INERTING HYDROCARBON FUELS with HALON ALTERNATIVES

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ABSTRACT

The legislated elimination of halon production due to ozone-layer depletion concerns has motivated the current drive to find effective and environmentally acceptable alternative fire suppressants. It has also focussed attention on appropriate laboratory screening tests for such agents. The cup-burner test is a standard screening test for the performance of a suppressant in extinguishing an established diffusion flame. This test has shown the superior performance of Halon 1301 (CF_3Br) and similar bromo and iodo fluorocarbons in extinguishing such flames, and has been found to correlate with the results of larger scale extinguishment of open flames. Another test used for screening inerting agents *to* replace CF_3Br involves the preparation of uniform gaseous mixtures of fuel, air, and inertant in a chamber, and the monitoring of pressure rise upon ignition. Normally, the highest flame temperatures, explosion pressures, rates of pressure rise, and required inerting gas concentrations are found for fuel concentrations just above the stoichiometric fuel-air compositions (about 10% for CH_4-air). Such mixtures, thus, represent a worst-case scenario for explosion inerting. Electric sparks are the most common and convenient ignition sources for the latter test. However, there can be a strong influence of ignition source and energy on the inerting requirements for halons[1,2]. It was considered desirable to avoid the issue of ignition quenching by the inerting agent through the use of chemical igniters of considerably greater energy than the normal spark sources. Commercial pyrotechnic igniters having a calorimetric energy of 1000 J were used for this study, since prior work at the Pittsburgh Research Center (part of the U.S. Bureau of Mines until 4/96) had shown that these igniters reproduced the accepted lower

flammability limit of 5% for CH_4-air mixtures in a 20-L explosion chamber[3]. The test results for the required inerting concentration of CF_3Br in 10% CH_4-air was 18%. a value which is much higher than that reported for spark ignition. The fluorinated hydrocarbons, C_4F_{10} and CF_3CHFCF_3 (C_3F_7H), required about 10% for 10% CH_4-air mixtures. The relative effectiveness of the above fluorocarbons vs CF_3Br is thus the reverse of that obtained in the cup-burner test. These results argue against the strategy of relying on a single laboratory screening test to gauge the relative effectiveness of candidate suppressants in various fire and explosion scenarios. Further testing of CH_4 and other fuels at various fuel/air ratios and various igniters is thus indicated, in order to provide a more complete data base for the effectiveness of proposed inerting agents under different ignition and fire scenarios.

INTRODUCTION

Much of the laboratory and field studies on the effectiveness of halons and halon alternatives in fire suppression have focussed on the extinguishment of open flames. There is another problematic fire scenario relevant to accidental impacts or military operations, however; that is, the explosion suppression of enclosed, premixed, gaseous fuel-air mixtures such as in the head space of fuel tanks. The ignition and pressure build-up of such fuel-air mixtures, e.g., by impact or penetration by incendiary projectiles is more difficult to suppress within the confines of the enclosure than the subsequent external fire, due to the much higher propagation velocities of an explosion relative to a diffusion flame. These mixtures can also be more energetic per unit volume, and less susceptible to chemical inhibition. Such distinctions are most pronounced for uniform stoichiometric mixtures, wherein the amount of oxygen in the air is just sufficient to completely oxidize the fuel component. Mixtures that approach the fuel-rich flammability limit, on the other hand, are expected to behave more like diffusion flames. All such uniform mixtures, however, fix an often uncontrolled variable, the concentration of oxygen in the flame front, and allow a more direct test of the relative contribution of thermal vs. chemical (chain stopping) mechanisms to fire suppression based on calculated flame temperatures. An explosion chamber such as the near-spherical 20-L stainless steel chamber developed at the Pittsburgh Research Center, is well suited for testing uniform fuel-air-suppressant mixtures since it is large enough to allow the use of energetic ignitors, yet sufficiently compact to fit into a standard laboratory hood. The latter consideration is important for safe operation since corrosive and toxic products are produced from inadequately inerted mixtures.

