

FINAL REPORT
CONTRACT NASW-1625

NASA HEADQUARTERS
Washington, D. C.

and

JET PROPULSION LABORATORY
Pasadena, California

INVESTIGATION OF POLYMERIC COATINGS
BY ELECTRODELESS DISCHARGE

By
J. P. Redmond & A. F. Pitas



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I SUMMARY

The intent of this program was to investigate the composition, structure, chemical and physical properties of polymeric films deposited via electrical discharge from low molecular weight organic compounds. To accomplish this a series of hydrocarbons were selected with varying hydrogen to carbon compositions as the reactants. These monomers included isobutylene (C_4H_8), ethylene (C_2H_4), acetylene (C_2H_2) and diacetylene (C_4H_2), a liquid. Also, plastic films were deposited from toluene (C_7H_8), trifluoroethylene (C_2HF_3) and tetrafluoroethylene (C_2F_4) to aid in the identification of the structure of the hydrocarbon films. Likewise, hydrogen or deuterium were premixed with the selected hydrocarbons, followed by chemical and infrared analysis to note the changes in the properties of the films. Besides infrared analysis, the films were quantitatively analyzed for carbon, hydrogen and residue. In addition, the solubility of the films were investigated in strong acids, bases and in organic solvents. The physical properties of the films such as color and thermal stability in air were characterized. Finally the deposition parameters were investigated to elucidate the reaction mechanism.

This program was carried out over a nine month period, and was divided into five phases. The first phase was the construction of a vacuum apparatus to deposit the films. The second phase was to deposit sufficient quantities of the films prepared from the four selected hydrocarbons to characterize these polymers. The third phase was to prepare polymers from the selected compounds after premixing them with hydrogen or deuterium in molecular ratios of 1/1, 2/1 and 4/1. The fourth phase was to investigate the structure of films prepared from toluene, trifluoroethylene and tetrafluoroethylene. The final phase was to evaluate the results of the study as to the nature of the film and to clarify as much as possible the deposition process.

The results from the infrared and chemical analysis data established that films deposited from ethylene have a structure analogous to a highly cross-linked polyethylene. The infrared spectra were strikingly similar to the spectra obtained from commercial plastics which were chemically cross-linked or cross-linked by high energy radiation. The films prepared from isobutylene were similar to those prepared from

ethylene except that in the infrared spectra of the isobutylene films aromaticity was detected. Thus the structure of this film was more analogous to a polyethylene-polystyrene copolymer. The films generated from acetylene or diacetylene were also similar to the polyethylene infrared spectras, however, the acetylene and diacetylene films possessed a larger fraction of carbon-carbon double bonds. From the infrared spectras it was clearly evident that diacetylene films contained a greater degree of unsaturated linkages than the acetylene. This was also consistent with their hydrogen/carbon ratios obtained by the chemical analysis of the film as well as their color. In fact, a correlation was obtained between the relative degree of unsaturation of the film and the hydrogen/carbon content of the film. Infrared analysis was further used to monitor the incorporation of deuterium into the polymeric films to verify that the composition of the films are more a factor of the atomic concentration rather than the chemical reactivities of the monomer. Toluene films exhibited considerable aromaticity in its spectra and more closely resembled the spectra of polystyrene. The infrared spectras of tri- and tetrafluoroethylene gave very broad bands, consequently, it was not possible to categorize these teflon-like films.

The presence of carbonyl groups was identified in the structure of all the deposited film; this was verified with the compositional analysis. While no systematic investigation was undertaken to establish the source of oxygen, it was found that pre-mixing oxygen with the hydrocarbon reactants inhibited or removed any film formation. We tend to support the explanation presented by others (see reference 4) that the presence of carbonyl groups in the films is due to oxidation of the film on exposure to air.

The color of the films varied from light yellow to a dark reddish brown. The higher the percentage of hydrogen in the film the lighter its color. All films were rather brittle. The films were insoluble in hydrochloric acid, sodium hydroxide and common organic solvents such as trichloroethylene and acetone. However, the films containing a relatively greater amount of hydrogen showed some reactivity to concentrated sulfuric acid.

In the evaluation of the deposition parameter data, it was found that gases containing a low ratio of hydrogen to carbon deposited films at a much faster rate than starting gases containing a higher hydrogen ratio. It was noted that when the plasma was initiated in the presence of acetylene the pressure in the system decreased while the opposite was true for gas mixtures containing higher hydrogen to carbon ratios such as isobutylene. In essence, the hydrogen inhibited the film deposition by reforming low molecular weight hydrocarbon products. The ratio of hydrogen to carbon in these films varied from 1/1 to 1.9/1 and was clearly dependent on the hydrogen to carbon ratios of the input gases.

The net result from this study is that continuous, homogeneous, adherent plastic coatings can be vapor deposited via an electrical discharge. These films are very highly cross-linked, consequently, they possess good thermal and chemical stabilities. In addition they are nonpermeable and would exhibit low outgassing characteristics. Even more significant is the fact that the film can be tailored to meet specific applications. For example, one could initially deposit a film from ethylene and then gradually switch the gas composition to deposit a teflon-like film from tetrafluoroethylene with no demarkation line. The chemical and thermal inertness of these films suggest they might find applications as nonpermeable coatings in fuel storage containers, however, more work is needed to establish commercial applications of these polymers. During this program it was not possible to investigate the dielectric properties of the polymers or to investigate other film forming materials such as the organosilanes, phosphines or boranes.

II INTRODUCTION

The use of an electrical discharge as a means of initiating unusual chemical reaction is receiving renewed attention⁽¹⁾. By the use of this technique a variety of organic polymeric films can be deposited. Vastola and Wightman⁽²⁾ employing a microwave discharge have prepared films from low molecular weight strength chain hydrocarbons plus benzene and naphthalene. While there is some question as to the structures of the polymeric films, it is evident that adherent, nonpermeable polymeric films can be deposited with unusual chemical and thermal stability. Thus the films may be utilized in applications requiring corrosion protection, a permeation barrier, or as coupling agents. Also, these films could be used in circumstances requiring a low vapor pressure material or a plastic with extreme chemical inertness. These properties make the plasma deposited polymer attractive candidate materials for aerospace applications.

Therefore, this process should be further investigated for the following reasons: To elucidate the nature of these hydrocarbon films, to establish the deposition mechanism and to deposit and evaluate other film forming materials. This program was initiated to accomplish these objectives and thus to provide a foundation for engineered coatings designed to meet specific aerospace requirements.

In order to clarify the structure of the polymeric films, a series of organic compounds were examined to determine the correlation between the starting compounds and their deposited films. The four hydrocarbon compounds selected for study were isobutylene ($i\text{-C}_4\text{H}_8$), ethylene (C_2H_4), acetylene (C_2H_2) and diacetylene (C_4H_2). These compounds were chosen because of their hydrogen to carbon ratios and total carbon content. These monomers were reacted and deposited in a plasma and the structures of their polymeric films were investigated by infrared analysis and by chemical analysis. The physical properties of the films were obtained by softening

1. "Symposium on Chemical Reactions in Electrical Discharges" American Chemical Society, 153d National Meeting, April 1967.

2. F. J. Vastola and J. P. Wightman, J. Appl. Chem. 14 69 (1964).

point or thermal degradation measurements and solubility test. The films were tested for solubility in concentrated hydrochloric and sulfuric acids and sodium hydroxide plus the common organic solvents such as trichloroethylene and acetone. The solubility of a material in a particular solvent provides a clue as to the functional groups and structure of the material.

The deposition process was studied by following the effect of system pressure, gas flow rates, power input to plasma and gas composition on the rate at which the film is deposited. In order to more fully understand the deposition process and the structure of the film, both hydrogen and deuterium were premixed with each of the four hydrocarbon compounds in molar ratios of 1/1, 2/1 and 4/1. The premixing of hydrogen with the starting monomer was used to correlate the composition of the starting gas with the composition of the film as well as the color and physical properties of the films and to determine the effect of added hydrogen on the deposition rate. The premixing of deuterium with each of the four starting compounds was designed to be used in the interpretations of the infrared spectras of the films, thus its purpose was to verify the extent which hydrogen enters into the deposited films.

Besides the four aliphatic compound, coatings were also prepared from toluene trifluoroethylene and tetrafluoroethylene. Toluene was included in the study to compare the structure and properties of films prepared from an aromatic compound with aliphatic hydrocarbons. The two fluoronated compounds were added to the program to evaluate as potential film materials. In addition, since hydrofluoric acid vapors were used to remove the deposited hydrocarbon films from the walls of the reaction tube there was the possibility of fluorine reacting with the coatings and confusing the interpretation of the infrared patterns.

Thus a research program was devised to extensively investigate the structure, composition and properties of polymeric-like materials deposited from an electrical discharge. This was a nine month program. It called for the design and construction of an apparatus to produce the films; the preparation and examination of samples prepared from isobutylene, ethylene, acetylene and diacetylene; the study of hydrogen and deuterium additions to the starting compounds and the examination of

films prepared from toluene and fluorinated ethylenes as well. All these objectives of the program were accomplished, and significant findings were obtained both as to the structure of the films and the deposition process and a basis has been laid for the extensive development of tailor-made coatings and free-standing specimens.

