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KSS-4386A

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"FREON" PRODUCTS LABORATORY
E. I. du Pont de Nemours & Company
TECHNICAL REPORT

Report Number: KSS-4386A

Subject: Flammability Properties of Propellant
Blends

Company: "Freon" Products Division

By: P. A. Sanders Date: August 13, 1963

Object: To report miscellaneous flammability data
for various propellant blends. These data
were obtained since the last report (KSS-4386)
on the flammability properties of propellant
blends.

Results: The following data were obtained:

1. The flammability limit curves in air of the following propellant blends:
 - a. "Freon" 12/isobutane blends
 - b. "Freon" 12/"Freon" 11 (50/50)/isobutane blends
 - c. "Freon" 12/propane blends
2. The lower flammability limits in air of "Freon" 12/"Freon" 11/
ethyl chloride blends.
3. The flash point of some common propellant blends.

EID10147

- 2 -

Comments:I. Flammability Limits in Air of "Freon" Propellant/
Hydrocarbon BlendsA. Procedure and Apparatus

The flammability limits in air of the various "Freon" propellant/hydrocarbon blends were determined with the modified closed drum apparatus using match ignition. This apparatus has been described in a previous report (Reference 1).

In order to obtain sufficient data to construct a flammability limit curve for the blends, varying concentrations of "Freon" propellant/hydrocarbon blends and also the hydrocarbons alone were discharged into the drum. The gas mixture in the drum was sampled for subsequent gas chromatographic analysis, after thorough mixing, and then tested for flammability using match ignition. If no explosion occurred, the drum was aired thoroughly and a larger quantity of the "Freon" propellant/hydrocarbon mixture was discharged into the drum and the mixture again tested for flammability. This procedure was repeated until an explosion was obtained. Only two gas samples were analyzed for each propellant blend - the mixture that exploded and the mixture immediately preceding that did not explode. This procedure has been described in detail in Reference 2.

By using a variety of blends having different "Freon" propellant/hydrocarbon ratios, it was possible to obtain a number of different concentrations of the mixtures in air that were both explosive and nonexplosive. These data were used to construct flammability limit curves in air.

B. Construction and Significance of the Flammability Limit
Curves

In order to construct the flammability limit curves in air, it is also necessary to have both the lower and upper flammability limits of the hydrocarbons alone. The lower limits were determined using the modified closed drum as described above. The published values for the upper limits were used in the curves (Reference 3). A comparison of the published values of the lower flammability limits of the hydrocarbons (Reference 3) with the limits that were obtained with the closed drum is shown in Table I and indicates that the agreement between the two sets of data is quite good.

EID10148

TABLE I

Flammability Limits of Hydrocarbons In Air

<u>Hydrocarbon</u>	<u>Lower Flammability Limit</u> <u>(Vol % in Air)</u>			<u>Upper Flammability</u>
	<u>Modified Closed Drum</u>			<u>Limit (Vol % in Air)</u>
	<u>Nonexplosive</u>	<u>Explosive</u>	<u>Published</u>	<u>Published Data</u>
Propane	1.9	2.4	2.2	9.5
Isobutane	1.3	1.7	1.8	8.4

The data are illustrated graphically for the following "Freon" propellant/hydrocarbon blends:

1. "Freon-12"/isobutane----- Figure 1
2. "Freon-12"/"Freon-11" (50/50)/isobutane ---- Figure 2
3. "Freon-12"/propane ---- Figure 3

On each graph, two different "Freon" propellant/hydrocarbon blends are shown in which the ratios are shown in wt %. The concentrations of the hydrocarbon in the blends differ by 1%. The blend with the higher concentration of hydrocarbon was found to explode in the drum while that with the lower concentration did not explode at any concentration in air. This is the lower flammability limit of the "Freon" propellant/hydrocarbon blend and these data have been reported previously (Reference 1). Since the blend with the lower concentration of hydrocarbon did not explode in air, the flammability limit curve cannot intersect this line since the line represents nonexplosive mixtures. In drawing the flammability limit curves, therefore, the lower limit was drawn to a point close to the lower flammability limit line and then curved and extended to the upper flammability limit of the hydrocarbon alone.

