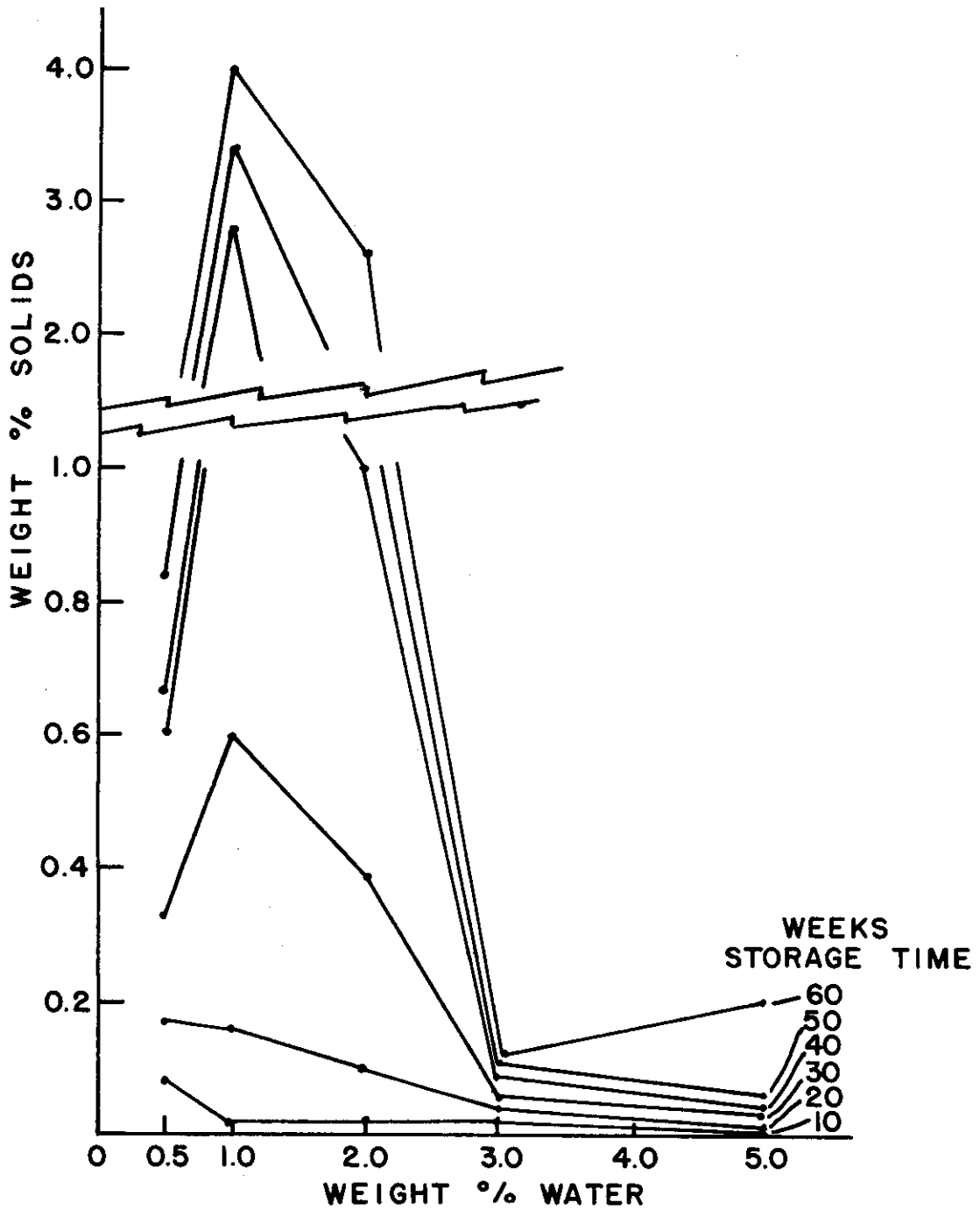


FIGURE 8
EFFECT OF WATER ON STORAGE
OF 8515 FLUID

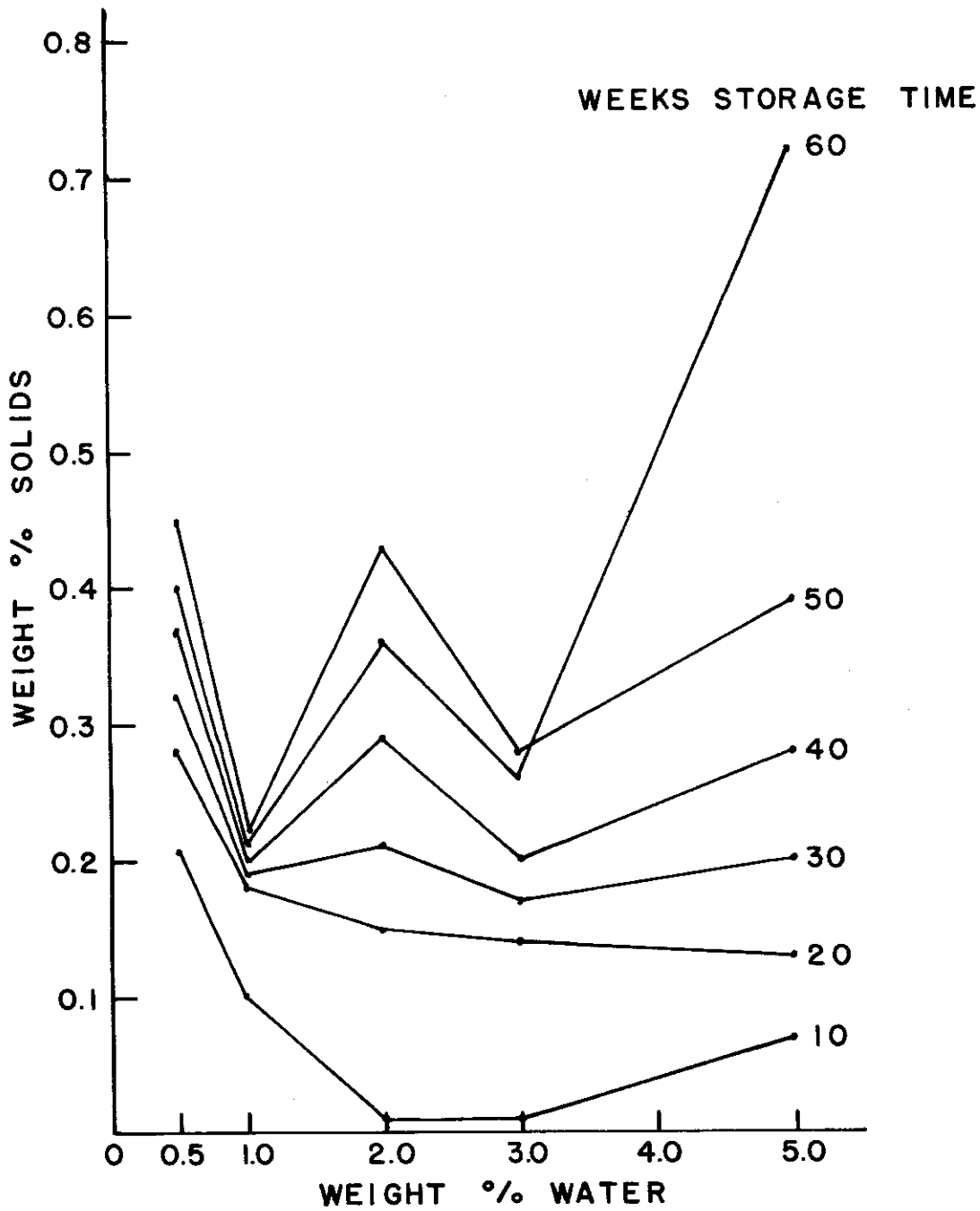