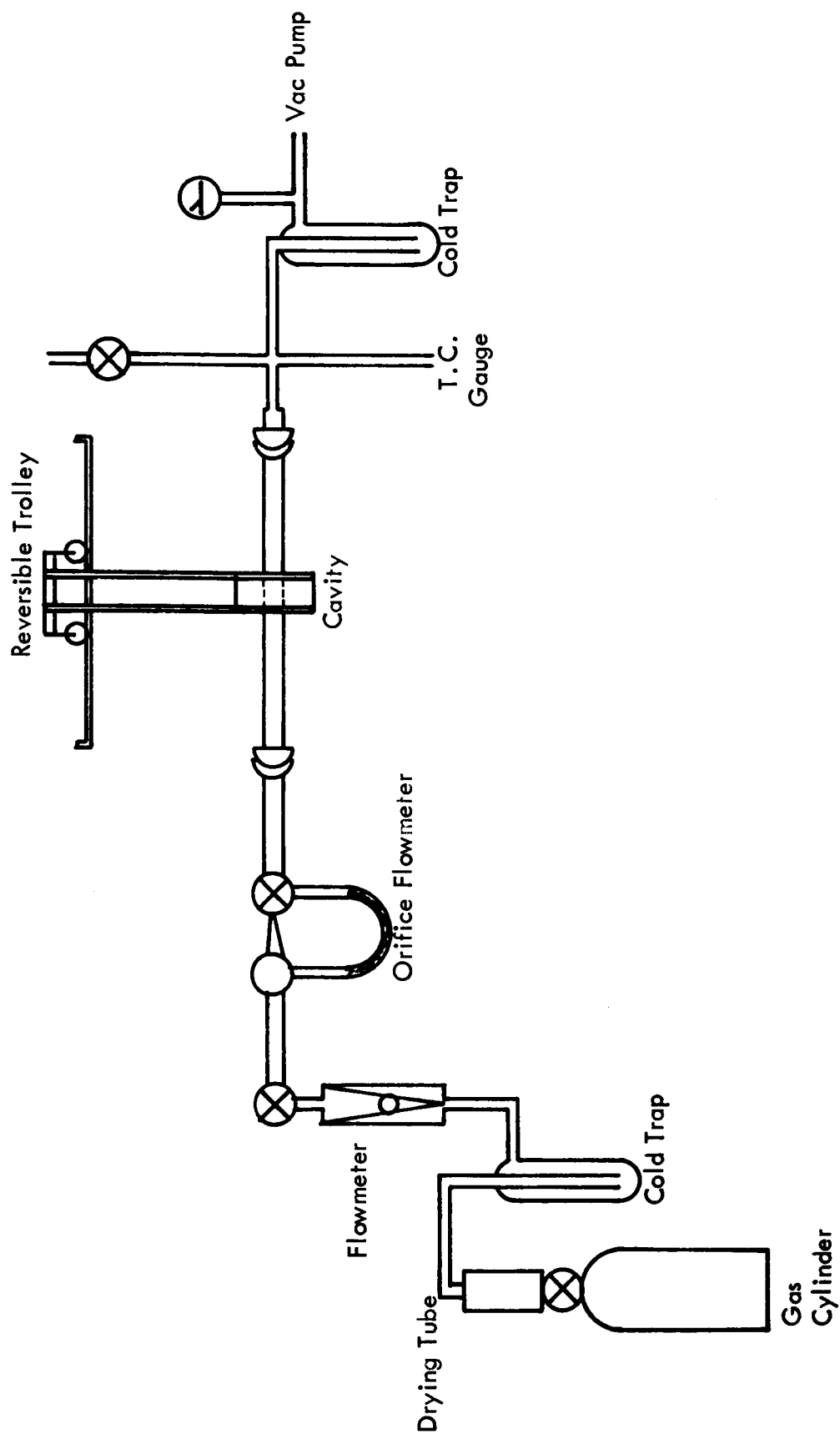
III EXPERIMENTAL APPARATUS

Essentially the coating apparatus consisted of a vacuum rig to control and monitor the gases, a microwave generator with a resonance cavity and a means of sliding the microwave cavity back and forth along the reaction chamber to provide for the collection of a sufficient quantity of sample.

A schematic drawing of the apparatus has been shown in Figure 1. Essentially, the experimental apparatus consisted of a gas purifying system to remove any impurities entrained in the gas being supplied to the system. A flowmeter (J. T. Baker) with both pyrex and stainless steel floats was used to measure the gas flow from 5.0 cc/min. to 150 cc/min. A Nupro needle valve was used to control the gas flow. An orifice type flowmeter was added to the system to increase the sensitivity of the measurement of gas flows particularly at low flow rates. This flowmeter consisted of a U-tube on which a stopcock with a hollow stopper was mounted. The stopper contains four orifices from approximately 1/4 to 2 mm. in diameter. Silicone fluid is used in the U-tube to measure the pressure drop across the orifice, this pressure drop is directly related to the gas flow rate. In addition, a U-tube manometer containing silicone oil was employed to measure the total pressure of the system, while a Televac thermocouple gauge was used to measure ultimate vacuum within the system. Finally, a Bourdon gauge was incorporated in the system to obtain a rough pressure measurement. A Welsh two-stage, duo-seal, model 1405 vacuum pump was used to evacuate the system.

A trolley was used to slide the cavity of the microwave generator back and forth along the reaction tube. The length of travel of the cavity is 3-1/2 ft. It required ten seconds for the cavity to traverse the length of the reaction tube. Microswitches and an impulse relay are employed to reverse the slo-syn synchronous motor at the end of the travel.

A Raytheon microwave generator model PGM-10 which operates at 2450 megacycles was used to produce the plasma. The generator transmitted the high frequency electromagnetic radiation to an Opthos quarter wave resonance cavity.



SCHEMATIC DIAGRAM OF
PLASMA DEPOSITION APPARATUS

This cavity was tuneable and was air cooled. The power input from the generator to the cavity was measured by a Micromatch reflected power meter. A Teslo coil was used to ignite the plasma.

Before a run, the system was evacuated to 0.1 torr and leak checked. The flow rate of the starting gas was measured along with the system pressure. When the plasma was generated the run was commenced, and, in general, the experiment duration was from ten minutes to an hour. The microwave power was generally set at 25 watts. The flow rate of starting gases was varied from 0.01 to 0.06 cubic feet per hour (CFH) and the pressure during a run ranged from 0.5 to 1.5 torr.

After a run, the reaction chamber was removed from the system and the deposited film was released from the walls of the tube by scratching the film with a wire and passing hydrofluoric acid vapor down the tube. By scratching the film, the acid vapors were able to undercut the film and release the coating. The film was then brushed off the walls into a collecting bottle. The sample was then weighed, examined microscopically and sent for analysis.

Aldridge Associates of Washington, D. C. performed the chemical analysis. The samples were analyzed for carbon, hydrogen and residue. Oxygen percentage content of the film was calculated by subtracting the sum of the carbon, hydrogen and residue from one hundred. The infrared analysis was done at the Jet Propulsion Laboratory under the direction of Mr. David Lawson. A Perkin and Elmer Model 421 Infrared Spectrometer was used. The films were examined by mixing approximately 0.05% of the ground plastic film with potassium bromide and pressing a 13 mm disc at 21,000 psi.

The hydrocarbon gases were purchased from Matheson Chemical Co. and no special purification treatments were given to the gases outside of passing through a drying tube prior to entering the system. Diacetylene was prepared in our laboratory by the procedure described by Armitage et al⁽³⁾.

3. Armitage, Jones & Whitney, J. Chem. Soc. 44 (1951).

IV RESULTS AND DISCUSSIONS

Sixty separate experiments were conducted during this program. Films were prepared from each of the four aliphatic compounds (isobutylene, ethylene, acetylene and diacetylene). Coatings were deposited from at least three separate runs for each compound to determine the reproducibility of the experiment and to aid in establishing the deposition parameters. Each of the starting compounds were then premixed with hydrogen and deuterium in mole ratio of 1/1, 2/1 and 4/1, to study the changes brought about in the structure and appearance of the deposited films. Ten experiments were concerned with the deposition of teflon-like coatings from trifluoroethylene and tetrafluoroethylene. Three experiments were used to deposit films from toluene and three runs were made to study the effect of premixing oxygen with the hydrocarbon on the deposition process. The experiments and the deposition parameters are presented in Table I. In general, the films are brittle and highly stressed. They tend to curl up after they were removed from the reaction tube.

A. Ethylene and Isobutylene Film.

Films prepared from isobutylene and ethylene were similar in appearance and are discussed together. The coatings varied in color from yellow to light yellow to clear. From Table II it is evident that their hydrogen-carbon composition were equivalent. However, as we shall see later there was some difference between their infrared spectras. Ordinarily, the films are quite transparent as they are first deposited, however, as the thickness increases the coating becomes more yellow in color. This is probably due to thermal degradation caused by the plasma sweeping back and forth over the deposited film.

The premixing of hydrogen or deuterium with isobutylene or ethylene increased the amount of hydrogen incorporated into the sample but does not obviously change the appearance of the deposited films. These and all the films were insoluble in concentrated hydrochloric acid, sodium hydroxide, trichloroethylene and acetone, however, both the ethylene and isobutylene films were classified as being soluble in concentrated sulfuric acid as the acid charred or reacted with these film. On heating in air both films started charring around 280°C.

TABLE 1
PROCESS CONDITIONS FOR DEPOSITION OF POLYMERIC COATINGS^a

Expt No.	Gases Moles	H/C Ratio	Flow Rate CFH ^c	Pres Torr	ΔP Torr	Dep'n Rate Mg/Min
5 ^b	1 C ₄ H ₈	2/1	0.06	1.5	0.5	0.6
7	1 C ₄ H ₈	2/1	0.05	1.1	0.1	1.0
8	1 C ₂ H ₄	2/1	0.02	1.0	--	3.5
9	1 C ₂ H ₄	2/1	0.05	1.4	0.4	0.6
10	1 C ₂ H ₂	1/1	0.05	1.0	0	3.0
11	1 C ₄ H ₈	2/1	0.07	0.7	--	--
13	1 C ₂ H ₄	2/1	0.02	0.8	0.2	--
15	1 C ₂ H ₂	1/1	0.01	0.5	0	--
16	1 C ₂ H ₂	1/1	0.01	1.3	-0.3	--
17	6 C ₂ H ₄					
	1 Ar	2/1	0.04	1.9	0	--
18	1 C ₂ H ₂					
	1 Ar	1/1	0.02	0.5	-0.2	--
19	10 C ₂ H ₂					
	1 H ₂	1.1/1	0.02	0.6	-0.1	19.0
20	1 C ₂ H ₂					
	1 H ₂	2.1	0.03	1.8	-0.1	1.7
21	1 C ₂ H ₂					
	2 H ₂	3/1	0.03	1.0	-0.1	1.8
22	1 C ₂ H ₄					
	1 H ₂	3/1	0.03	2.6	--	0.5
23	1 C ₂ H ₄					
	2 H ₂	4/1	0.01	0.6	0	7.0
24	1 C ₂ H ₄					
	1 D ₂	3/1	0.02	1.3	--	1.7

a. Power input from microwave generator was set at 25 watts, runs lasted from 15 min. to 180 min.

b. Data for runs 1 thru 5 were not recorded.

c. CFH = Cubic feet per hour at STP condition.