A line is also drawn on the charts which indicates the compositions of blends having a concentration of 13 volume % in air. The reason for this is that it indicates which particular blends may be shipped as nonflammable. According to Agent T. C. George's Tariff No. 13, Interstate Commerce Commission Regulations, paragraph 73.300, a compressed gas is classified as a flammable compressed gas if:

- (1) A mixture of 13% or less (by volume) with air forms a flammable mixture or,
- (2) the flammability range with air is greater than 12 per cent regardless of the lower limit.

A survey of Figures 1 and 2 shows that there are certain mixtures which will explode in air but which are classified as nonflammable by the ICS regulations since the concentrations at which they explode in air are greater than 15 volume per cent. Examples of mixtures of this type shown in Figures 1 and 2 are "Freon-12"/isobutane (88/12) wt % and "Freon-12"/propane (89/11) wt % mixtures. All mixtures of "Freon-12"/"Freon-11" (50/50)/isobutane that explode in air do so at concentrations less than 15 volume per cent and, therefore, would be classified as flammable by the ICS regulations.

The flammability limits in air of "Freon-12"/propane mixtures have also been determined by the Bureau of Mines (Reference 4). A comparison of the limits of flammability of the mixtures as determined by the Bureau of Mines with the limits obtained by the "Freon" Products Laboratory is shown in Figure 4. The "Freon" Products Laboratory data indicates the flammability limits of the "Freon-12"/propane mixtures to be slightly lower than the Bureau of Mines data. For example, mixtures containing more than 10.2 wt % propane would be flammable by the "Freon" Products Laboratory data. According to the Bureau of Mines data, mixtures could contain up to 11.5% propane before the mixtures were flammable.

The reason for the slightly lower limits obtained at the "Freon" Products Laboratory is that the 55-gallon modified drum used for the determinations tends to give lower limits than the small eudiometer tube used by the Bureau of Mines. This has been discussed in detail in Reference 5.

II. Lower Flammability Limits of "Freon-12"/"Freon-11"/Ethyl Chloride Blends

The lower flammability limits of the "Freon" propellents with blends of dimethyl ether, isobutane, propane, and vinyl chloride have been reported in Reference 1. The present data for ethyl chloride blends was obtained in exactly the same way as that for the blends reported in Reference 1. The data for the "Freon-12"/"Freon-11"/ethyl chloride blends are illustrated on the triangular coordinate chart in Figure 5. Compositions that do not form explosive mixtures in air when completely vaporized are illustrated in Figure 5 and also compositions that do not form explosive mixtures in air at any time during evaporation.

Vapor pressure data for all blends of "Freon-12", "Freon-11", and ethyl chloride are illustrated on the triangular coordinate chart in Figure 6. The procedure for obtaining the vapor pressure data is described in Reference 1.

III. Flash Point of Common Propellant Blends

The flash points of propellant blends are of interest in connection with the proposed New York City Fire Department Regulations. The flash points of the following propellant blends were determined using the Tagliabue open cup. The blends were cooled to below -50°F. before starting the flash point determination. The results are listed in Table II. Duplicate determinations were carried out and both results are given.

TABLE IIFlash Points of Common Propellant Blends

<u>Propellant Blends</u>	<u>Flash Point (°F)</u>
"Freon-12"/propene (91/9)	-8°, -72
"Freon-12"/vinyl chloride (91/9)	No flash to dryness
"Freon-12"/"Freon-11" (50/50)/vinyl chloride (85/15)	No flash to dryness
"Freon-11"/vinyl chloride (92/8)	No flash to dryness
"Freon-11"/dimethyl ether (94/6)	-9°, -13
Propellant A ("Freon-12"/"Freon-11" (50/50)/isobutane (90/10)	No flash to dryness
Propellant F ("Freon-12"/"Freon-11"/dimethyl ether (75/20/15)	3, 8

