3M
COMPANY

Fluorochemicals

HEPTAFLUOROBUTYRIC ACID

3M
COMPANY

MINNESOTA MINING & MANUFACTURING CO.
NEW PRODUCTS DIVISION
SAINT PAUL 6, MINN.

Exhibit
1008
State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

TABLE OF CONTENTS

APPENDIX

HEPTAFLUOROBUTYRIC ACID

$\boxed{CF_3CF_2CF_2COOH}$

INTRODUCTION

The Central Research Department of Minnesota Mining and Manufacturing Company, in its investigation of Fluorochemicals, has studied the fluorination of aliphatic acids. The physical and chemical properties of these acids have been investigated by the Central Research Department and the New Products Laboratory. The data summarized here have resulted from these investigations. Most of this information has been presented in papers by D. R. Husted and A. H. Albrecht, T. S. Reid and G. H. Smith, E. A. Kauck and A. R. Diesslin, and D. G. Weiblen at the 116th National Meeting of the American Chemical Society at Atlantic City, N. J., September, 1949.

This summary is being presented to acquaint chemists with this example of a completely fluorinated reactive Fluorochemical. Heptafluorobutyric acid is the first new reactive Fluorochemical to be studied extensively at 3M laboratories. Other reactive and non-reactive Fluorochemicals are currently under investigation.

Research quantities of heptafluorobutyric acid are available. Samples will be supplied on request.

Inquiries are solicited concerning this and other 3M Fluorochemicals. Please write:-

Minnesota Mining and Manufacturing Company
New Products Division
St. Paul 6, Minnesota

PHYSICAL PROPERTIES

Formula	$CF_3CF_2CF_2COOH$
Form	Colorless liquid
Formula Weight	214
Odor	Sharp, similar to butyric acid
Boiling Point	120.0°C (735 mm)
Freezing Point	-17.5°C
Density g/cc[1]	1.641 (25°C) 1.562 (60°C)
Viscosity,[1] Centistokes	1.622 (25°C) 0.828 (60°C)
Index of Refraction[2]	n_D^{25} 1.290
Vapor Pressure[1]	44 mm at 56°C 455 mm at 107.4°C 735 mm at 120°C
Heat of Vaporization	11,200 cal./mole 52.3 cal./g } at b.p. (calc.)
Trouton Ratio	28.5
Surface Tension	15.8 Dynes/cm (30°C)

Equivalent Conductance	Concentration (molar)	pH at 29°C	Equivalent Conductance at 27°C mhos/equivalent
	Infinite dilution		390*
	0.001	3.1	383
	0.005	2.3	374
	0.01	2.1	367
	0.02	1.7	357
	0.04	1.5	346
	0.1	1.1	319

*Extrapolated Value

---

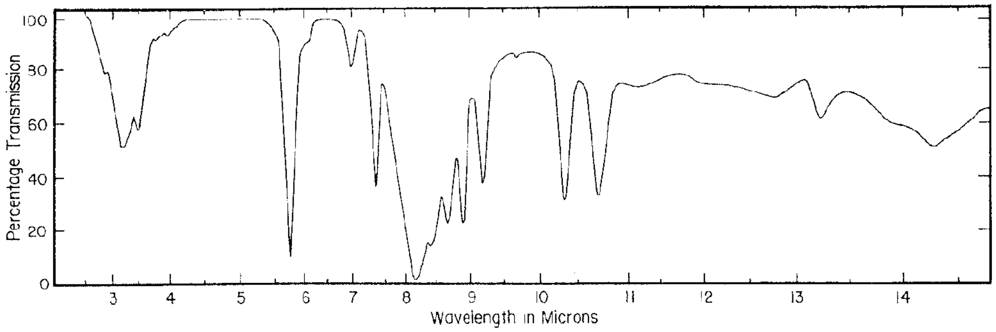
1. See appendix for graph.
2. Varies in fourth place; hygroscopic.

Solubility

Grams acid per 100 grams solvent at 20°C

Acetone	misc.
Benzene	22.3
Carbon Disulfide	insol.
Carbon Tetrachloride	44.3
Ether	misc.
Heptane	2.4
Methanol	misc.
Mineral Oil	insol.
Petroleum Ether (b.p. 30-75°C)	misc.
Water	misc.
Xylene	3.8

Infra-red Spectrum



Cell Thickness 0.013 mm

Corrosion

Aluminum, brass, copper, Monel, nickel, and cold rolled steel showed continuous weight loss when immersed in heptafluorobutyric acid throughout a 120 hour test period at 50°C. Stainless steel showed weight loss in 100 percent acid but was passive to 50 percent and 5 percent solutions for the first 48 hours immersion, and showed unappreciable weight loss in 50 percent and 5 percent concentrations for the duration of the 120 hour test period. Corrosion was generally more severe in half immersed samples than in completely immersed samples. Detailed quantitative results are appended.