Expt No.	Gases Moles	H/C Ratio	Flow Rate CFH	Pres Torr	ΔP Torr	Dep'n Rate Mg/Min
25	1 C ₂ H ₄ 2 D ₂	4/1	0.01	2.1	--	1.3
26	1 C ₂ H ₂ 1 D ₂	2/1	0.02	0.4	-0.37	--
27	1 C ₂ H ₂ 1 D ₂	2/1	0.02	1.5	-1.0	--
28	1 C ₂ H ₂ 2 D ₂	3/1	Experiment Terminated -- See Expt. No. 34			
29	1 C ₄ H ₈ 1 H ₂	2.5/1	0.02	0.8	0	1.8
30	1 C ₄ H ₈ 2 H ₂	3/1	0.02	1.1	0.9	1.4
31	1 C ₄ H ₈ 4 H ₂	4/1	0.03	0.9	0.2	0.9
32	1 C ₂ H ₄ 4 H ₂	6/1	0.03	1.5	0.3	0.3
33	1 C ₂ H ₂ 4 H ₂	5/1	0.03	0.4	0.15	0.4
34	1 C ₂ H ₂ 2 D ₂	3/1	0.02	0.2	--	0.73
35	1 C ₄ H ₈ 1 D ₂	5/2	0.03	--	--	--
36	1 C ₄ H ₈ 2 D ₂	3/1	0.02	0.7	0.14	1.3
37	1 C ₄ H ₈ 4 D ₂	4/1	0.03	1.0	0.1	--
38	1 C ₂ H ₄ 4 D ₂	6/1	0.03	1.3	0	0.5
39	1 C ₂ H ₂ 4 D ₂	5/1	0.03	--	--	--
40	1 C ₄ H ₂	1/2	0.17	6.8	--	--
41	1 C ₄ H ₂	1/2	0.05	0.2	0.4	5.0
42	1 C ₄ H ₂ 2 D ₂	3/2	0.01	0.7	0.74	1.8

Expt No.	Gases Moles	H/C Ratio	Flow Rate CFH	Pres Torr	P Torr	Dep'n Rate Mg/Min
43	1 C ₄ H ₂ 1 D ₂	1/1	0.02	--	--	2.6
44	1 C ₄ H ₂ 4 D ₂	5/2	0.02	0.8	-0.3	1.25
45	1 C ₄ H ₂ 1 H ₂	1/1	0.02	0.4	0.8	0.70
46	1 C ₄ H ₂ 2 H ₂	3/2	0.01+	0.5	--	0.6
47	1 C ₄ H ₂	1/2	Experiment terminated			
48	C ₂ HF ₃	1/2	0.01+	0.15	--	4.93
49	C ₂ HF ₃	1/2	0.005	--	--	1.73
50	1 C ₂ HF ₃ + 1 Ar	1/2	0.02	0.07	0.07	1.93
51	C ₂ HF ₃ + H ₂	3/2	0.01	--	--	4.9
52	C ₂ HF ₃	1/2	0.005	.15	--	3.1
53	C ₂ HF ₃ + O ₂	1/2	0.005	--	--	No coating
54	C ₂ H ₂ + O ₂	1/1	0.06	--	--	No coating
55	CH ₃	8/7	0.01	.88	0.3	4.33
56	CH ₃ + O ₂	8/7	0.005	--	--	No coating
57	C ₂ F ₄	--	0.01	Varied	--	--
58	C ₂ F ₄	--	0.005	0.15	--	--
59	C ₂ F ₄	--	0.005	.15	--	--
60	C ₂ F ₄	--	0.01	--	--	1.7

TABLE II
CHEMICAL ANALYSIS OF POLYMERIC
FILMS

Expt No.	Gases Mole/Ratio	H/C Ratio Input	Analysis C	Wt % H	Res.	Dif. (a)	H/C Ratio(b) Film
<u>Isobutylene</u>							
11	C_4H_8	2	72.9	8.8	5.8	0.52	1.46
31	$C_4H_8 + 4H_2$	4	55.8	8.3	14.8	21.1	1.79
<u>Ethylene</u>							
13	C_2H_4	2	79.1	9.5	4.8	6.6	1.44
17	$C_2H_4 + Ar$	2	81.5	9.3	TR	9.2	1.37
23	$C_2H_4 + 2H_2$	4	78.0	10.5	4.0	7.6	1.62
32	$C_2H_4 + 4H_2$	6	59.5	8.7	12.4	23.3	1.76
38	$C_2H_4 + 4D_2$	6	71.4	10.5	6.1	12.0	1.79
<u>Acetylene</u>							
15	C_2H_2	1	83.5	8.4	2.4	5.7	1.2
18	$C_2H_2 + Ar$	1	71.7	7.1	9.2	12.0	1.2
21	$C_2H_2 + 2H_2$	3	83.6	9.7	TR	6.7	1.39
33	$C_2H_2 + 4H_2$	5	61.3	8.9	8.9	21.	1.75
<u>Diacetylene</u>							
41	C_4H_2	0.5	64.5	6.2	2.5	26.8	1.15
43	$C_4H_2 + D_2$	1	74.5	8.4	5.3	11.8	1.35
42	$C_4H_2 + 2D_2$	1.5	59.0	7.8	2.0	31.2	1.58
<u>Fluorinated Ethylene</u>							
51	$C_2HF_3 + H_2$	1.5	36.8	2.9	52.7	--	0.94
60	C_2F_4	2	29.7	0.7	68.4		1.45

(a) The difference is obtained by subtracting the combined weight percentages from 100. The difference is taken as the oxygen content of the films.

(b) This is calculated from the respective atomic mole fractions.

B. Acetylene Films.

The films prepared from acetylene were brown to orange-brown in appearance. The addition of hydrogen tended to lighten the film color to a yellow. The compositional analysis of the acetylene film which is listed in Table II showed a lower hydrogen/carbon ratio in the film as compared to isobutylene or ethylene films. This evidence combined with the color of the film suggest increased unsaturation in this film. This is verified from the infrared results which will be discussed later. The acetylene film did not react with the concentrated sulfuric acid and was classified as insoluble. On heating these film, they started charring near 340°C .

C. Diacetylene Films.

The films prepared from diacetylene were black to dark red-brown in color. Table II shows that these film have the lowest hydrogen to carbon ratio. Pre-mixing hydrogen with the diacetylene while passing the mixture through the plasma deposits a film with a higher hydrogen ratio in addition it lightens the color from a black to an orange-brown. As we shall see later from the infrared results, the diacetylene films contain the highest percentage of carbon-carbon double bonds. Though the films are also insoluble in sulfuric acid, they do start to char on heating to above 300°C .

D. Fluorinated Films.

Coatings were deposited from trifluoroethylene and tetrafluoroethylene. In physical properties the film were similar to each other but they differed in appearance. Both films were insoluble in all the solvents previously mentioned. They both had a charring point in the range of 320° to 340°C . However, the tetrafluoroethylene gas produced a dirty-white polymeric material greatly resembling teflon; whereas, the trifluoroethylene produced a brown film similar to the hydrocarbon films. The chemical analysis of these films showed that the tetrafluoroethylene had a stoichmetric composition of C_2F_3 while the trifluoroethylene had a composition of $\text{C}_2\text{F}_2\text{H}_{1.5}$. The infrared patterns for the films were very similar. Both samples showed a very diffuse, broad, poorly resolvable spectra.

E. Toluene Films.

Toluene deposited at a relatively high deposition rate (3 mg/min). The pressure in the system decreased (-0.3 torr) when the plasma was initiated indicating a fairly efficient deposition process. The films were yellow in color much like the aliphatic hydrocarbon films. Unfortunately no chemical analysis were made on the deposited film. The infrared spectra suggested that films were analogeous in structure to a polystyrene plastic. This will be discussed in more detail in the section on infrared.

V DEPOSITION PARAMETERS

A. Kinetics.

The deposition rate of the plasma deposited films was directly related again to the hydrogen-carbon ratio of the input gases. The deposition rates for over twenty runs has been plotted in Figure 2. The microwave power input used in these runs to generate the plasma was approximately 25 watts. The flow rate for the gases was varied from 0.01 to 0.04 CFH. The pressure during a run ranged from 0.5 to 1.5 torr. The system was evacuated to a pressure of 0.1 torr and leak checked before a run commenced. It should be noted in Figure 2 that over a ten-fold change in deposition rate was observed over the range of gas compositions studied. The low deposition rate for the gas mixtures containing a high hydrogen concentration was due to formation of low molecular weight products such as methane in the plasma. This was substantiated by the data shown in Figure 3 where the pressure change in the system was measured before and after when the plasma was initiated and this differential pressure change was plotted against the hydrogen-carbon ratio of the input gases. Again, to obtain this differential pressure change, the pressure in the system was measured with reactant gases flowing, and then the system pressure is re-measured after the plasma was ignited. This pressure change could have been an increase or decrease depending on the hydrogen content of the starting gases. Evidently the hydrogen was inhibiting the deposition process by forming low molecular weight exhaust products.

The results of the kinetic data indicate that the deposition rate was more of a function of the element content of the reactants than the concentration of the individual compounds. No effort was made to determine a rate expression from the data as there was too much scatter in the data.

B. Composition.

In order to clarify the relationship between the starting gases and their film, the four aliphatic compounds were premixed with hydrogen in molar ratios of 1/1, 2/1 and 4/1 and the resulting films deposited by the plasma were quantitatively analyzed. The plot of data for the hydrogen-carbon compositional ratio for the