Flammability Limits of "Freon-12"/Isobutane Mixtures in Air

Figure 1

Volume P cent Isobutane

Compositions of blends at a concentration of 13 volume per cent in air

"Freon-12"/Isobutane (13/87) in air
at 101.3 kPa (1 atm) and 25°C

Flammable Region

"Freon-12"/Isobutane (13/87) in air
at 101.3 kPa (1 atm) and 25°C

O = Explosion
X = No explosion

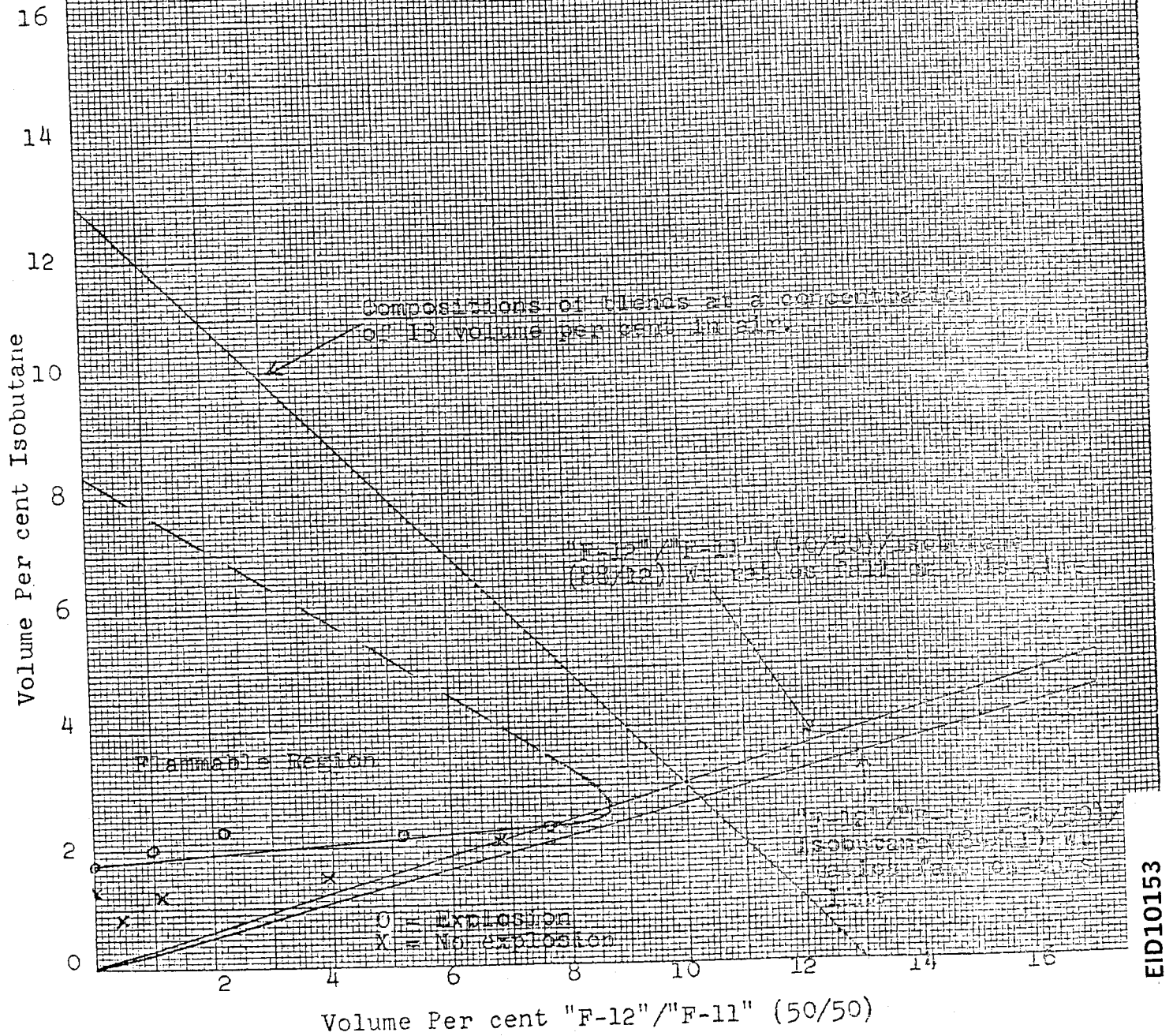
0 2 4 6 8 10 12 14 16

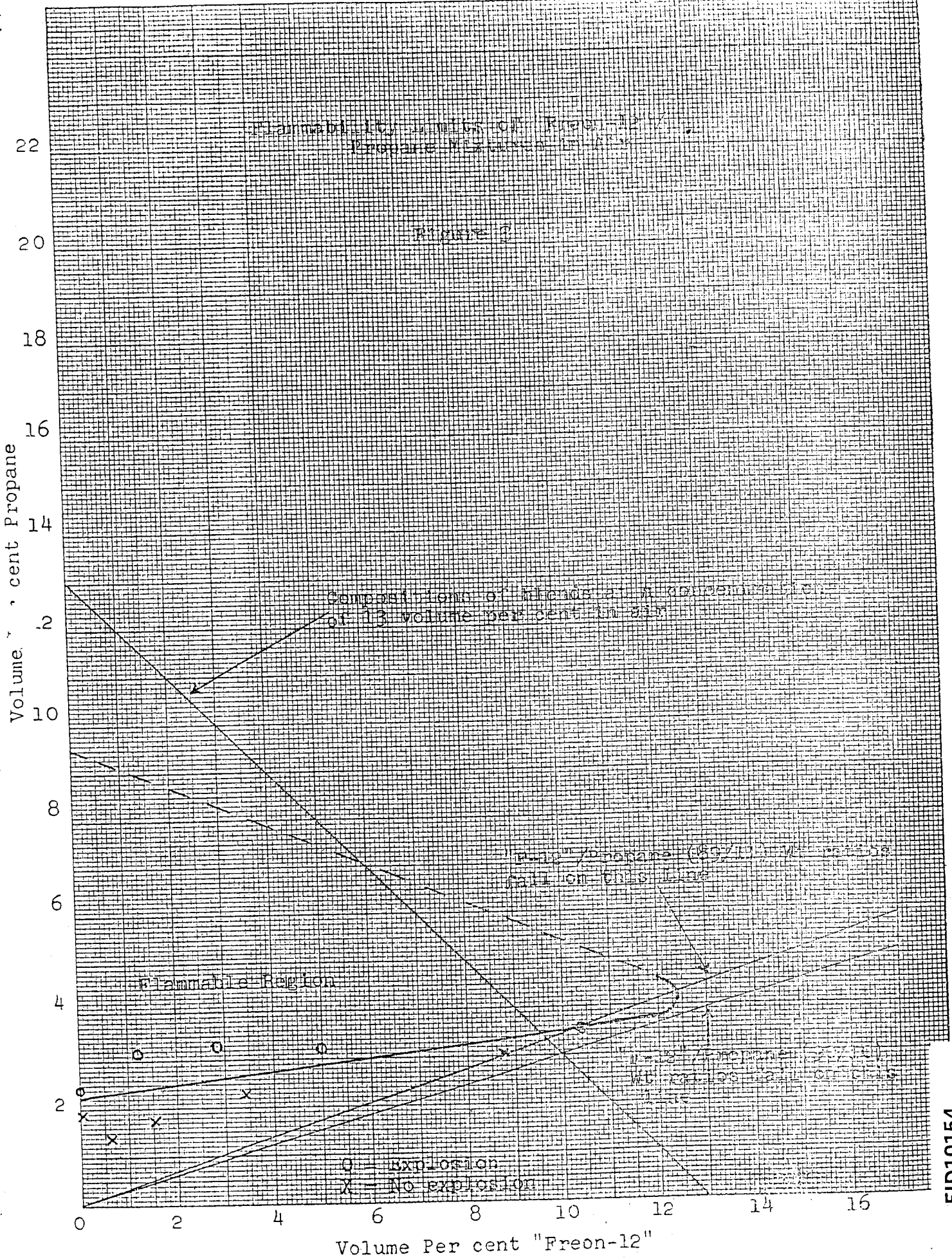
Volume Per cent "Freon-12"