EXPERIMENTAL

The 20-L steel chamber used for the studies reported here (figure 1) is of the type that has been adapted by U.S. and international testing agencies as the standard laboratory explosion chambers for dispersed fuel dusts, since they have been shown to reproduce the results from much larger (1000-L) explosion chambers'. The chamber was modified for gas explosion studies by inserting a small mixing fan, and by providing valved inlets for gas admission. The gas mixtures were prepared by first evacuating the chamber and adjusting the partial pressures of the inertant, fuel (CH_4), and air to give the desired concentrations. It should be noted that the stated CH, concentrations (10% and 14%) are computed from the component partial pressures on an agent-free basis, that is, they are the ratios of CH, to CH_4 + air in the mixtures. These ratios determine the "richness" and exothermicity of the mixture that is to be inerted. The agent concentrations, in contrast, are the actual mole% (volume %) values in the overall mixture. The admitted gases were mixed by fan for 3 minutes and then allowed to come to rest for 1 minute prior to electrical activation of the 1000 J pyrotechnic igniter. The igniters contain a 0.24g mixture of 40% Zr, 30% BaO_2, and 30% $BaNO_3$ that produces a jet of incandescent particles[3]. The ignition time, absolute pressures and rates of pressure rise were stored, and displayed using a high-speed AID data aquisition board in a PC.

RESULTS and DISCUSSION

The pressure rise after ignition was used to determine the inerting concentration of an agent. The pressure rise of 0.16 bar (2.3 psig) due just to the 1000 J igniter was subtracted from the overall pressure rise of the ignited mixtures. Normally, there was a sharp drop in pressure at the inerting level to less than 0.35 bar (5 psig), and a very gradual subsequent decrease in pressure at higher concentrations. A pressure rise above 0.35 bar (5 psig) is, therefore, taken as the empirical criterion of a flammable mixture. A lower pressure (below several psig) should result from the use of the same igniter in larger chambers at the inerting concentrations reported here, due to the smaller volume fraction occupied by the initial fireball. The above explosion criterion was found to be simpler and more easily applied than the more theoretically based criteria previously used in Bureau publications involving the **20-L chamber**[3]. **It** is also more consistent with the criteria generally used in gas inerting studies. The resulting values for inerting concentrations are also relatively insensitive to the exact criteria used to decide on the explosivity of a mixture.

Figure 2 shows the pressure rise vs. the concentration of nitrogen (N_2) in 10% CH_4-air. **It** is noted that there is a gradual decrease in explosion pressure until a concentration of about **37%** N_2 is reached. At that point there is a large drop in pressure. From **38%** N_2 **(430** g/m^3) and above, only pressure rises less than **5** psig. are noted. Such results characterize a purely thermal type suppressant. The agent reduces the energy density of the mixture, absorbs heat released by the fireball, and reduces the burning velocity to the point where the flame can no longer propagate into the unburned gas mixture against the competing hydrodynamic forces'. The pressure developed in the chamber is then dependent on the initial fireball size, shape, and location relative to the chamber walls, which is, apparently, sensitive to the action of the igniter. Hence, the scatter in pressure near the inerting concentration.

Figures **3** and **4** show similar plots for CF_3CHFCF_3 (C_3HF_7) and C_4F_{10}, which are among the leading replacement candidates for CF_3Br. Note the precipitous drop in pressure that they exhibit at concentrations above **9%** and 10%. respectively. The inerting concentrations are taken as **9.5%** (650 g/m^3) for C_3HF_7 and **10%** (960 g/m^3) for C_4F_{10}. In contrast, figure **5** shows the more gradual pressure drop with CF_3Br concentration. The pressure rise appears limited to about 5 psig. at **18%** (1080 g/m^3). On a volume basis, the above fluorocarbons are twice as effective as CF_3Br and four times as effective as N_2 On a mass concentration basis, C_4F_{10} is comparable in effectiveness to CF_3Br, while C_3HF_7 is **40%** more effective. Nitrogen is more effective than the other agents on a mass basis. **It** has the disadvantage, however, that it must be stored at high pressure in heavy-walled vessels in order to discharge the required mass for suppression. In contrast, the other agents are stored as liquids at moderate pressures.