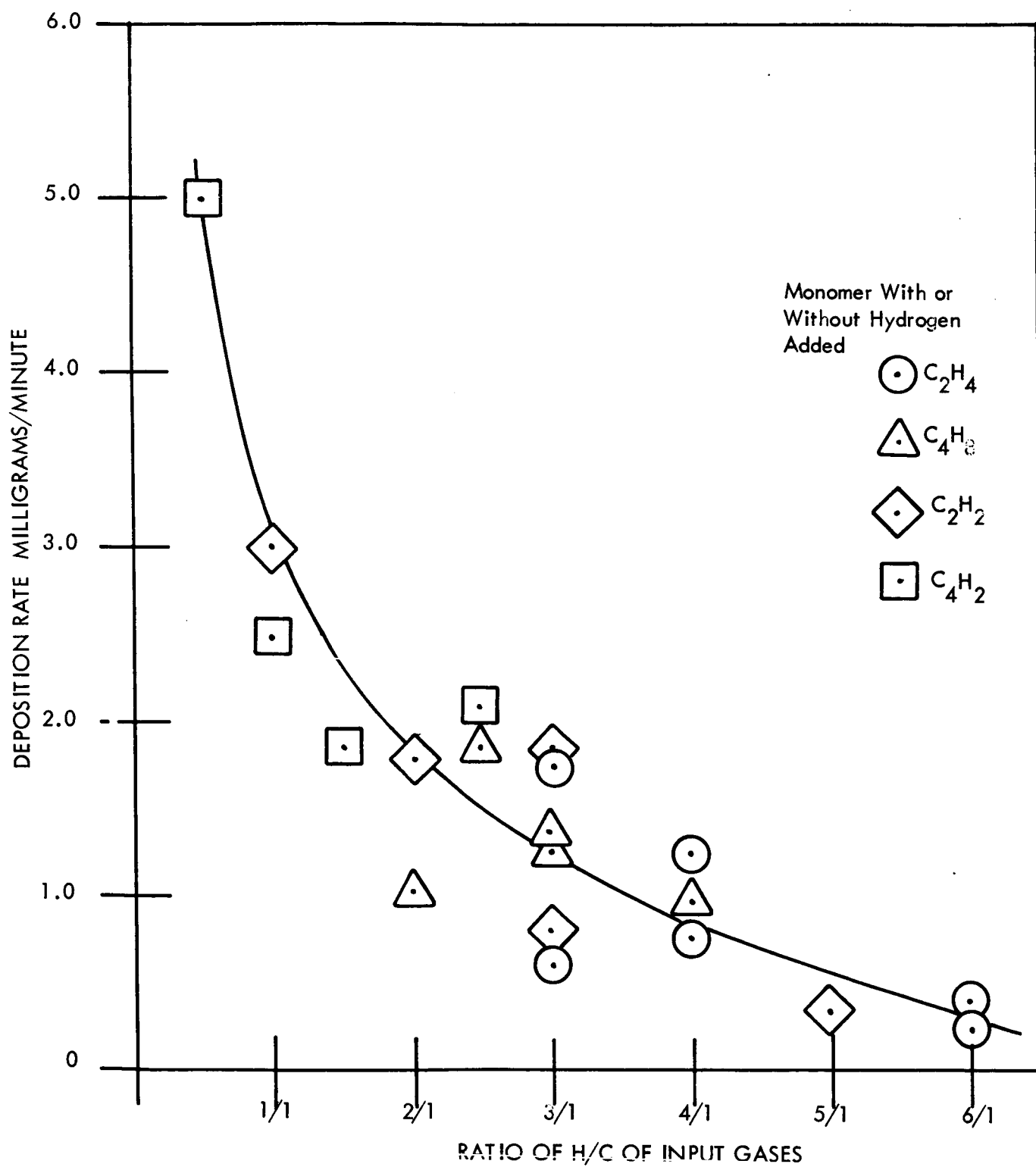


FIGURE 2

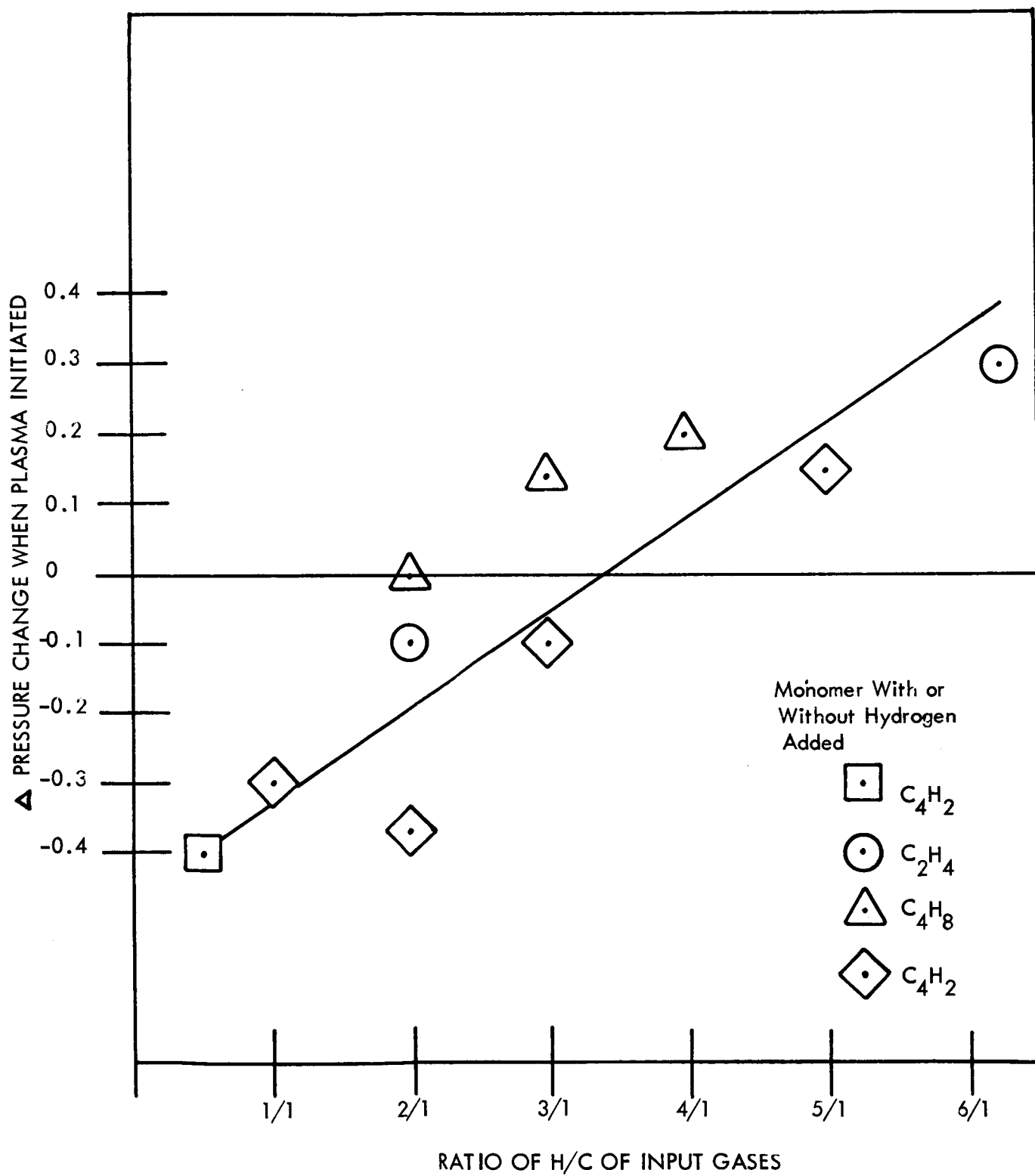


FIGURE 3

various deposited film against the total hydrogen to carbon content of the input gases has been shown in Figure 4. While there was some data scatter, it was clearly evident there is a nearly linear correlation between the film composition and starting gases. While this was expected, the relative amount of hydrogen contained in the film was not directly equal to the relative amount of hydrogen present in the starting gas. As more and more hydrogen was added the hydrogen-carbon ratio in the film should asymptotically approach a ratio of 2.0 which was the value for a linear chain film of polyethylene. A line has been marked on the graph which notes the solubility of the films in concentrated sulfuric acid. The film containing a H/C ratio of greater than 1.4 were soluble in the acid and had a lower charring temperature which was an indication of the reactive hydrogen content in the films.

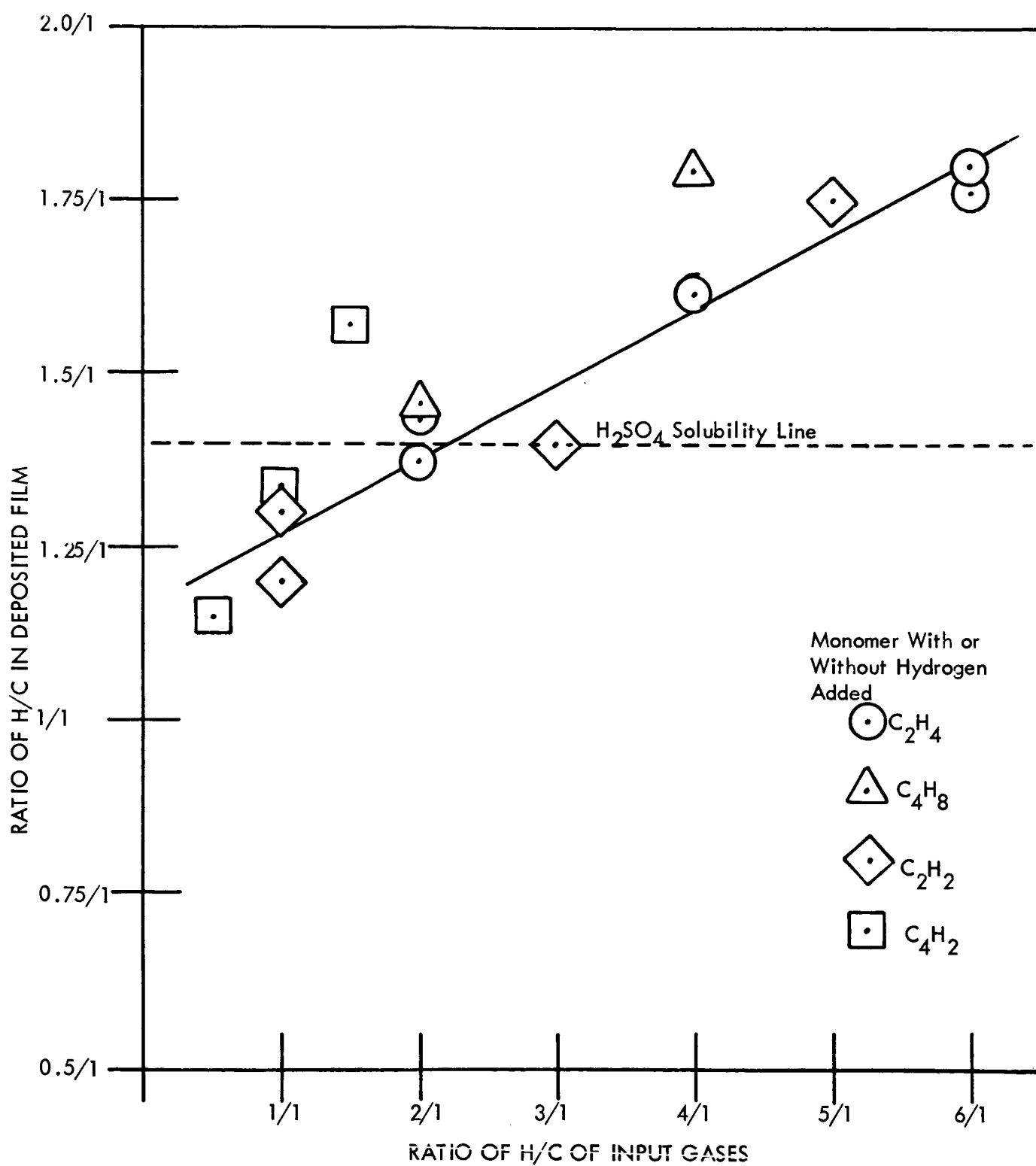


FIGURE 4

C. Oxygen Studies.

During the course of this study it became obvious that there was a relatively large amount of oxygen in the film. This was evident from the infrared results as well as the chemical analysis of the film. The question arose as to the source of oxygen. Therefore to help resolve this problem runs were made in which oxygen was premixed with the reactant gas, and the deposition process studied. Oxygen was premixed with acetylene, trifluoroethylene and toluene as starting gases. In each and every case a measurable amount of oxygen inhibited, or removed the polymeric film. At low oxygen concentration the deposition rate was reduced by a factor of ten. At higher concentrations the oxygen completely eliminated the formation of an acetylenic film. Since oxygen was such an efficient getter, later on in the program it was used to preclean the reaction tube before a run. Oxygen plasma has long been used to ash hydrocarbon solids for analysis of the inorganic material present in the sample. Thus we tend to support the conclusion of Neiswender⁽⁴⁾ who states that the oxygen in the film was due to the reaction with molecular oxygen on exposure of the films to air.