CHEMICAL PROPERTIES

Decarboxylation

Decarboxylation of heptafluorobutyric acid on heating in the presence of pyridine and silver oxide gave heptafluoropropane, C_3F_7H, boiling at -17°C to -19°C (741 mm). Heating the acid at 200°C for 4 hours in a sealed tube with excess five percent potassium hydroxide gave a high yield of C_3F_7H, as was the case with ten percent sodium carbonate solution under similar conditions. In water at 150°C, the acid decarboxylated at a much slower rate.

Salts

Heptafluorobutyric acid forms salts with the ease expected of a strong acid. All metallic salts which have been prepared are crystalline except the lead salt; both lithium and lead salts are very hygroscopic. The table gives solubilities and melting points of typical metallic salts.

MELTING POINT AND SOLUBILITY OF METALLIC SALTS

	Heptafluorobutyrate				
	Sodium	Lithium	Calcium	Lead	Silver
Melting Point, °C	240±5	210±2	>350	130d.	130d.

Solubility g/100 g Solvent

Solvent	Sodium	Lithium	Calcium	Lead	Silver
Acetone	127	234	209	75.3	147
Benzene	0.1	0.1	0.1	0.1	101
Ether	0.3	12.2	1.2	5.7	56.5
Methanol	128	124	158	368	59.9
Petroleum Ether (b.p.30-75°C)	0.0	0.0	0.0	0.0	0.0
Water	297	403	130	493	42.2

The S-benzylthiouronium salt of heptafluorobutyric acid melts at 183-4°C, and is soluble only to the extent of 0.4 gram per 100 grams water at 20°C.

For identification purposes, X-ray analysis of the metallic salts has been found useful. The three most prominent Debye-Scherrer X-ray lines (Cu K_{α}) are tabulated for these same salts.

DEBYE-SCHERRER X-RAY LINES OF METALLIC SALTS

	Heptafluorobutyrate				
	Sodium	Lithium	Calcium	Lead	Silver
Interplanar distance in Angstroms	5.13	4.64	5.36	amorphous	12.3
	4.24	4.18	3.87		4.24
	4.64*	2.64	7.21		6.29

*Probably K_{β}

Esters

A number of typical esters of heptafluorobutyric acid have been prepared and characterized. Esters of primary and secondary alcohols have been prepared by direct esterification with a mineral acid catalyst. For example, ethyl heptafluorobutyrate was obtained in 83 percent yield (crude).

$$C_3F_7COOH + C_2H_5OH \xrightarrow{HCl} C_3F_7COOC_2H_5$$

Methyl heptafluorobutyrate was obtained in 89 percent yield by reaction of the acid with an excess of methanol in the presence of sulfuric acid.

$$C_3F_7COOH + CH_3OH \xrightarrow{H_2SO_4} C_3F_7COOCH_3$$

The ester was also formed from heptafluorobutyramide and methanol in the presence of an excess (more than two moles) of sulfuric acid; the yield was 52 percent.

$$C_3F_7CONH_2 + CH_3OH \xrightarrow{H_2SO_4} C_3F_7COOCH_3$$

Use of the anhydride offers the usual preparative advantage. The n-octyl ester was prepared in good yield using an excess of anhydride, which was recoverable along with the acid formed.

$$(C_3F_7CO)_2O + C_8H_{17}OH \longrightarrow C_3F_7COOC_8H_{17} + C_3F_7COOH$$

The t-butyl ester was prepared from t-butyl chloride and silver heptafluorobutyrate.

$$C_3F_7COOAg + C_4H_9Cl \longrightarrow C_3F_7COOC_4H_9$$

Due to the reactivity of the ester, this preparation had to be accomplished under anhydrous conditions.

The polymerizable ester, vinyl heptafluorobutyrate, was obtained by the catalyzed addition of heptafluorobutyric acid to acetylene.

$$C_3F_7COOH + CH \equiv CH \longrightarrow C_3F_7COOCH = CH_2$$

Ethylidene heptafluorobutyrate, $CH_3CH(OOCC_3F_7)_2$, was also obtained in this manner.

The table gives physical properties of typical esters of heptafluorobutyric acid.

ESTERS OF HEPTAFLUOROBUTYRIC ACID

	B.P., °C	n_D^{20}	d_4^{20}
Methyl Heptafluoro - butyrate [1]	79 (737 mm)	1.293	1.483
Ethyl Heptafluoro-butyrate [2]	95 (744 mm)	1.3032	1.394
Isopropyl Heptafluoro-butyrate [3]	106 (739 mm)	1.310	1.324
n-Butyl Heptafluoro-butyrate	132 (740 mm)	1.3249(25°)	1.296
s-Butyl Heptafluoro-butyrate	126 (741 mm)	1.3212(25°)	1.284
t-Butyl Heptafluoro-butyrate [4]	116 (740 mm)	1.318	1.278
4-Hydroxybutyl Heptafluorobutyrate	141.6-142 (742 mm)	1.3579	
Vinyl Heptafluoro-butyrate	79 (748 mm)	1.3086	1.405
2-Hydroxyethyl Heptafluorobutyrate	44 (3.5 mm)	1.3325	1.542
n-Octyl Heptafluoro-butyrate	108 (27 mm)	1.3582(25°)	1.185
n-Dodecyl Heptafluoro-butyrate	158 (23 mm)	1.3802(25°)	1.120
n-Hexadecyl Heptafluoro-butyrate	208 (31 mm)	1.3950(25°)	1.074
n-Octadecyl Heptafluoro-butyrate	185 (4 mm)	1.4020(25°)	
1,3-Bis(heptafluoro-butyroxy) - 2-ethylhexane	145 (35 mm)	1.3488(25°)	1.413