For **14%** CH_4-air mixtures, the limited data set for N_2 first shows a large pressure drop at 23%, and the pressure rise becomes less than **5** psig. at over **28%** (figure 6). The inerting level is taken as 28% (320 g/m^3). Figures 7 and 8 show the corresponding results for C_3HF_7 and C_4F_{10}. For both fluorocarbons, the first large pressure drop occurs at **4%** and the pressure rise stays within **5** psig for

concentrations above 5%. The inerting concentration is therefore 5% (340 g/m^3) for C_3HF_7 and 5% (480 g/m^3) for C_4F_{10}. Figure 9 shows the results for CF_3Br. Here the first major pressure drop occurs at 5%. but the 5 psig. level is not reliably reached until a concentration of 10% (600 g/m^3).
The latter is taken as the inerting concentration of CF_3Br in "rich" (14%) CH_4-air mixtures. On a volume basis, the above fluorocarbons are seen to be twice as effective as Halon 1301 and about 5 times as effective as N_2. On a mass concentration basis, C_3HF_7 requires 40% less agent than CF_3Br, while C_4F_{10} requires **20%** less than CF_3Br.

CONCLUSIONS

In summary, the relative effectiveness of the above agents in inerting CH_4-air mixtures in the **20-L** chamber is as follows:
$C_3HF_7 = C_4F_{10} > CF_3Br > N_2$ on a volume (mole) percent basis, and
$N_2 > C_3HF_7 > C_4F_{10} > CF_3Br$ on a mass concentration basis.
For extinguishing established heptane diffusion flames in the cup-burner test, the following relative effectiveness has been found:
$CF_3Br > C_4F_{10} = C_3HF_7 > N_2$ on a volume percent basis, and
$CF_3Br > N_2 = C_3HF_7 > C_4F_{10}$ on a mass concentration basis.

The considerable difference in the relative effectiveness of CF_3Br vs. the above fluorocarbons in the two types of screening tests argues against the use of a single laboratory test to rank the relative effectiveness of halon replacement candidates. The cup-burner test models the extinguishment of open diffusion flames, and has been accepted as an adequate screening tool for such applications. Inerting a premixed fuel-air mixture with a fire/explosion inhibitor agent is simulated better by a laboratory sized explosion chamber containing the fuel-air-inertant mixture with an adequate ignition source. More work is needed, however, in establishing the energy and nature of the ignition source that will not be quenched by the mixture and will not "overdrive" the contents of the chamber. More work is also needed in establishing the mechanisms of quenching of premixed flames by the various agents.

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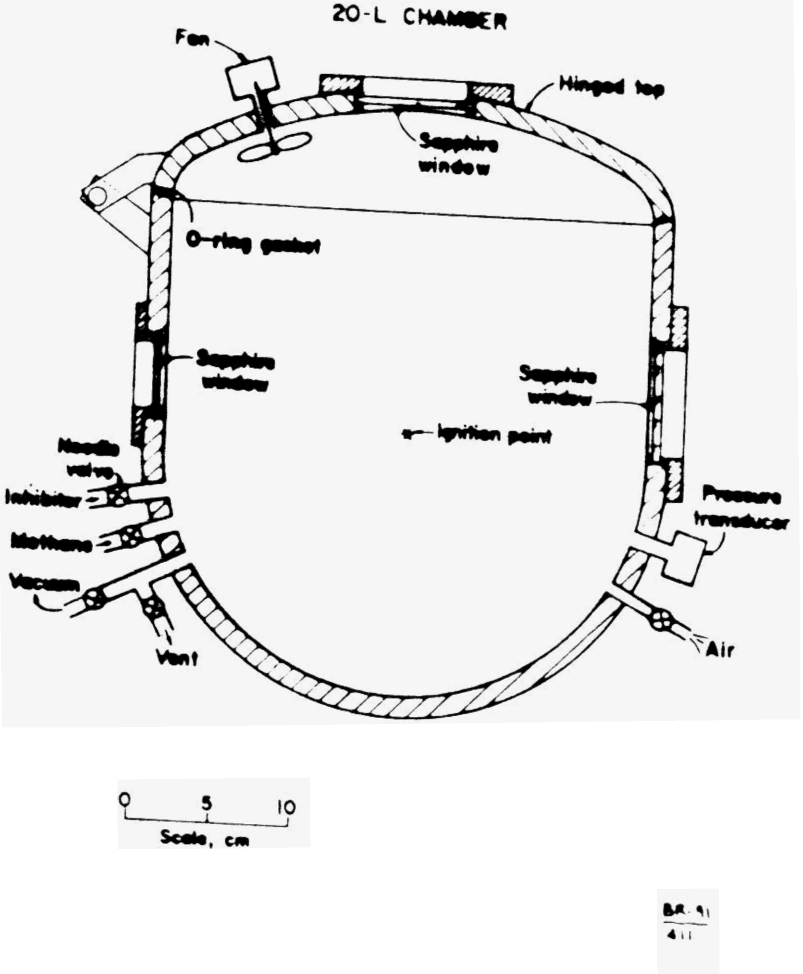
Figure 1A.