4. D. D. Neiswender "Polymerization of Benzene in a Radio Frequency Discharge", American Chemical Society's "Symposium on Chemical Reactions in Electrical Discharges" 153d National Meeting, p. 274-81, April 1967.

VI INFRARED RESULTS

A comparison of the infrared spectra of the polymeric films produced from the five hydrocarbon monomers (isobutylene, ethylene, acetylene, diacetylene and toluene) revealed that the infrared patterns of the deposited films were remarkably similar in appearance. Infrared spectra of the films prepared from these five compounds plus four spectra for other starting gases are shown in Figures 5, 6 and 7. Though the spectra were similar, on closer examination it was evident that there were significant differences in the patterns. For example, some additional peaks were found in the toluene spectra. These peaks have been attributed to the aromatic structure present in the film. Of the previously mentioned aliphatic compounds these same peaks (to a lesser degree) were found only in the spectra of the film deposited from isobutylene. A thorough examination of the infrared spectra have provided a clearer understanding of the structure of the films.

A. Aliphatic Films.

In general, the infrared patterns of the polymeric films deposited from the aliphatic compounds exhibited the following characteristics: A broad medium intensity band at 3400 cm^{-1} ; a strong reasonable sharp band between 3100 cm^{-1} to 2800 cm^{-1} ; a very broad band around 1700 cm^{-1} of medium intensity; two reasonably sharp medium intensity peaks appear at 1450 and 1380 cm^{-1} ; a shallow very broad band is seen between 1100 and 1000 cm^{-1} and finally a variable peak is found near 740 cm^{-1} . Analogous infrared spectra have been reported by Vastola and Wightman⁽²⁾ employing a similar experimental apparatus.

The infrared patterns for diacetylene gave a more diffuse spectra than the other three aliphatic hydrocarbons. However when hydrogen was premixed with diacetylene the resulting film produced infrared patterns closely resembling the other aliphatic patterns. No acetylenic or allenic linkages were found in the diacetylene patterns only a higher percentage of olefinic bond were observed.

In the interpretation of the patterns, the band at 3400 cm^{-1} has been assigned to the OH stretching vibration. Since the samples were enmeshed in

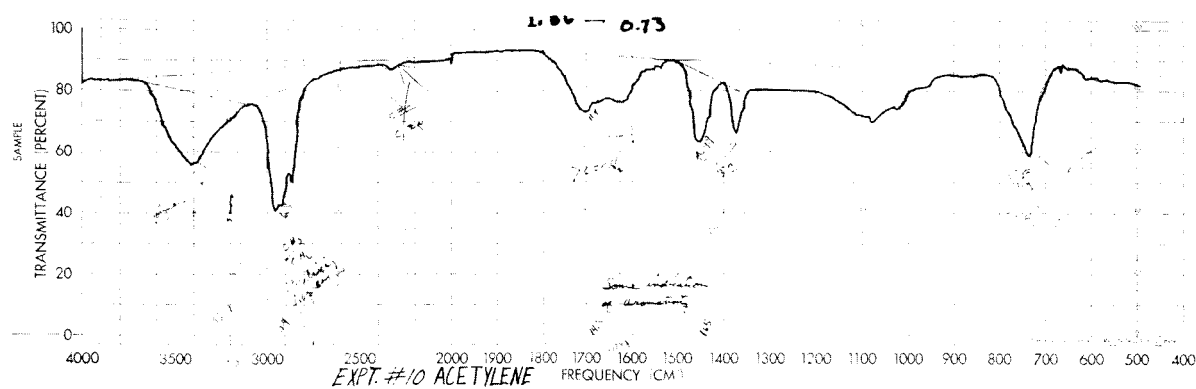
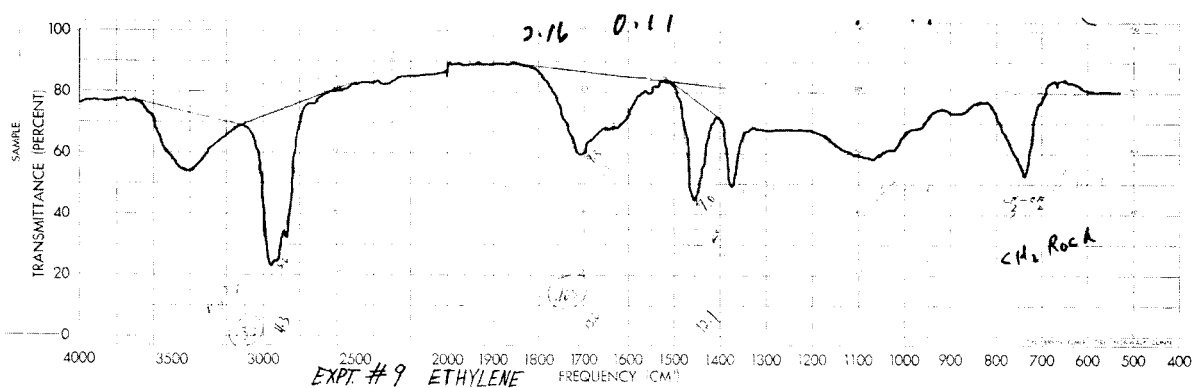
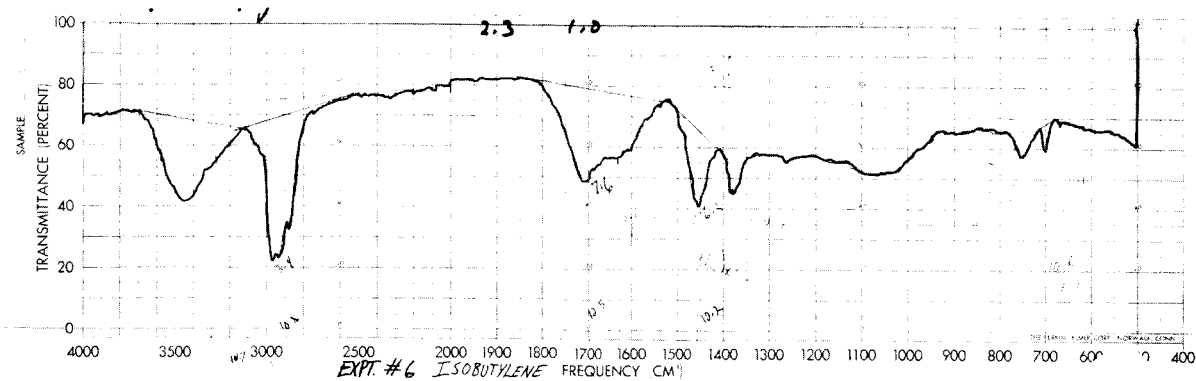


FIGURE 5

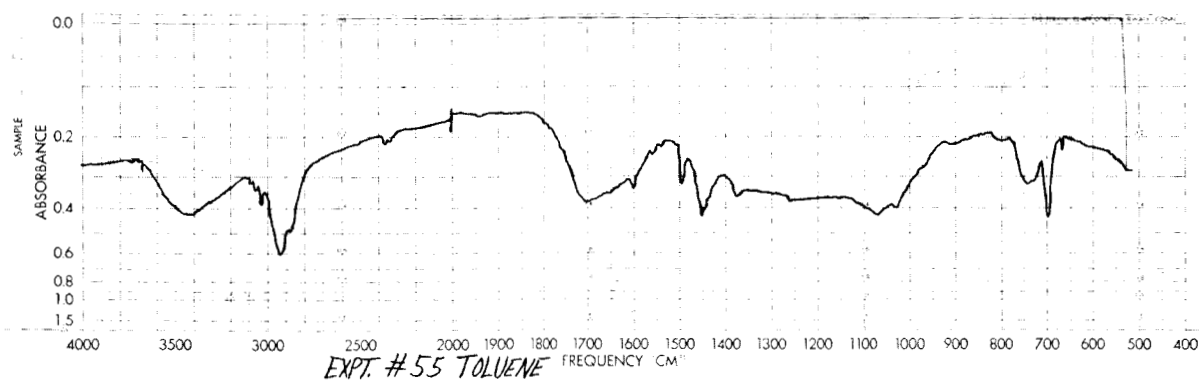
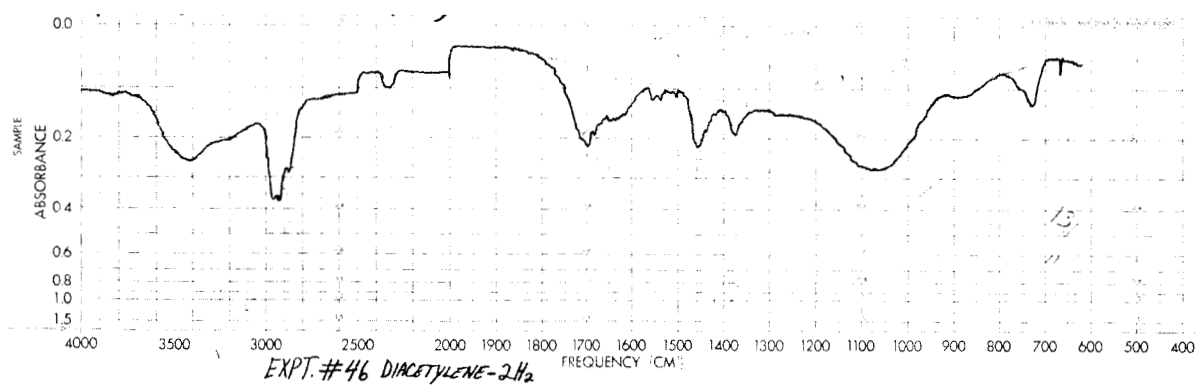
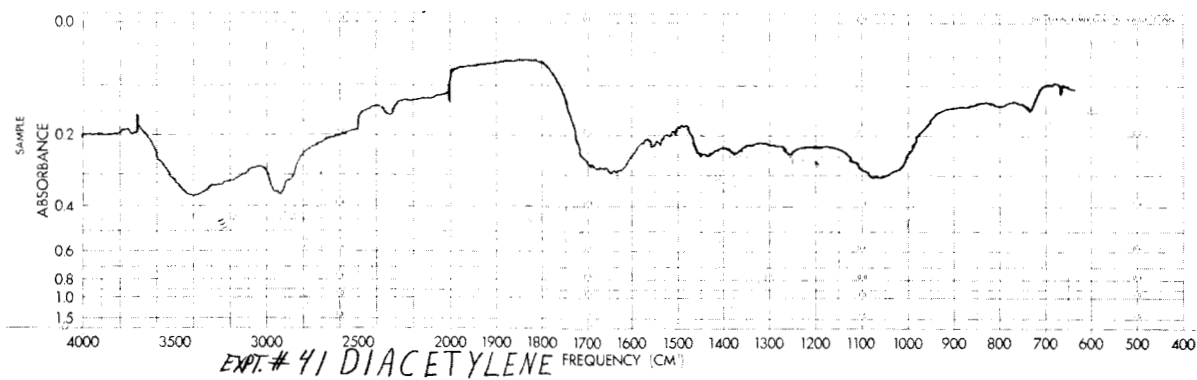