[1] m.p. -86°C
[2] pour point -99 ± 3°C
[3] m.p. -84°C to -90°C
[4] m.p. -92°C

A qualitative study of the rates of hydrolysis of n-butyl, s-butyl, and t-butyl heptafluorobutyrates in heterogeneous systems has shown that all three esters are relatively susceptible to attack by 0.025 N sodium hydroxide solution at 20°C. In water and in 0.03 N hydrochloric acid, the primary and secondary esters hydrolyzed slowly; the tertiary ester hydrolyzed more rapidly than the other two.

In homogeneous solution with acetone as a co-solvent, all three esters hydrolyzed very rapidly in the presence of dilute alkali, the tertiary ester rate being considerably slower than the others, which were practically instantaneous. In the absence of alkali, hydrolysis of all three esters was slower in homogeneous systems.

Anhydride

Heptafluorobutyric anhydride was prepared in 95 percent yield by the action of an excess of phosphorous pentoxide on the acid.

$$2\ C_3F_7COOH \xrightarrow[\text{reflux}]{P_2O_5} (C_3F_7CO)_2O$$

The compound was also prepared from the acid chloride and the sodium salt.

The physical properties of heptafluorobutyric anhydride are as follows: b.p. 107-107.5°C (730 mm); m.p. -45 ± 1°C; n_D^{20} 1.285; d_4^{20} 1.665 g/cc.

Acid Halides

Heptafluorobutyryl chloride has been synthesized from the acid and phosphorous pentachloride in better than 90 percent yield.

$$C_3F_7COOH \xrightarrow{PCl_5} C_3F_7COCl$$

The acid bromide resulted from the action of bromine and phosphorous on heptafluorobutyric acid. The acid iodide was formed from the acid chloride and calcium iodide. The acid fluoride was isolated from the reaction of the acid chloride and silver fluoride.

Physical properties of the four acid halides are tabulated:

HEPTAFLUOROBUTYRYL HALIDES

Heptafluorobutyryl	B.P., °C	n_D^{20}	d_4^{20}
Fluoride	7-7.5 (741 mm)		
Chloride	38-9 (740 mm)	1.288	1.55
Bromide	52-4 (748 mm)	1.3261	1.735
Iodide	75-6 (736 mm)	1.3562	2.00

Amides

Heptafluorobutyramide has been prepared by acylation of ammonia with either the acid halide, anhydride, or ester.

$$C_3F_7COCl + NH_3 \longrightarrow C_3F_7CONH_2$$

$$(C_3F_7CO)_2O + NH_3 \longrightarrow C_3F_7CONH_2$$

$$C_3F_7COOCH_3 + NH_3 \longrightarrow C_3F_7CONH_2$$

The synthesis of N-substituted amides has been accomplished in straightforward fashion.

$$C_3F_7COCl + (C_2H_5)_2NH \longrightarrow C_3F_7CON(C_2H_5)_2$$

The table lists physical constants of heptafluorobutyramide and some of its derivatives.

HEPTAFLUOROBUTYRAMIDES

	M.P., °C	B.P., °C
Heptafluorobutyramide	105	sublimes
N,N-Diethylheptafluorobutyramide		161 (734.5 mm)
Heptafluorobutyranilide	92.5-93	
p-Bromoheptafluorobutyranilide	105.4-106	
N-Octadecylheptafluorobutyramide	67.5	
Heptafluorobutyric acid hydrazide	76	

Nitrile

Heptafluorobutyronitrile (b.p. -1 to +5°C) has been prepared by dehydration of the amide.

$$C_3F_7CONH_2 \xrightarrow{F_2O_5} C_3F_7CN$$

Alcohol

The alcohol, 1,1-dihydroheptafluorobutyl alcohol, has been formed by reduction of heptafluorobutyric acid or its derivatives. Hydrogenolysis of methyl heptafluorobutyrate over copper chromite catalyst and reduction of the free acid or acid chloride with lithium aluminum hydride have been used to prepare the alcohol.

$$C_3F_7COOCH_3 \xrightarrow[CuCrO]{H_2} C_3F_7CH_2OH$$

$$C_3F_7COOH \xrightarrow{LiAlH_4} C_3F_7CH_2OH$$

$$C_3F_7COCl \xrightarrow{LiAlH_4} C_3F_7CH_2OH$$

This alcohol is comparable to a phenol in acidity. It also resists conversion to an alkyl halide. It can be esterified under conditions used for a phenol.

$$C_3F_7CH_2OH + CH_2{=}CHCOCl \longrightarrow C_3F_7CH_2OOCCH{=}CH_2$$

$$C_3F_7CH_2OH + (CH_3CO)_2O \xrightarrow{C_5H_5N} C_3F_7CH_2OOCCH_3$$

Properties of the alcohol and some of its derivatives are reported.