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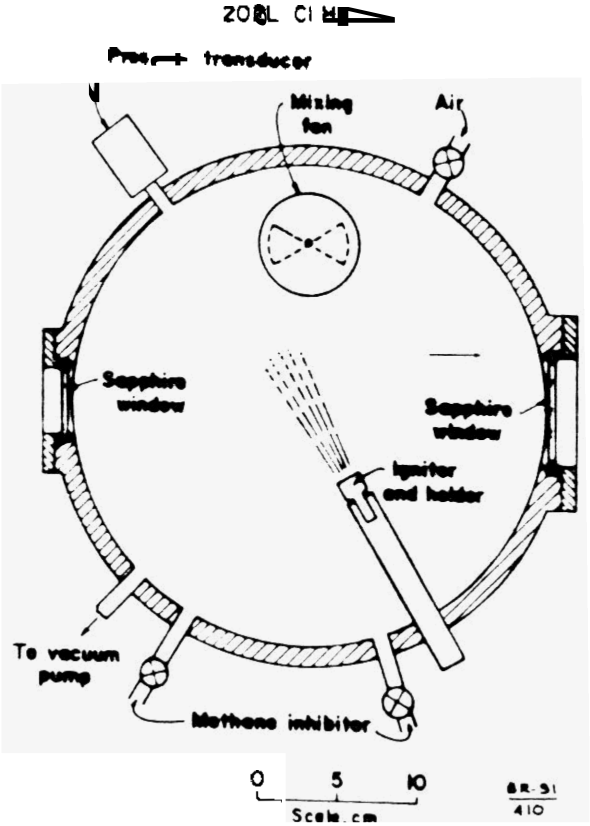
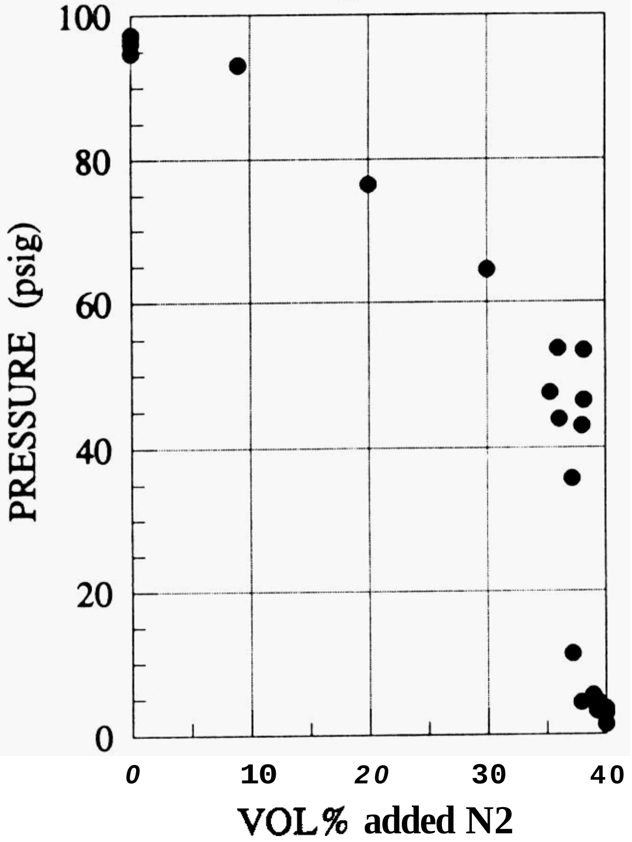


10%CH4 - AIR vs % INERTANT

Figure 2.