FIGURE 6

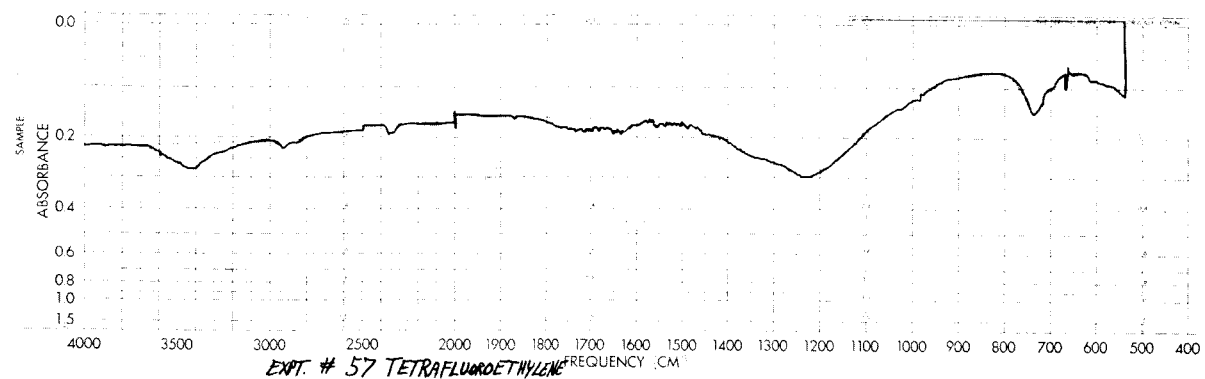
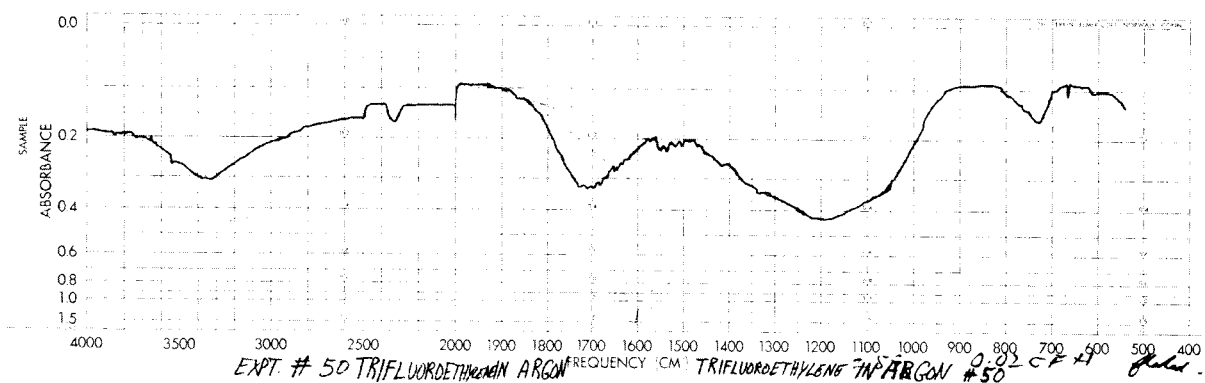
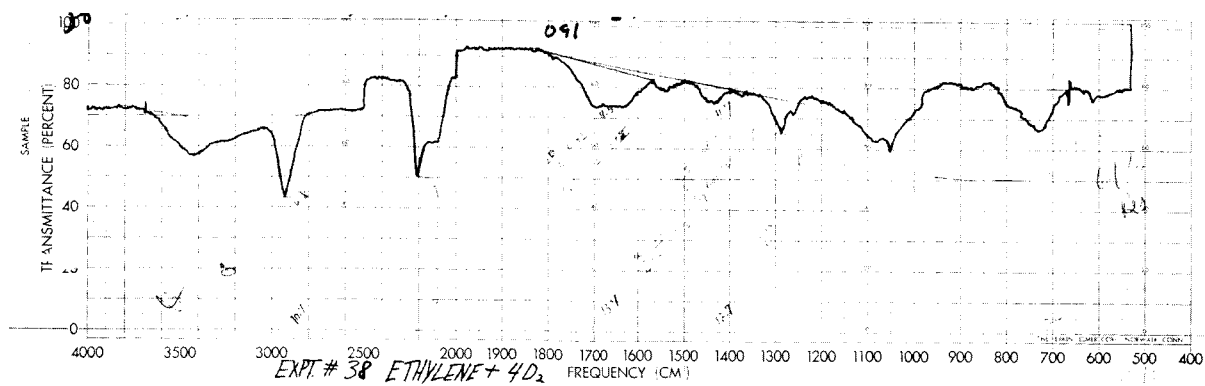


FIGURE 7

potassium bromide pellets no efforts were made to determine what fraction of the OH band was due to the film and what part was contributed by the potassium bromide. The strong absorption peak around 2900 cm^{-1} was resolvable into at least three distinct peaks; one at 2960 another at 2930 and a final one at 2870 cm^{-1} . These resolvable peaks have been assigned to the CH_3 and CH_2 stretching vibrations. Since this band extends to a slightly higher wave number than 3000 cm^{-1} , there is evidence of olefinic linkages as well as the carbon hydrogen stretching frequencies. The broad band covering from 1800 to 1550 cm^{-1} has been found to contain at least two peaks. The one at 1700 cm^{-1} is assumed to be due to carbonyl and the peak at 1620 cm^{-1} is conjectured to be the stretching vibrational frequency of a carbon-carbon double bond. There is evidence to support these peak assignment, as we shall see later. The peaks at 1450 and 1380 cm^{-1} have been ascribed to the carbon-hydrogen bending vibration frequency. The variable weak broad band covering the region from 1100 to 1000 cm^{-1} has been identified as silica. The silica contaminate is due to its entrapment in the film during the removal of the films from the walls of the reaction tube. Finally the variable peak at 740 cm^{-1} has been assigned to a methylene rocking vibration which occurs in a long carbon chain such as polyethylene.

A search of the literature for infrared spectras of plastic material was made in order to determine if any of the reported patterns were similar to the spectra obtained in this work, particularly for the ethylene film. We found that the spectras reported by Stemler and Kagarese⁽⁵⁾ for cross-linked polyethylene were similar. Their reported infrared spectra for Cabot's (CAB-XL1411) chemically cross-linked polyethylene, duPont's Suryln A a cross-linked polyethylene resin containing both covalent and ionic chemical bonds and Electronized Chemical Corporation's insulrod, a polyethylene cross-linked by irradiation all were characteristic of the spectras reported in this work. This similarity of spectras applies in some degree

5. S. S. Stimler & R. E. Kagarese, NRL Report 6392, AD #634 427 (1966)

to the plastic film that we prepared from toluene in spite of the fact that its infrared spectra indicate the presence in some degree of aromaticity in the plastics.

B. Absorbency Ratio.

It was reasoned that a comparison of the infrared patterns between the different starting materials would lead to the identification of the structures of the films and would provide some insight as to reaction mechanism. While a qualitative examination of the patterns did reveal that films consisted primarily of a highly cross-linked polyethylene with some unsaturation and aromaticity, it did not reveal the exact relationship between the structure of the film and the starting material. Therefore, a quantitative evaluation of the absorption peak intensity was undertaken to determine if a correlation between the peak intensity and composition of the starting gas did exist.

Using Beer's Law the logarithm of the intensity of a peak was directly proportional to the concentration. By selecting a particular peak in the infrared pattern as an internal standard it was feasible to devise a method to determine the relative concentrations. Therefore by dividing the absorbancy of a specified peak by the absorbancy of the standard peak it is possible to obtain a value for the relative concentration. Thus this absorbancy ratio provides a means of comparing the infrared spectras from different samples and a means of establishing whether a correlation exists between the starting compound and the structure of the resultant film. The peak at 1450 cm^{-1} was taken as the standard, and the absorbancy ratio of the following peaks were calculated: A_{2900}/A_{1450} ; A_{1700}/A_{1450} ; A_{1620}/A_{1450} ; and A_{740}/A_{1450} plus the absorbancy ratio of A_{2900}/A_{2160} for the deuterated samples. The A_{2900}/A_{1450} ratio was chosen to compare the carbon-hydrogen stretching vibration with the deformation vibration for the series of hydrocarbons. The ratio of A_{1700}/A_{1450} was selected to determine if there was a relationship between the carbonyl present in the film and the starting materials. The absorbancy ratio of $1620\text{ cm}^{-1}/1450\text{ cm}^{-1}$ was evaluated to determine if there was a correlation between degree of double bonding in the film and the hydrogen content of the starting materials. The ratio of A_{740}/A_{1450} was considered to be an indication

of the extent of the build-up of the linear ethylenic type structure with starting material. The substitution of deuterium for hydrogen in the films was monitored by A_{2900}/A_{2160} .

