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A CONVAIR DIVISION OF GENERAL DYNAMICS CORPORATION

FR-3063

PREPRODUCTION TEST REPORT

FOR

THE DETERMINATION OF HYDROCARBON CONTAMINANTS IN TRICHLOROETHYLENE IN CONCENTRATIONS OF APPROXIMATELY 10 PARTS PER MILLION

Spec. No. AR-270-1-11A

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1.0 INTRODUCTION:

The investigations described in this report were carried out to develop a method of determining low concentrations of greases and oils in commercial trichlorethylene which would be more economical than the present procedure described in AR-270-1-11A. The test request specified that infra-red spectrophotometric and vapor phase chromatographic methods be considered, and that the method developed should be capable of detecting hydrocarbons in concentrations below 12.5 ppm with an accuracy of ± 1.25 ppm.

2.0 SUMMARY OF RESULTS:

Analysis of the samples by gas chromatography was ruled out because of the lack of volatility of the hydrocarbon contaminants.

Infra-red techniques applied in this test were incapable of accurately determining hydrocarbons in trichlorethylene in concentrations below 50 ppm.

The application of nuclear magnetic resonance techniques to the problem was found to be impractical because commercial trichloroethylene has an NMR spectra whose secondary peaks coincide with those due to hydrocarbons.

3.0 TEST SPECIMENS:

The trichloroethylene from which the sample solutions were made was the commercial grade of tricholoethylene, inhibited, manufactured by Dupont Corp. under the name "Triclene-D".

The material used to simulate a hydrocarbon contaminant was USP heavy grade mineral oil, having a specific gravity at 70°F of 0.885.

4.0 TEST PROCEDURE:

4.1 Gas Chromatography - To determine if the sample under consideration was suitable for analysis by gas chromatography, the maximum temperature at which all the material volatilezed was determined. A sample of trichloroethylene which had been used for degreasing was obtained and the solvent evaporated at 80°C. The oily residue was transferred to a ceramic crucible, placed on an aluminum heating block, and surrounded with insulating material. The temperature of the block was increased and when it had reached 225°C, the residue began to smoke. When the temperature reached 300°C, there remained some oily material in the crucible, but considerable charring had taken place.

4.2 Infra-Red Spectrophotometry - To determine if low concentrations of hydrocarbons in trichlorethylene could be quantitatively determined by infra-red methods, standard samples of mineral oil in trichloroethylene were made up ranging in concentration of hydrocarbons from 100 ppm to 10 ppm. The infrared absorbance of these solutions was determined using a Beckman IR4 instrument. Mineral oil was selected as a hydrocarbon contaminant most similar to those present in trichloroethylene which had been used as a degreaser.

A double beam technique was used in analyzing the solutions, the reference cell containing commercial trichloroethylene from the same source as used to prepare the standard solutions. The cell windows were KBr. The cell path length was 2 mm. Absorbance of the solutions at the 3.45 micron C-H stretching frequency was measured.

In an effort to achieve the best resoltuion of the spectra and the most reproducible data, a variety of combinations of such variables as slit width, gain and scanning speed was used. Final data was taken from spectra run at a gain of 2% and slit width of 0.10 at 3.45 microns. The scanning speed across the peak was .08 microns/minute.

A scale expander was used for all the measurements. It was adjusted so that the height of the 3.45 micron peak of the 100 ppm solution was at a maximum.

An attempt was made to measure the solutions using cells of 4 mm path length, but the energy transmission through cells of this size filled with trichloroethylene was so low that the absorbance of even the 100 ppm concentrations of mineral oil could not be determined.

As a comparison, a similar set of measurements, using the same operating parameters, was made on a set of solutions of carbon tetrochloride containing mineral oil in the same concentrations as the trichloroethylene solutions.

4.3 Nuclear Magnetic Resonance - The nuclear magnetic resonance spectra of commercial trichloroethylene, and standard concentrations of mineral oil in the solvent were determined in an attempt to apply the technique to the analytical problem.

5.0 TEST RESULTS:

5.1 Gas Chromatography - On heating a sample of trichloroethylene which had been used for degreasing purposes, it was found that there were components present which had comparatively high boiling points or were not volatile at all. Because of the lack of volatility of these components, analysis by gas chromatography is obviously not indicated.

5.2 Infra-Red Spectrophotometry - Under none of the operating conditions described under the test procedure was it possible to produce reproducible infra-red spectra of hydrocarbons in trichloroethylene in concentrations less than 50 ppm. A plot of the absorbance function of concentrations from 50 to 100 ppm is included as Figure 1.

Absorption measurements were made in corresponding solutions of carbon tetrachloride containing hydrocarbons in concentrations as low as 10 ppm with none of the difficulty experienced in measuring the trichloroethylene solutions. Variation of measurement of the carbon tetrachloride solutions at the 10 ppm level resulted in errors in hydrocarbon concentration within the specified limits (1 ppm at 12.5 ppm concentration). A plot of the absorbance functions of these solutions ranging in concentration from 10 to 100 ppm is included as Figure 2.