FIGURE 9
EFFECT OF WATER ON STORAGE
OF OS-45 FLUID

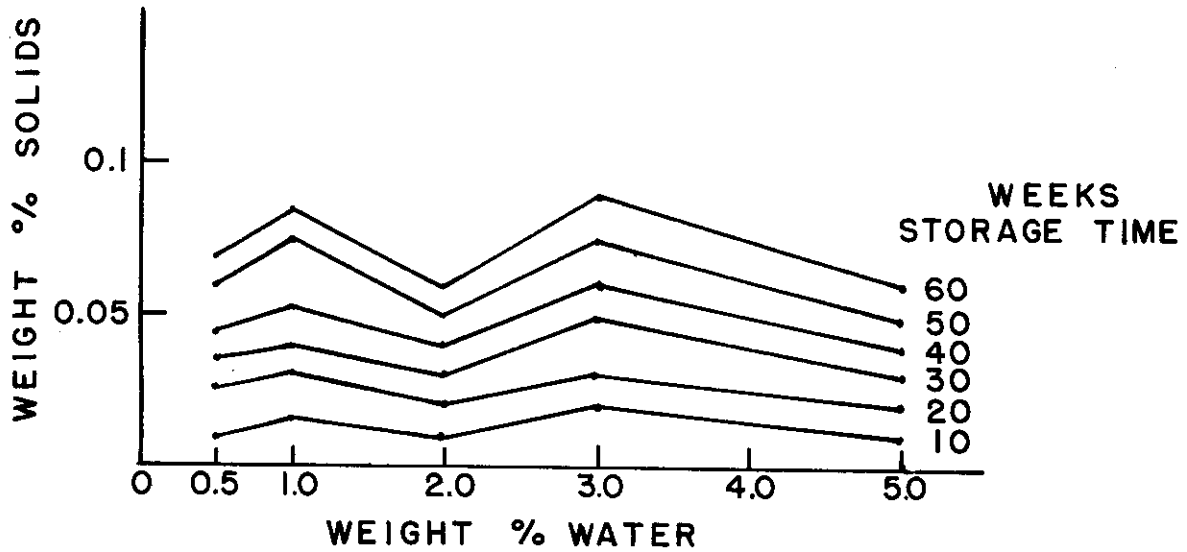


FIGURE 10

EFFECT OF WATER ON STORAGE
OF 8200 FLUID