The tabulation of the absorbancy ratio data has been listed in Table III along with the composition of the starting materials. It should be mentioned that the deposited films were reasonably homogeneous; infrared patterns prepared from different portions of the same sample gave identical patterns (absorption intensities within 90% of each other) even though many of the second spectra was prepared after a time lapse as long as a month. Spectra obtained from samples prepared under identical conditions gave absorption coefficient ratios within 10 to 20%.

Correlations were found not only for the degree of carbon-carbon double bonding in the film with the composition of the reactants (A_{1620}/A_{1450}) and the deuterium incorporation in the film with the amount of deuterium in the starting gases (A_{2900}/A_{2160}), but a correlation was found between the ratio of A_{1700}/A_{1450} and the oxygen content of the film. While no trend was observed for the ratio of A_{2900}/A_{1450} , the values were fairly consistent only varying from 1.9 to 2.5 over the whole range of compositions studied. The absorbancy ratio values for the methylene chain (A_{740}/A_{1450}) scattered considerably and no consistent trend was evident. The categorizing of this peak near 740 cm^{-1} as a CH_2 rocking mode is not completely substantiated other than by the contour of the peak.

C. Degree of Unsaturation Present in Films.

An obvious correlation exist for the degree of unsaturation (carbon-carbon double bonds) (A_{1620}/A_{1450}) and the hydrogen/carbon (H/C) ratio of the input gases. The absorbancy ratio for isobutylene and ethylene both with a H/C ratio of 2/1 for the gases varies from 0.4 to 0.66. While the "A" ratio for acetylene is in the range of $1.7 \pm .2$; while the absorbancy ratio is near 3.0 for diacetylene which has a H/C ratio of 0.5/1 for the compound. Also, it is evident that if you premix hydrogen with the last two compounds (acetylene and diacetylene) the number of double bond in the film decreases accordingly. This correlation

TABLE III
INFRARED ABSORBANCY RATIOS $\text{cm}^{-1}/\text{cm}^{-1}$ OF
POLYMERIC FILMS

Expt No	Composition	2900/1450	1700/1450	1620/1450	700/1450	2900/2160
<u>Isobutylene</u>						
6	C_4H_8	2.3	1.0	0.66		
7	C_4H_8	2.2	0.5	0.40		
35	C_4H_8 & D_2	--	0.8	--	3.1	5.9
37	C_4H_8 & 4D_2	--	0.2	--	0.2	2.9
<u>Ethylene</u>						
8	C_2H_4	2.0	--	--	--	--
9	C_2H_4	2.2	0.2	0.41	--	--
17	C_2H_4	2.1	0.3	0.66	0.2	--
22	C_2H_4 & H_2	2.5	0.1	0.45	--	--
23	C_2H_4 & 2H_2	2.4	0.2	0.40	0.2	--
24	C_2H_4 & D_2	--	0.9	--	1.5	6.6
38	C_2H_4 & 4D_2	--	2.1	--	2.6	0.9
<u>Acetylene</u>						
10	C_2H_2	2.2	0.7	1.90	--	--
18	C_2H_2	2.2	0.7	1.52	--	--
20	C_2H_2 & H_2	1.9	0.3	0.87	1.4	--
21	C_2H_2 & 2H_2	2.1	0.2	0.51	--	--
27	C_2H_2 & D_2	--	0.2	--	0.9	2.4
39	C_2H_2 & 4D_2	--	1.4	--	0.5	1.0
<u>Diacetylene</u>						
41	C_4H_2	--	2.9	2.97	0.9	--
45	C_4H_2 & H_2	2.2	1.9	0.7	0.7	--
46	C_4H_2 & 2H_2	2.4	1.5	0.6	0.8	--
43	C_4H_2 & D_2	--	2.1	--	0.5	6.55
42	C_4H_2 & 2D_2	--	3.1	--	1.6	3.75
44	C_4H_2 & 4D_2	--	2.9	--	--	2.52

is shown in Figure 8 where the absorbancy ratio is plotted against the H/C ratio present in the film. Because not all the films were chemically analyzed, it was necessary to estimate the hydrogen-carbon composition for some of the films reported in the graph. This was done by referring to Figure 4 and using the data presented there as a calibration curve. Since this curve is fairly linear, it is relatively easy to estimate the composition. Thus by knowing the H/C ratio of the reactant gases one could arrive at an estimate of the H/C ratio in the film. This procedure was used because it was felt that this approach gave a clearer picture of the degree of unsaturation of the films. However a similar shaped plot would have obtained for Figure 8 if instead we had used the H/C ratio of the reactant gases. Some of the significant aspects of this correlation is that it demonstrates that the composition of the deposited films is more of a function of the atomic ratio of the input gases than it is on the chemical reactivity of the reactant gases and it also substantiates our interpretation of the infrared patterns. For example, it is unlikely that if the absorption peak at 1620 cm^{-1} did not correspond to an olefinic grouping we would find a correlation with the peak intensity and chemical composition. Naturally if the film has a polyethylene like structure, the decrease of hydrogen content in the film would lead to more unsaturated linkages in the polymer.

D. Deuterium Content of Films.

The fact that deuterium is readily incorporated in the film also supports the first conclusion mentioned above; i.e., the composition of the deposited polymer is more of a function of the atomic constituents of the gases present in the plasma rather than the chemical reactivity of these gases. Figure 9 is a plot of the absorbancy ratio for the stretching frequency of C-H and C-D in the polymers versus the hydrogen-deuterium ratio of the input gases. As more and more deuterium is premixed with the hydrocarbon monomer the intensity of the peak at 2160 cm^{-1} increases relative to the band around 2900 cm^{-1} . While there is some variation of the slopes of the data plots for different hydrocarbon gases studied, all curves show the same trend. No quantitative analysis has been made to determine the weight percent of deuterium on the film at this time, but this could have been obtained by a mass spectrometry analysis of the pyrolysis products of the films.