HEPTAFLUOROBUTYL ALCOHOL

	B.P., °C	n_D^{20}	d_4^{20}
1,1-Dihydroheptafluorobutyl			
Alcohol	95 (750 mm)	1.2944	1.601
Acetate	105 (735 mm)	1.3110	1.435
Acrylate	43 (40 mm)	1.3299	1.420
N-α-Naphthyl-1,1-dihydroheptafluorobutylurethan	m.p. 77-8°C		

Aldehyde

Heptafluorobutyraldehyde has been prepared in 40 percent yield as a co-product with the alcohol by reduction of heptafluorobutyric acid with lithium aluminum hydride. Reduction of heptafluorobutyramide (see under "Amine") also results in the formation of some aldehyde.

$$C_3F_7COOH \xrightarrow{LiAlH_4} C_3F_7CHO$$

This aldehyde resembles chloral in that it forms a stable solid hydrate as well as a diacetate. It is sensitive to alkali. Polymerization occurs readily at room temperature. The behavior in the Grignard reaction is described later (see under "Miscellaneous").

The physical properties of the aldehyde, hydrate, and diacetate are given below:

HEPTAFLUOROBUTYRALDEHYDE

	B.P., °C	M.P., °C	n_D	d_4^{20}
Heptafluorobutyraldehyde	28		1.2730 (4°C)	1.505
Hydrate	93.5	61		
Diacetate	164(743 mm)		1.3378 (20°C)	1.431

Amine

A fluorinated amine, 1,1-dihydroheptafluorobutylamine, has been prepared from heptafluorobutyronitrile and heptafluorobutyramide by the reductive action of lithium aluminum hydride.

$$C_3F_7CN \xrightarrow{LiAlH_4} C_3F_7CH_2NH_2$$

$$C_3F_7CONH_2 \xrightarrow{LiAlH_4} C_3F_7CH_2NH_2$$

Amide reduction gave a 60 percent yield of amine, most of the remaining material being recovered as acid and aldehydrol.

As is the case with the alcohol, the amine bears a closer resemblance to aromatic than to aliphatic hydrocarbon analogs. It is a relatively weak base.

With phosgene, 1,1-dihydroheptafluorobutyl isocyanate was formed.

$$C_3F_7CH_2NH_2 \xrightarrow{COCl_2} C_3F_7CH_2NCO$$

The isocyanate reacted typically with active hydrogen compounds.

Diazotization of the amine hydrochloride in a dichloroethyl ether - water system at low temperature has been accomplished. Subsequent reaction with hydriodic acid gave 1,1-dihydroheptafluorobutyl iodide.

Physical properties of the amine and some of its derivatives are given.

HEPTAFLUOROBUTYLAMINE

	B.P., °C	M.P., °C	n_D^{20}	d_4^{20}
1,1-Dihydroheptafluorobutyl-				
Amine	68 (743 mm)		1.298	1.493
Hydrochloride	sublimes	130-5		
Acid Sulfate		105-20d.		
Isocyanate	91 (737 mm)	-78	1.3152	1.512
Bis(1,1-dihydroheptafluoro-butyl)-urea		118-9		

Miscellaneous Reactions

Grignard

Methyl magnesium iodide added to methyl heptafluorobutyrate, and on hydrolysis there was obtained 2-heptafluoropropyl-2-propanol in 75-77 percent yield.

$$C_3F_7COOCH_3 \xrightarrow{CH_3MgI} C_3F_7C(CH_3)_2OH$$

The carbinol has the following physical properties: b.p. 105-6°C (749 mm); n_D^{20} 1.3279; d_4^{20} 1.415. Dehydration gave 2-heptafluoropropylpropene in 85 percent yield.

$$C_3F_7C(CH_3)_2OH \xrightarrow{H_2SO_4} CH_2{=}C(CH_3)C_3F_7$$

The olefin has the following physical properties: b.p. 53.6°C (733 mm); n_D^{20} 1.3002; d_4^{26} 1.303.

By subjecting heptafluorobutyraldehyde to the action of methyl magnesium iodide, 1-heptafluoropropylethanol was obtained.

$$C_3F_7CHO \xrightarrow{CH_3MgI} C_3F_7CH(CH_3)OH$$

Malonic Ester

Heptafluorobutyryl chloride condensed with diethyl malonate to give the expected product.

$$C_3F_7COCl + CH_2(COOC_2H_5)_2 \longrightarrow C_3F_7COCH(COOC_2H_5)_2$$

(b.p. 122°C, 22 mm)

APPLICATIONS

Known applications for this entirely new acid are obviously unavailable today. It is anticipated that this acid will find an increasing number of uses as a chemical intermediate. The data presented here are reported in an effort to stimulate application testing by others. As additional types of chemical reactions are identified by 3M, they will be reported in the literature and in technical bulletins.