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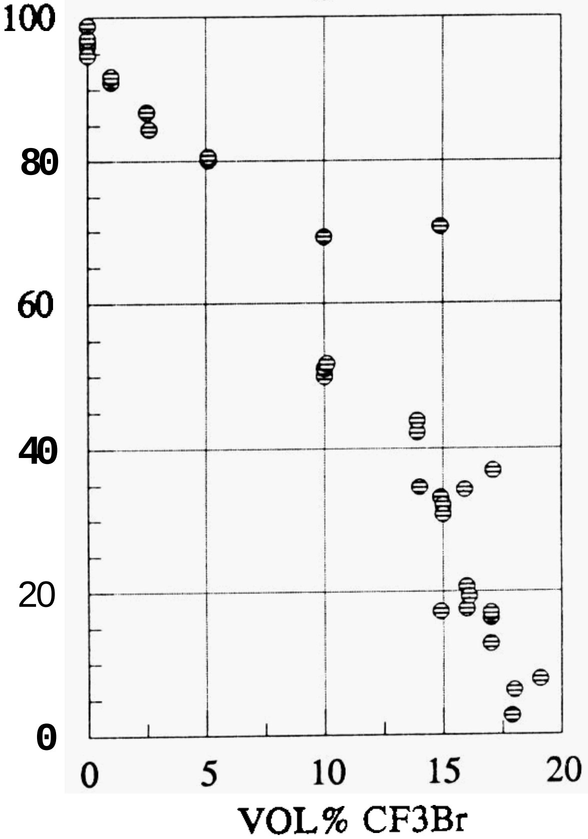

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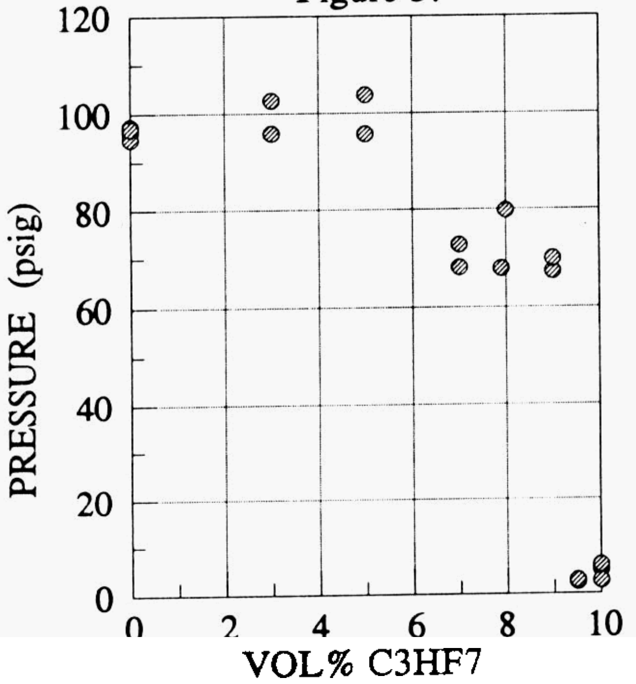

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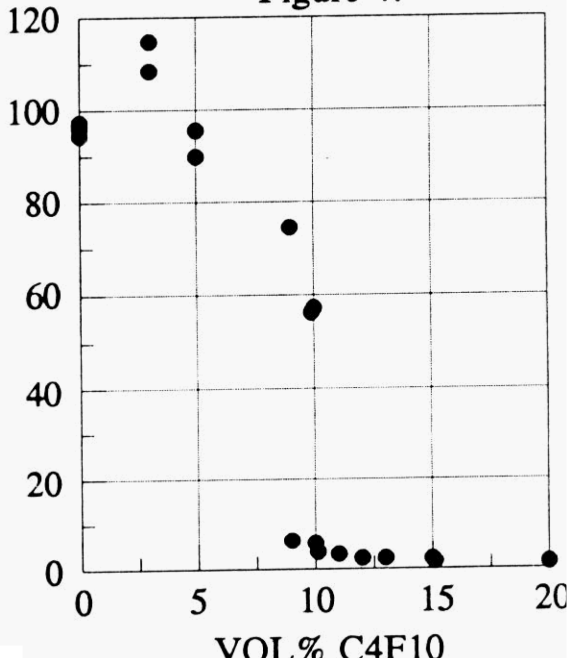
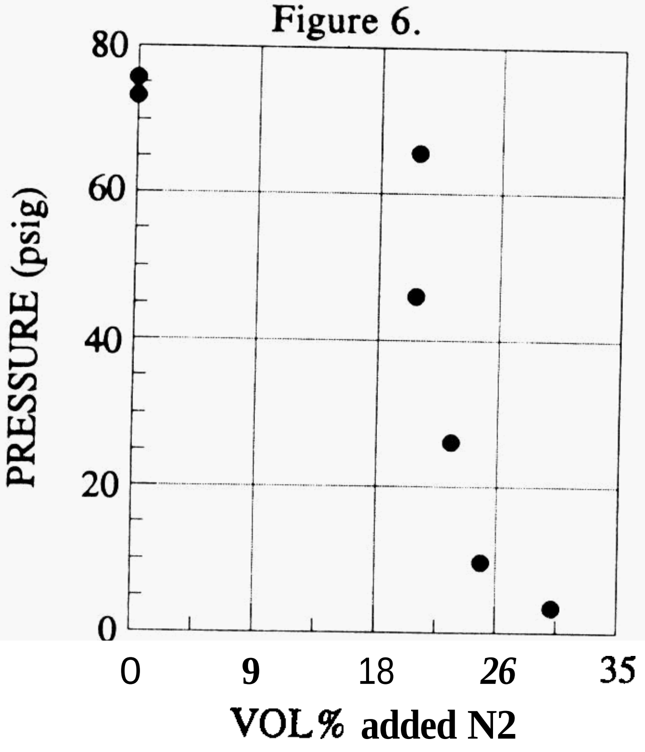