EID10152

Flammable Limits of
"Freon-12"/"Freon-11" (50/50)/
Isobutane Mixtures in Air

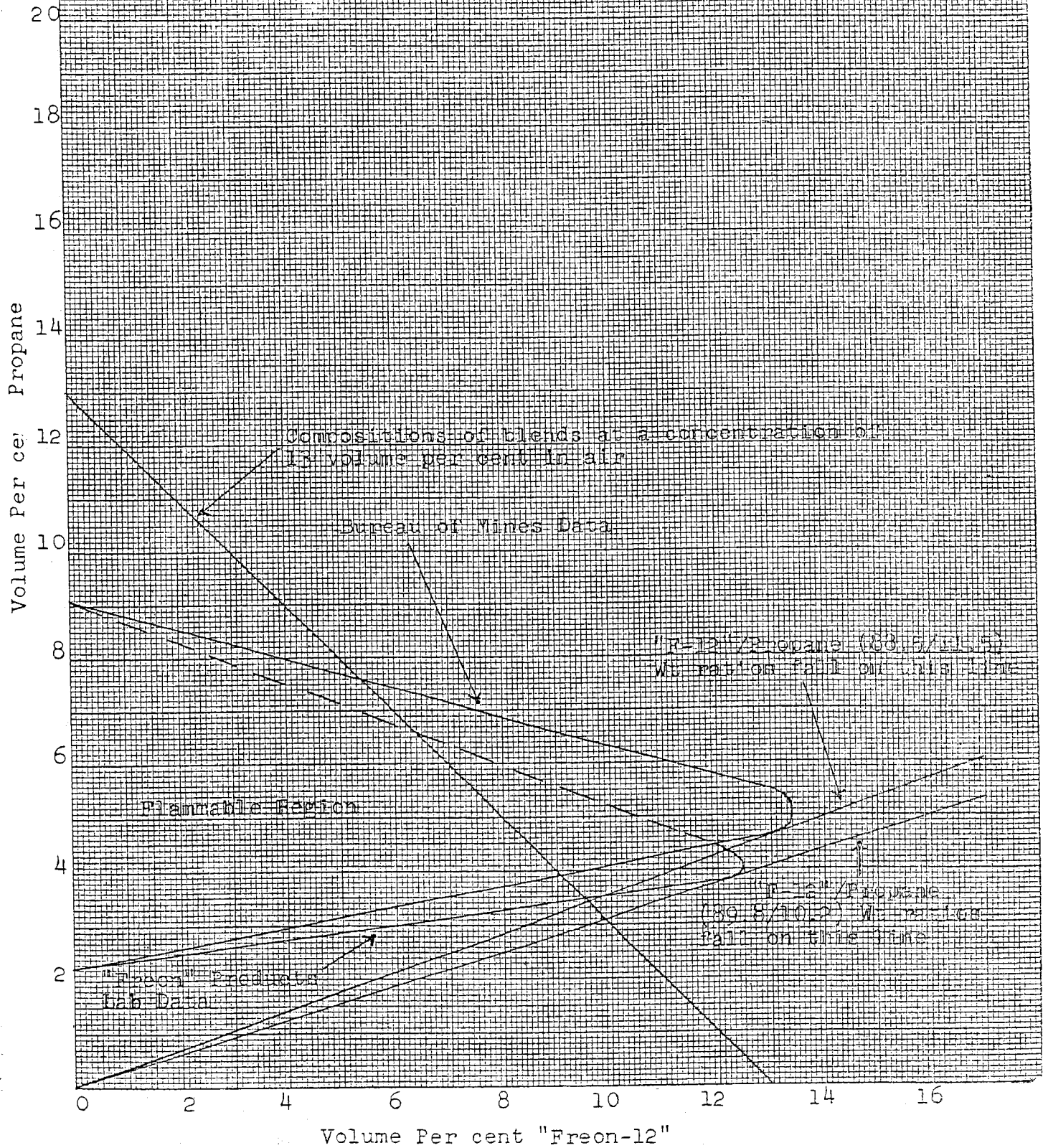
Figure 2





Comparison of Flammability Limits
of "Freon-12"/Propane Mixtures As
Determined by the Bureau of Mines
and the "Freon" Products Laboratory