Of particular interest are the low surface tension of the acid, and therefore its high penetrating power; the possibility of introducing the hydrophobic heptafluoropropyl group into organic molecules; and the strong acidity of the compound, coupled with its non-oxidizing and non-oxidizable nature.

The common salts of heptafluorobutyric acid are unusually soluble in water. Since the acid is strong, salts of strong bases are hydrolyzed very little. This may be of interest to metallurgical chemists.

HANDLING

Heptafluorobutyric acid is a very strong acid, and all normal precautions should be observed. Corrosiveness to the skin is due to high acid strength and dehydrating action. In case of accident, exposed areas of the body should immediately be flooded with water, followed by sponging with five percent sodium bicarbonate solution or dilute ammonia.

Heptafluorobutyric acid is very hygroscopic. Sample shipments are made in glass bottles sealed with polystyrene caps containing a Teflon liner. Closures such as cork, rubber, bakelite, and polyethylene are all attacked by the acid. Low surface tension makes tight sealing difficult, as the acid tends to "creep".

TOXICITY

The physiological and toxicological properties of heptafluorobutyric acid are still being investigated. Due precaution should be exercised in its handling and use.

The compound possesses an odor similar to that of butyric acid, and gives adequate warning of the presence of its vapor.

* *

The data contained herein are based on the best available information and are believed to be correct. However, no warranty is expressed or implied regarding the accuracy of these data or the use of these products.