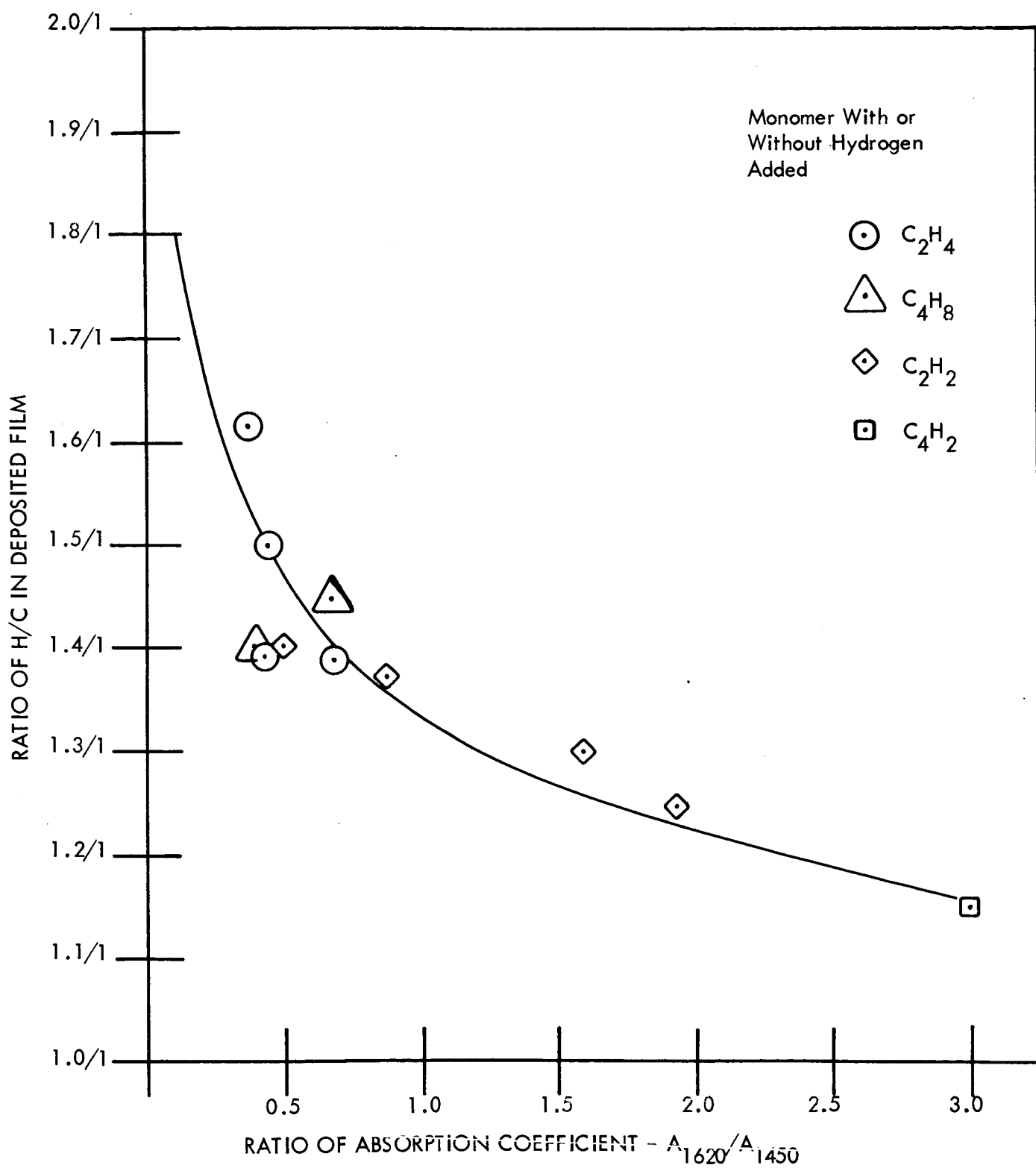


FIGURE 8

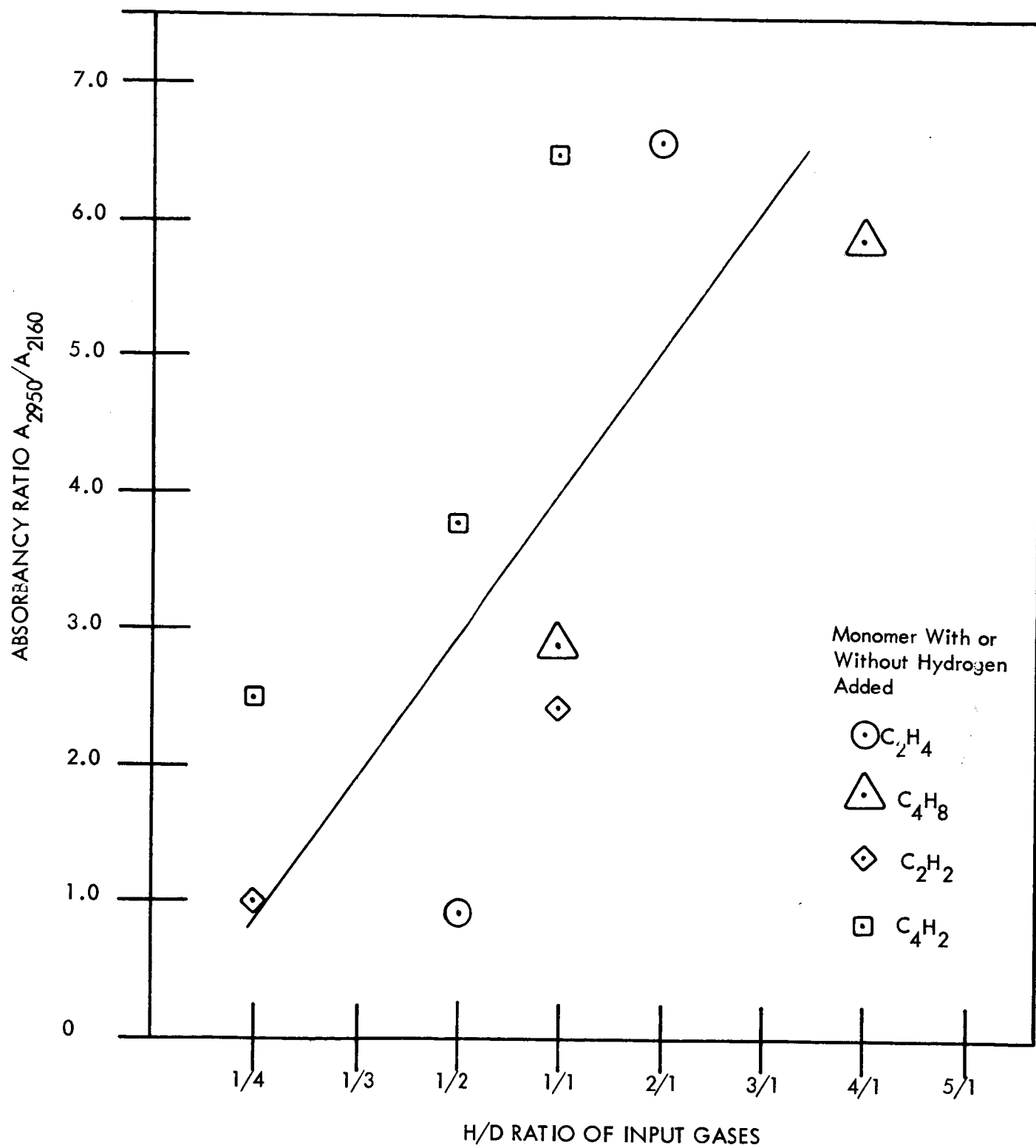


FIGURE 9

E. Presence of Carbonyl Groups in Films.

The assumption that the peak at 1700 cm^{-1} is due to carbonyl groups is substantiated by the fact that there is a relationship between the amount of oxygen present in the film and the ratio of the absorption coefficient at 1700 cm^{-1} with respect to the absorption coefficient at 1450 cm^{-1} . This data is presented in Table IV. While there is some scatter in the data the trend towards higher ratios with increasing oxygen content of the film is clearly evident. This brief investigation was not sufficient to establish the source of the oxygen contamination on the films, however, from Table IV it was also obvious there was no correlation between the oxygen content of the film and the addition of hydrogen or deuterium to the hydrocarbons. The large amount of oxygen in the films was rather anomalous, however, the presence of oxygen containing groups was observed in the spectra published by Wightman⁽²⁾ in addition to the previously mentioned plastics analyzed by Stemler and Kagarese⁽⁵⁾ and in the spectra of Neiswender⁽⁴⁾. Thus we conclude the presence of oxygen is not unique to our system and we tend to support the conclusion of Neiswender⁽⁴⁾.

TABLE IV
OXYGEN CONTENT OF FILM AND THE
CARBONYL ABSORPTION COEFFICIENT RATIO

<u>Expt No.</u>	<u>Gas Composition</u>	<u>Wt %* O₂</u>	<u>A₁₇₀₀/A₁₄₅₀</u>
17	C ₂ H ₄	9.2	0.3
23	C ₂ H ₄ & 2H ₂	7.6	0.2
38	C ₂ H ₄ & 4D ₂	12.0	2.1
18	C ₂ H ₂ & Ar	12.0	0.7
21	C ₂ H ₂ & 2H ₂	6.7	0.2
41	C ₄ H ₂	26.8	2.9
43	C ₄ H ₂ & D ₂	11.8	2.0
42	C ₄ H ₂ & 2D ₂	30.4	3.1

*The oxygen weight % is determined from the chemical analysis by the differences.

F. Polyethylene Chain.

There is a variable absorption peak that appears in the infrared patterns between 700 to 800 cm^{-1} . The peak not only fails to appear on occasion, but its location in the pattern may vary, generally the peak appears at 740 cm^{-1} . It is speculated that this peak is primarily the result of the "CH₂ rock" of an ethylene chain. This shift in absorption frequency may be due to a variation in length of the ethylene chain. However, the peak could also be the result of a "CH wag" on alkyl substituted olefins or due to the crystalline content of the polymer. However, the fluorinated ethylene deposited polymers also have been found to absorb in this frequency range which is very perplexing, but to our best estimate, this peak is judged to be the result of the rocking of the ethylene chain; this was based on the contour of the peak as well as its frequency.

G. Infrared Spectra of Films Produced from Toluene.

Toluene was employed in the investigation to aid in the identification of the structure of the plasma deposited films. While there was a striking similarity of the spectras between the film produced from this aromatic compound and that from the aliphatic materials it is apparent toluene film contain a relatively high degree of aromatic character and more closely resembles the spectra of a polystyrene plastic. The narrow sharp band at 700 cm^{-1} with a broad band adjacent to it is characteristic of an aromatic compound. The same goes for the very broad band from 1000 to 1300 cm^{-1} and the sharp peaks at 1500, 1580 and 1600 cm^{-1} . These plus the additional small detail in the C-H stretching band which extend above 3000 cm^{-1} and which has not been observed in the polymers deposited from most of the aliphatic materials supports the aromatic character of the films. It should be mentioned again that the film prepared from isobutylene display a small degree of aromaticity in their spectras. The cause of this is unknown but the significance of this finding warrants further study.

H. Infrared Spectra of Films Produced from Trifluoroethylene and Tetrafluoroethylene.

Since hydrofluoric acid vapor are used to release the polymeric film

from the reaction tube it was thought advisable to prepare polymeric films from trifluoro and tetrafluoroethylene and determine if the hydrofluoric acid vapors are reacting with the deposited polymer to give an infrared spectra of a fluorinated hydrocarbon polymer instead of the primary deposited polymer. Thus by a comparison of these infrared patterns with the aliphatic patterns we could establish whether the hydrofluoric acid vapor are interfering. However, the infrared spectra of both films produced from tri- and tetrafluoroethylene were rather amorphous. These polymers displayed a relatively strong intense very broad band from 1000 to 1400 cm^{-1} which was impossible to separate out. Outside of a medium intense band at 740 cm^{-1} the infrared patterns revealed little else except a variable hydroxyl group band at 3400 cm^{-1} and a small variable band at 1700 cm^{-1} corresponding to the carbonyl functional group. However, the band at 740 cm^{-1} is perplexing. The infrared patterns of fluorinated ethylene plastics in the literature show an absorption peak in this region. However these reported peaks as well as our fluorinated peaks have a different profile from the peak at 740 cm^{-1} for the hydrocarbons. The hydrocarbon peak is asymmetric almost characteristic of two adjunct peaks having different intensities relative to each other. Additional work is needed to determine the exact nature of the peak to insure that the peak observed at 740 cm^{-1} for the aliphatic films is not due to the methylene chain.

VII CONCLUSION

Coatings deposited via an electrodeless, microwave discharge process from relatively low molecular weight hydrocarbons produce highly cross-linked adherent films. In general these films are resistant to most solvents as well as having a high thermal resistance. The color of the films vary from light yellow to dark brown, depending on the composition of the reactant gases.

1. Films deposited from ethylene are light yellow to clear in color, char or react with only concentrated sulfuric acid and are thermally stable in air to 280°C . Their infrared spectra indicates that the film have a highly cross-linked polyethylene structure.

2. Films prepared from isobutylene are similar in appearance and properties to the polyethylene films but their infrared spectra indicates a small degree of polystyrene like structure in the films in conjunction with the polyethylene structure.

3. The films prepared from acetylene are orange to brown in color. The films are insoluble in all solvent and do not thermally degrade in air to 340°C . The infrared spectra indicates a polyethylene structure with a high degree of unsaturated groups.

4. Diacetylene films are black to red brown in color. Their chemical analysis supports the fact that these films are highly unsaturated. These polymers contain the least amount of hydrogen in their structures. They are insoluble in all solvents and withstand heating in air to above 300°C .

5. Premixing hydrogen with the aliphatic monomers increases the hydrogen content of the film up to a certain point, decreases the degree of unsaturation in the films, lightens their color and causes them to be soluble in concentrated sulfuric acid.

6. By mixing deuterium with the aliphatic reactants in various ratios it is possible to follow the incorporation of deuterium into the polymers structure by infrared analysis indicating that the incorporation of hydrogen into films is independent of its source.

7. Toluene films are yellow in color and similar in appearance to the films prepared from polyethylene. Their infrared spectra suggest the films have a structure analogous to a polystyrene-polyethylene copolymer.

8. The deposition rate of the various films are reduced by the addition of hydrogen to the reactant gas and the deposition rate correlates with the gas composition.

9. The infrared and chemical analysis of the various films indicates the presence of oxygen in the films as carbonyl groups. Neiswender⁽⁴⁾ claims the carbonyl bands are formed by a rapid oxidation by molecular oxygen on exposure of the sample to air. No verification of this claim was made except to note that when oxygen was premixed with the aliphatic monomer it inhibited the deposition or stripped the polymeric film from the reactor.

10. The films produced from trifluoroethylene and tetrafluoroethylene are similar in physical properties. Both films are insoluble in all solvents; they do not degrade until heated to a temperature near 330°C. However, the trifluoroethylene produces a brown colored film while the tetrafluoroethylene produces a dirty white, teflon-like film. The infrared patterns do not reveal enough detail for identification of functional grouping in the films.