5.3 Nuclear Magnetic Resonance - Examination of the trichloroethylene solutions by nuclear magnetic resonance techniques indicated that commercial trichloroethylene has an NMR spectra whose secondary peaks occur at the same frequency as those due to hydrocarbons in the solvent. The presence of these peaks, which presumably are caused by organic inhibitor in the solvent, make it impossible to detect the presence of hydrocarbons in low concentrations.

6.0 RECOMMENDATIONS:

Of the analytic approaches applied in this test to the determination of hydrocarbons in trichloroethylene, infra-red spectrophotometry appears to be most appropriate. However the sensitivity of the method described in this report is not satisfactory for determining concentrations as low as 12.5 ppm. It appears from a comparison of solutions of hydrocarbons in both trichloretnylene and carbon tetrachloride that the difficulties experienced in analyzing trichloroethylene solutions are caused by the solvent. Presumably, the presence of a C-H band in trichloroethylene reduces the intensity of radiation passing through the sample, thus decreasing sensitivity of the infra-red beam to the presence of hydrocarbons.

Low concentrations of hydrocarbons in solvent can be determined by this method only by using solvents in which the C-H structure is absent, such as carbon tetrachloride or one of the freons.

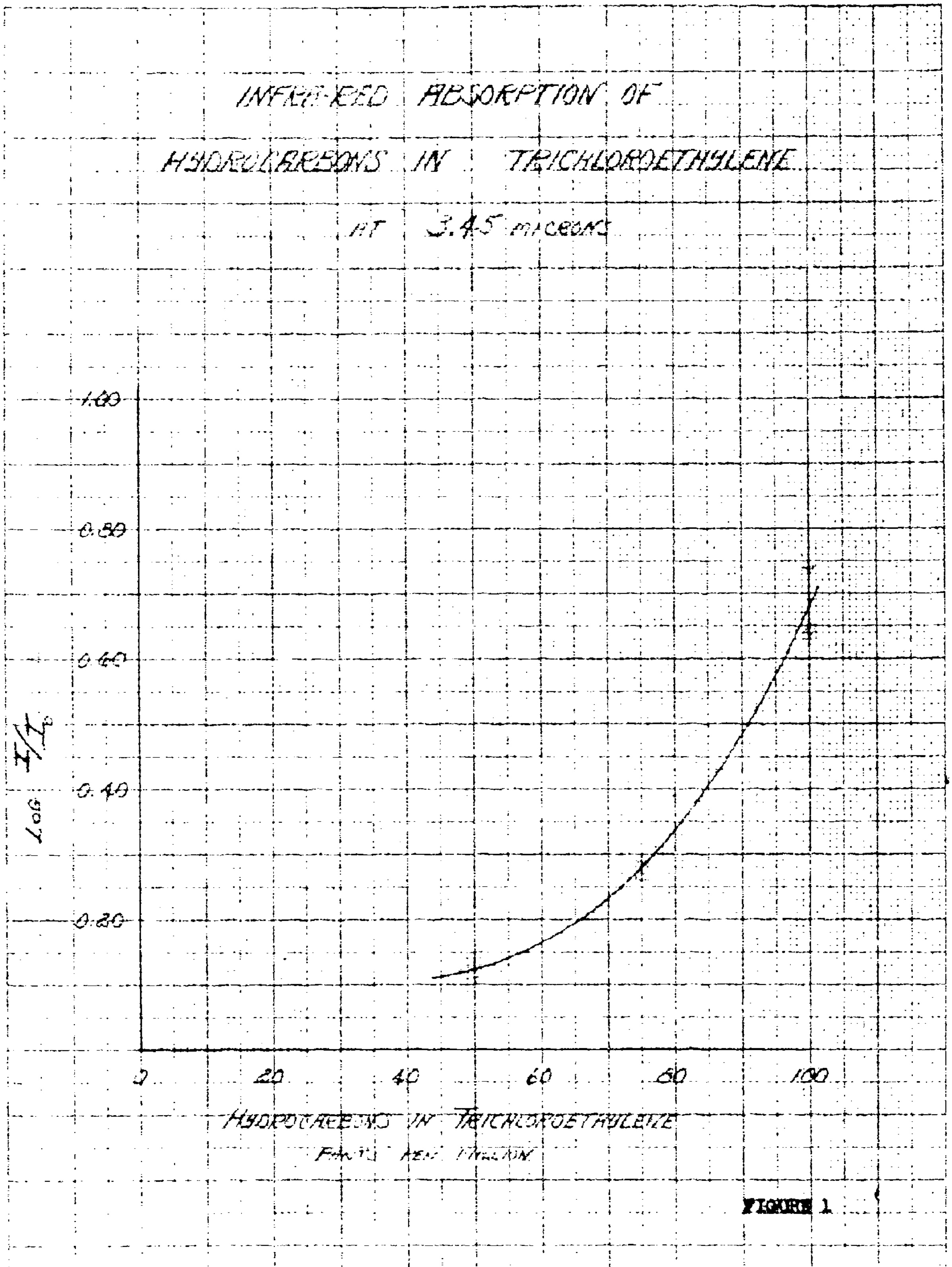
INFRA-RED ABSORPTION OF
HYDROCARBONS IN TRICHLOROETHYLENE
AT 3.45 MICRONS
LOG I/I₀
1.00
0.80
0.60
0.40
0.20
0
20
40
60
80
100
HYDROCARBONS IN TRICHLOROETHYLENE
PARTS PER MILLION