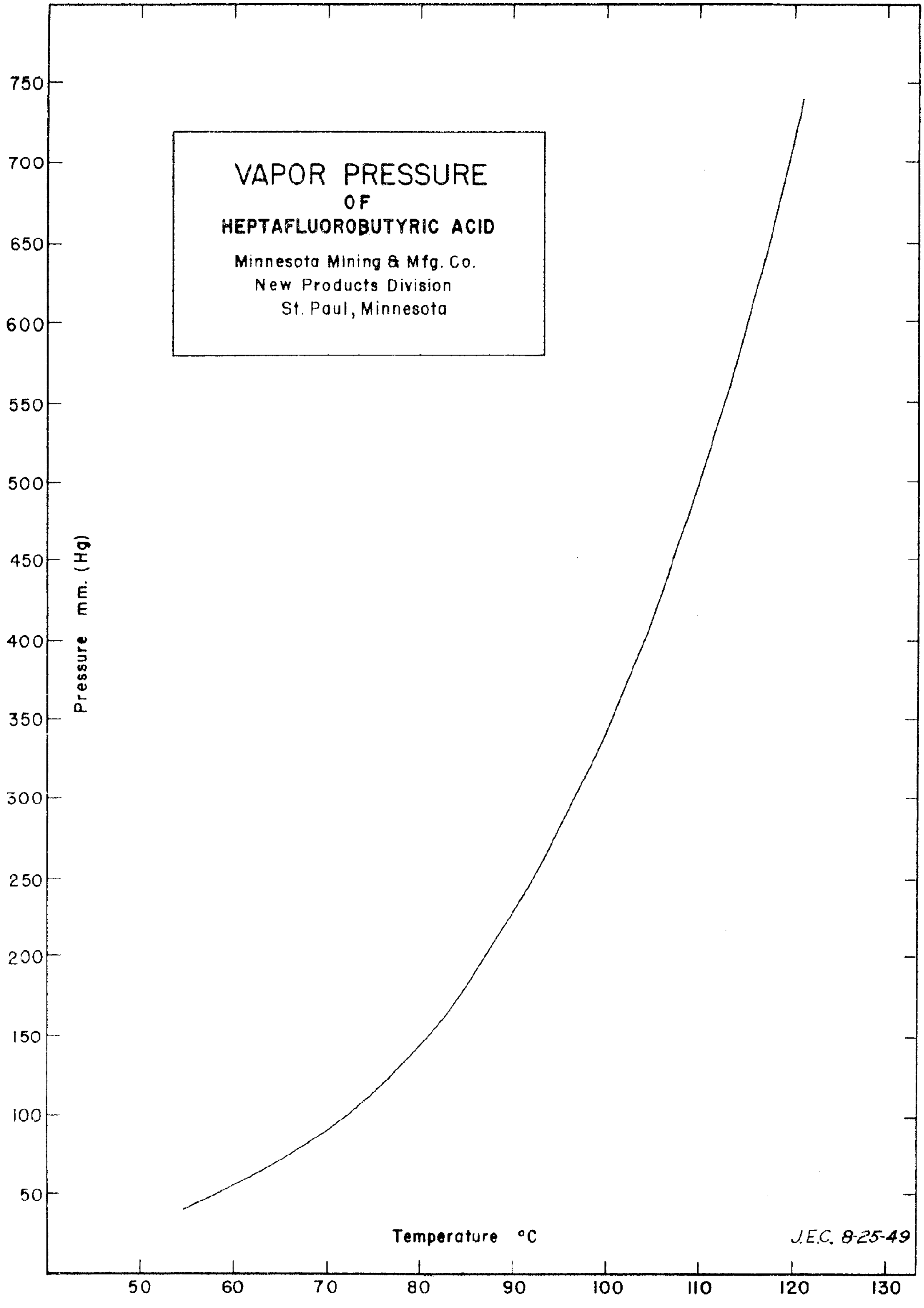
CORROSION OF VARIOUS METALS IN HEPTAFLUOROBUTYRIC ACID

Weight Loss as an Average for 120-Hour Immersion Period

METAL	ALUMINUM 24S		BRASS		COPPER		MONEL		NICKEL		COLD ROLLED STEEL		STAINLESS STEEL-304	
Test Temperature	50°C		50°C		50°C		50°C		50°C		25°C		50°C	
Percent Immersion in Liquid	100	50	100	50	100	50	100	50	100	50	100	50	100	50
Wt. Loss-Mg./Cm.^{2}/24 hr. in 100 Percent Acid	0.31	0.19	3.45	2.97	1.73	2.49	1.99	1.68	4.19	3.98	4.44	4.55	0.49)† 3.90)	0.60)† 2.86)
50 Percent Acid	1.65	2.28	1.19	8.28	2.24)* 0.82)	7.24	1.20	4.55	1.61	4.14	4.27	7.57	0.006	0.008
5 Percent Acid	1.10	0.58	0.68	1.80	0.51	1.62	0.22	1.61	0.28	1.26	1.99	1.73	0.006	0.01
Water	0.01		0.04		0.03		0.03		0.03		0.13		0.03	

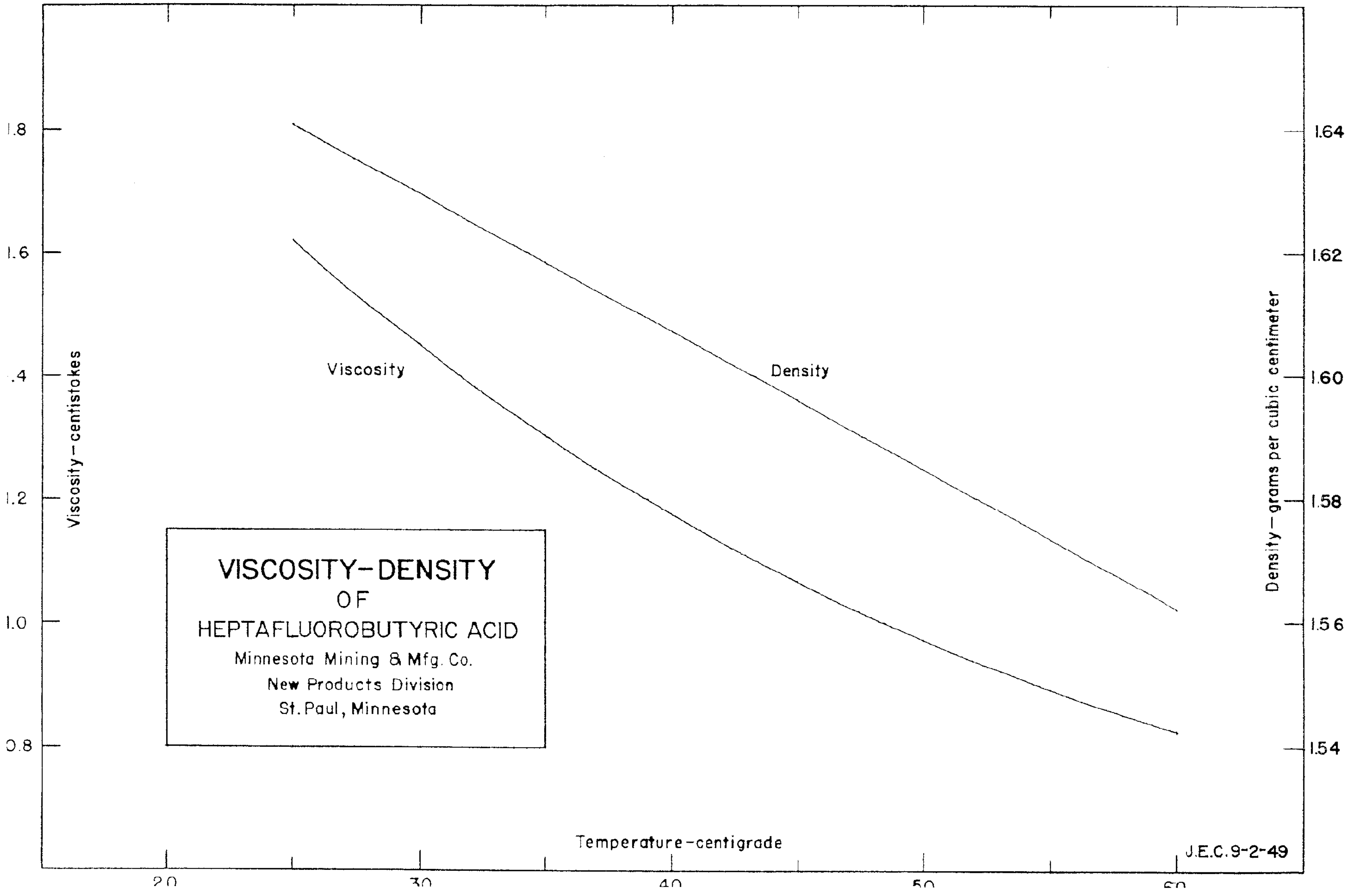
* Smaller value - continuous immersion (120 hours),
larger value - intermittent immersion (24 hour weighings).