Figure 2



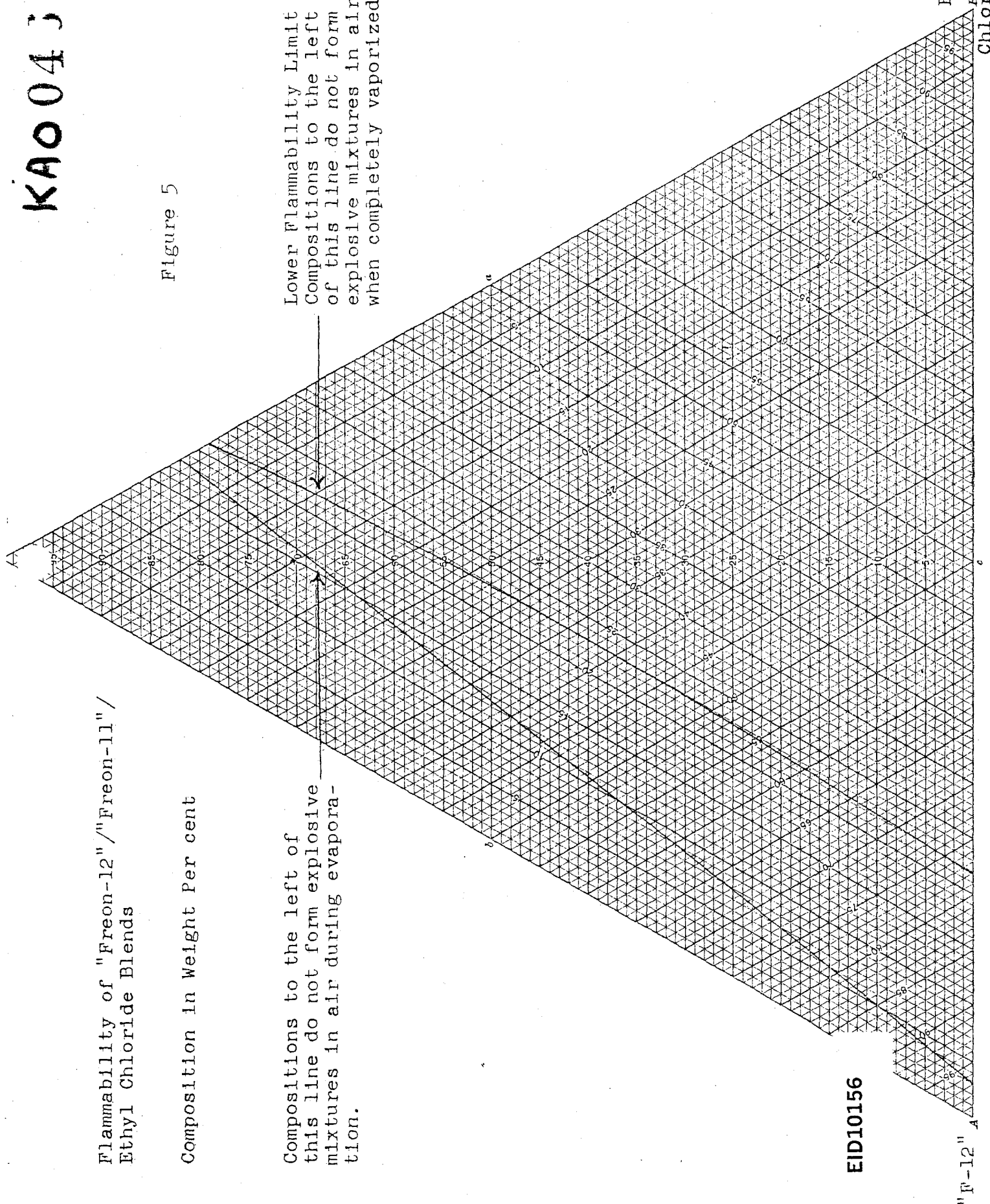
Flammability of "Freon-12"/"Freon-11"/
Ethyl Chloride Blends

Composition in Weight Per cent

Compositions to the left of
this line do not form explosive
mixtures in air during evapora-
tion.

Lower Flammability Limit -
Compositions to the left
of this line do not form
explosive mixtures in air
when completely vaporized.

Figure 5



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"F-12"