FIGURE 1

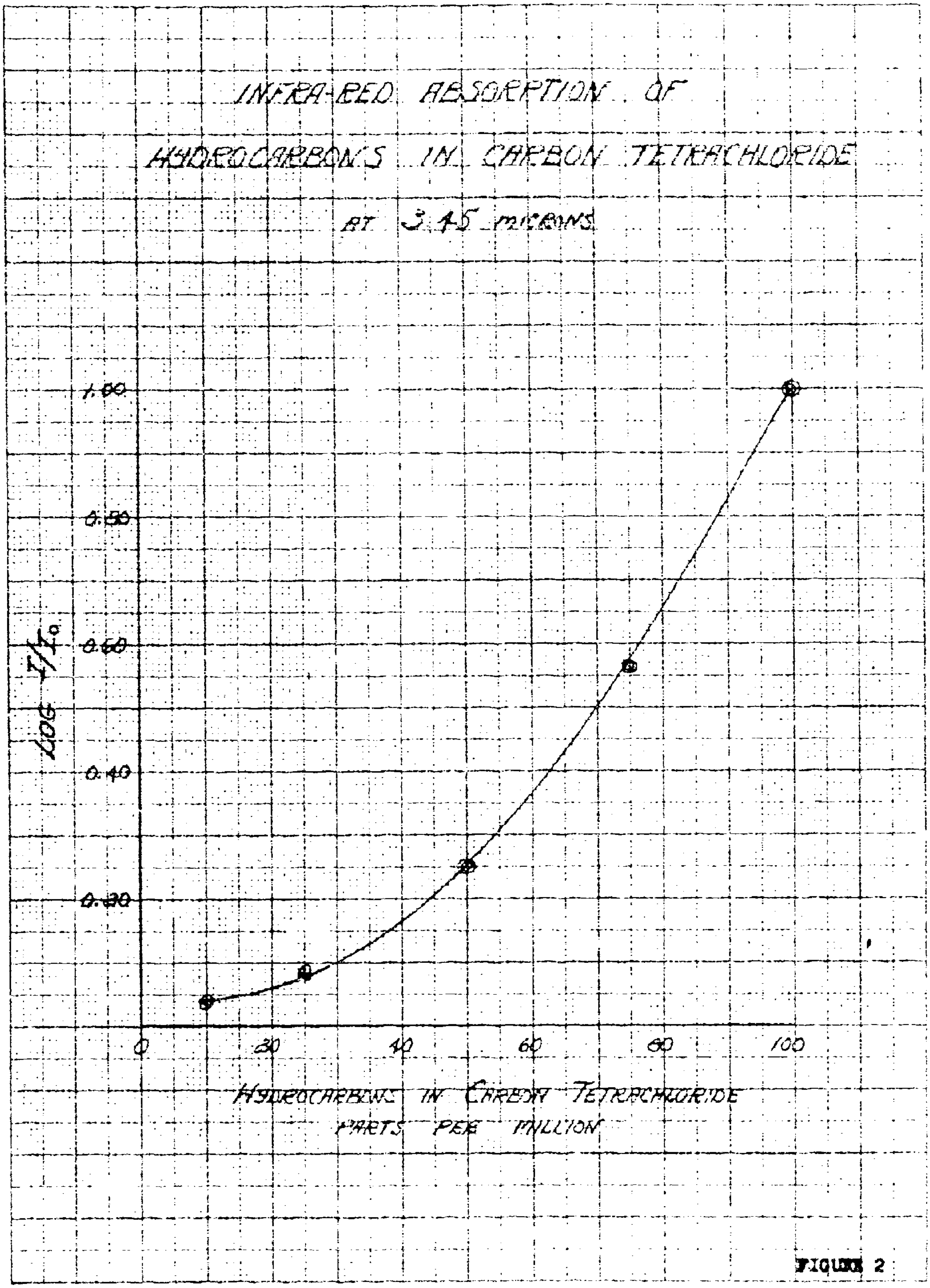

FIGURE 2

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