† Smaller value - intermittent immersion (24 hour weighings),
larger value - continuous immersion (120 hours).



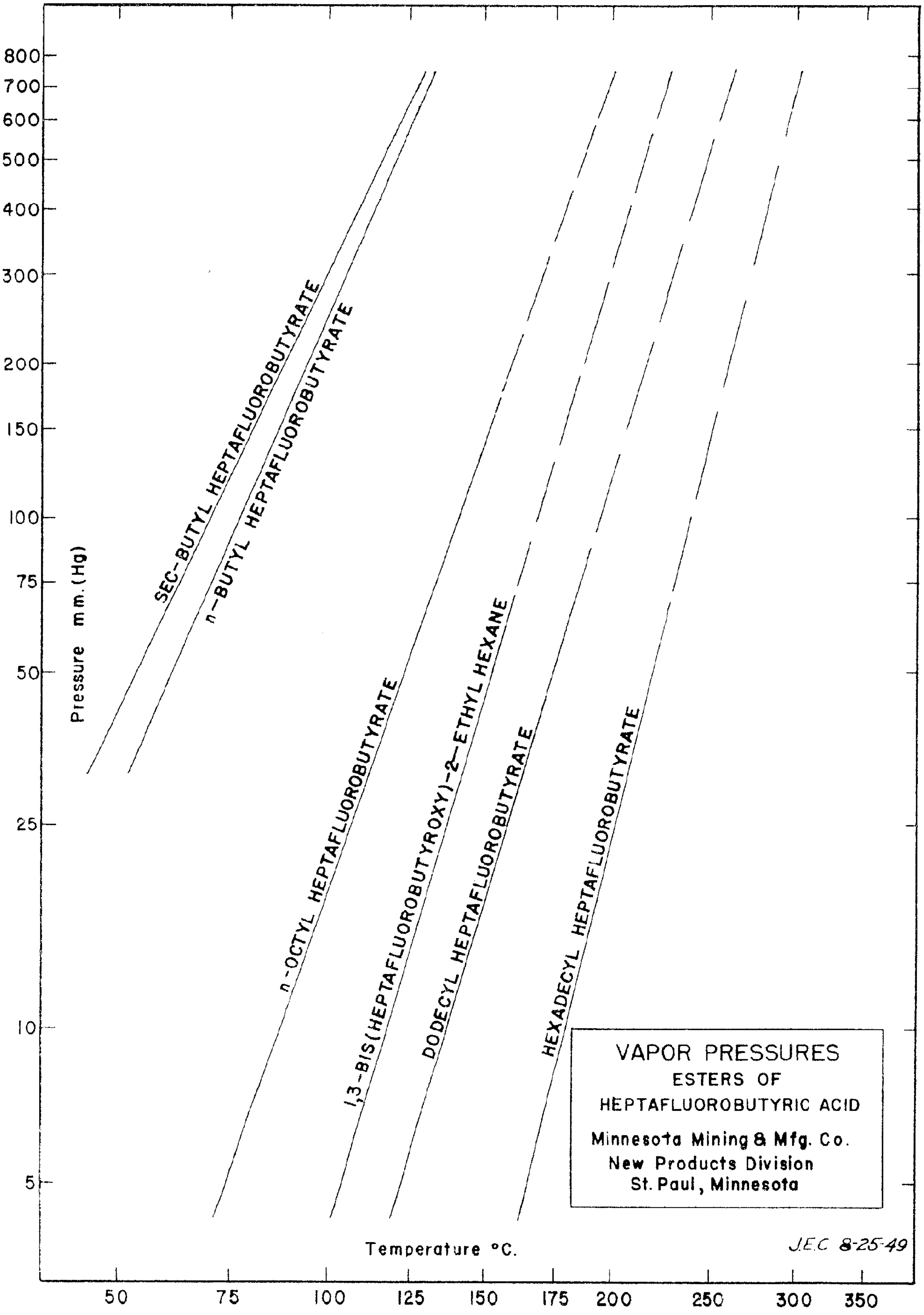
VAPOR PRESSURE
OF
HEPTAFLUOROBUTYRIC ACID
Minnesota Mining & Mfg. Co.
New Products Division
St. Paul, Minnesota