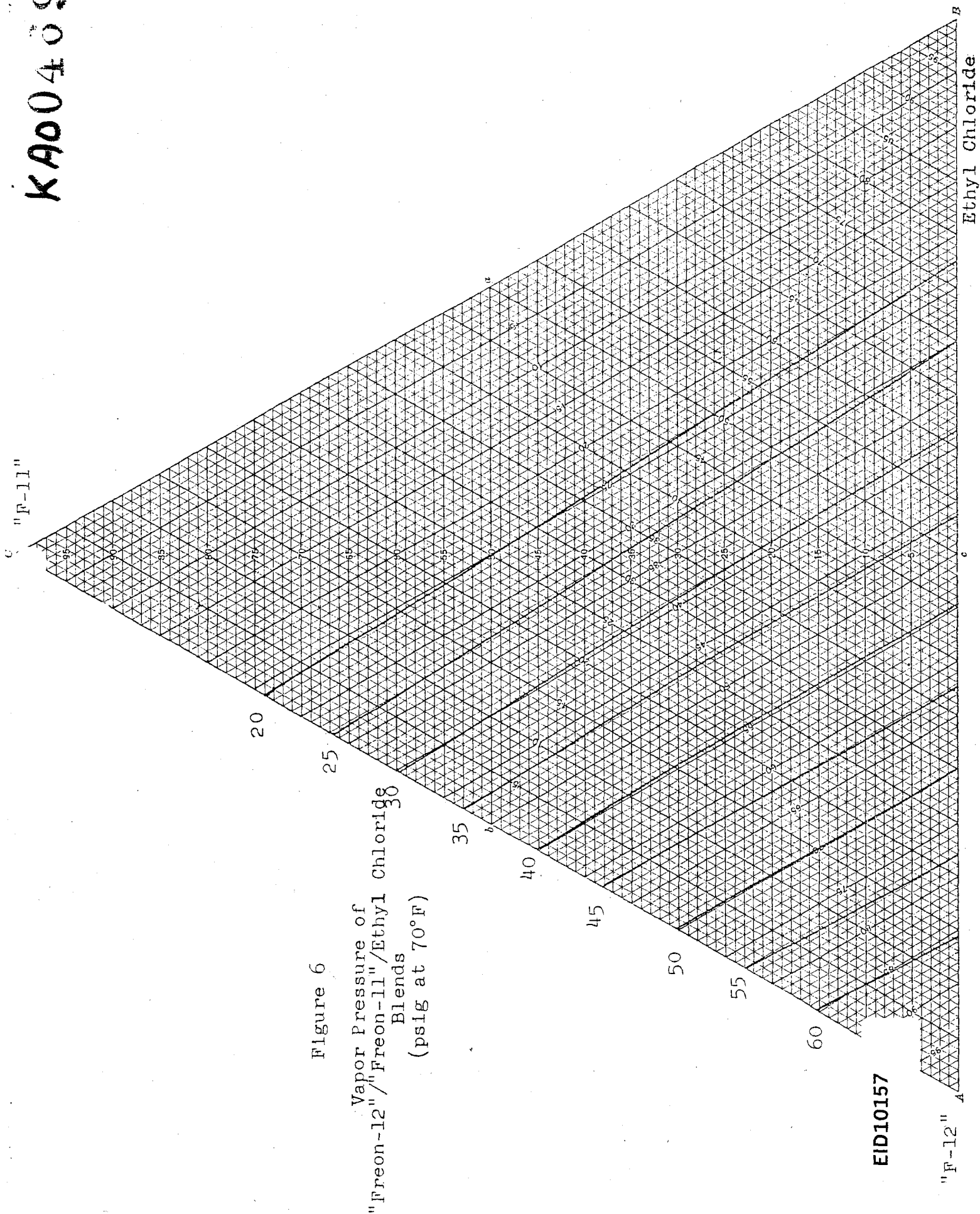
A

B

C

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Report Number:

KSS-4386A

Company:

"Free" Products Division

Action:

None

References:

1. KSS-4386
2. KSS-2858A
3. Matheson Gas Data Book, The Matheson Company, Inc., 1961
4. Bureau of Mines Report RI 4502
5. KLLB-317, 334
6. Memo, PIRed to PASanders, 1/29/63

Period Covered by Experimental Work:

2/14/63 - 7/12/63

Chemist's Time:

10 hours

Technician's Time:

42 hours

Total Cost:

\$400

District:

Wilmington

Class:

II

Investment Account:

Aerosol

Classification:

Nontechnical

MSS Date:

7/30/63

Date Typed:

8/13/63

/pb

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A-2310
PAS

CC: D. E. Kvalnes - Orchem, Wilmington
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"FREON" PRODUCTS LABORATORY
CHESTNUT RUN

January 29, 1963

TO: P. A. SANDERS

FROM: F. T. REED

FLASH POINT OF NONFLAMMABLE PROPELLANT BLENDS

At the Ponte Vedra sales meeting I mentioned that I was concerned about the flash point of the so-called nonflammable propellant blends when the flash-point method prescribed by the New York City Fire Department is used. Would you please select a few blends which are near the borderline of being nonflammable both as gases and liquids and run flash points on these blends starting at -50°F.

Our data implies that these blends would have no flash point but we cannot be certain of this when the flash point is started at -50°F. In developing our data on flammable fractions I believe the starting temperatures were much higher than -50°F; therefore, it is possible that a flammable fraction could be produced at a lower starting temperature. If this is so, the blend would be considered flammable or extremely flammable by the proposed New York City Fire Department Regulations.

FTR:bkf