J.E.C. 8-25-49



VISCOSITY-DENSITY
OF
HEPTAFLUOROBUTYRIC ACID

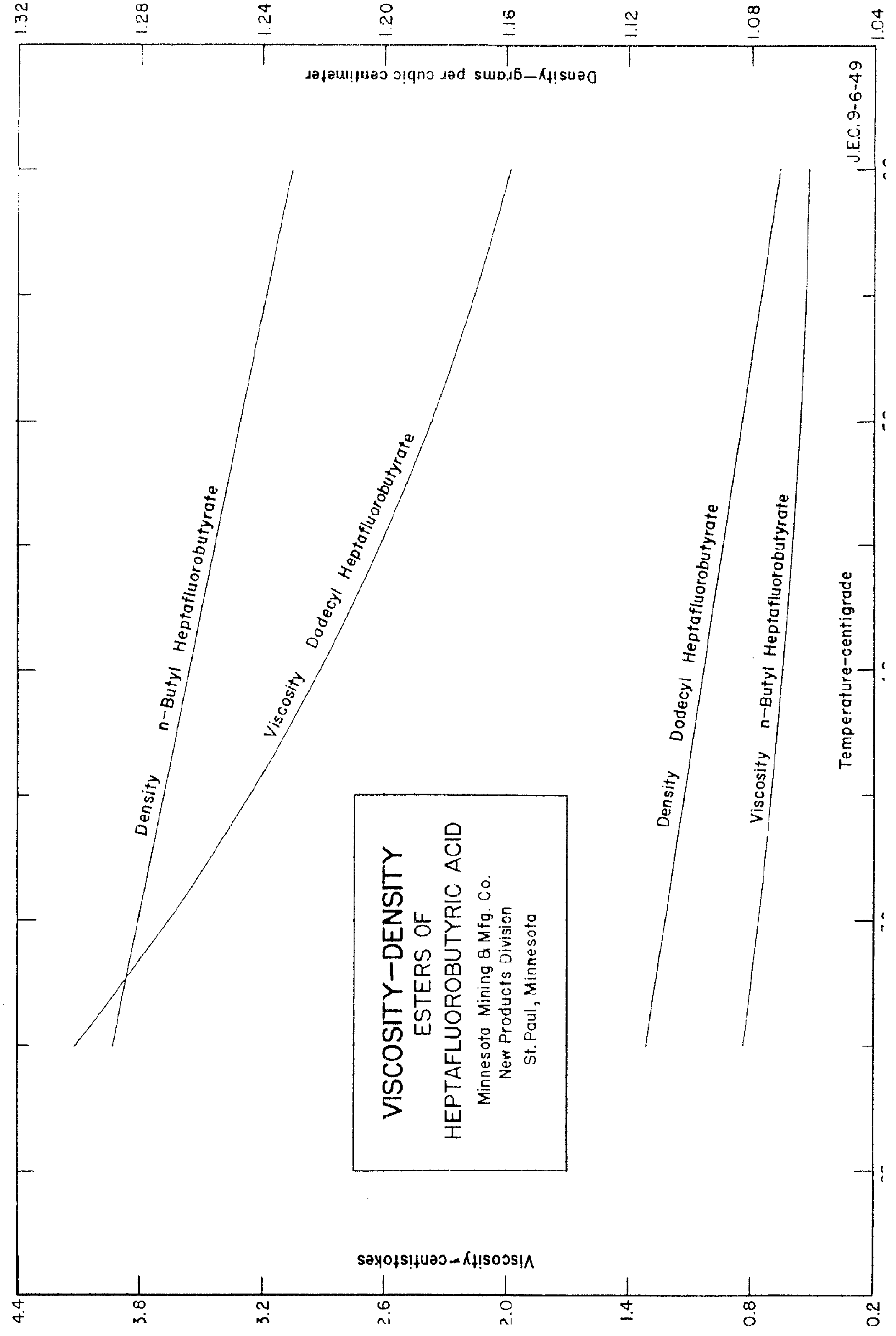
Minnesota Mining & Mfg. Co.
New Products Division
St. Paul, Minnesota



VAPOR PRESSURES
ESTERS OF
HEPTAFLUOROBUTYRIC ACID

Minnesota Mining & Mfg. Co.
New Products Division
St. Paul, Minnesota

J.E.C 8-25-49

VISCOSITY—DENSITY
ESTERS OF
HEPTAFLUOROBUTYRIC ACID
Minnesota Mining & Mfg. Co.
New Products Division
St. Paul, Minnesota
J.E.C. 9-6-49
Density—grams per cubic centimeter
1.32
1.28
1.24
1.20
1.16
1.12
1.08
1.04
Viscosity—centistokes
4.4
3.8
3.2
2.6
2.0
1.4
0.8
0.2
Temperature-centigrade
Density n-Butyl Heptafluorobutyrate
Viscosity Dodecyl Heptafluorobutyrate
Density Dodecyl Heptafluorobutyrate
Viscosity n-Butyl Heptafluorobutyrate

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