14%CH4 - AIR vs % INERTANT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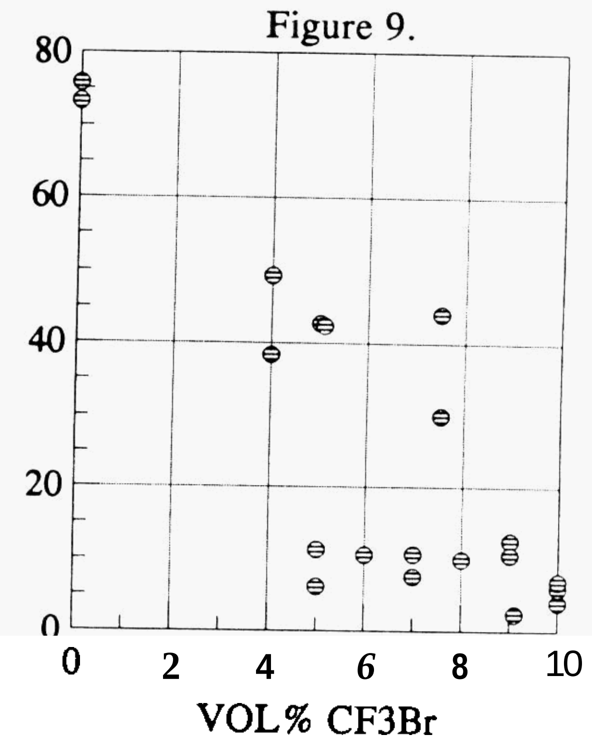
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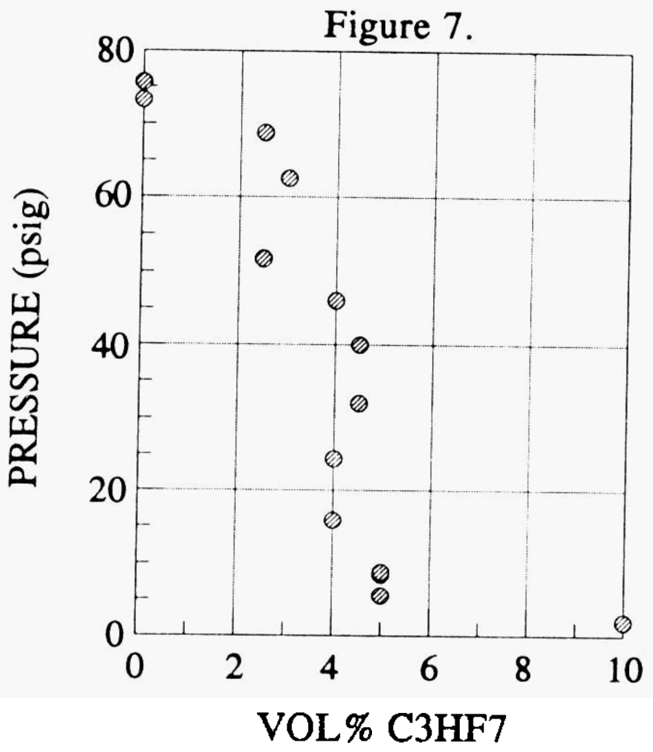
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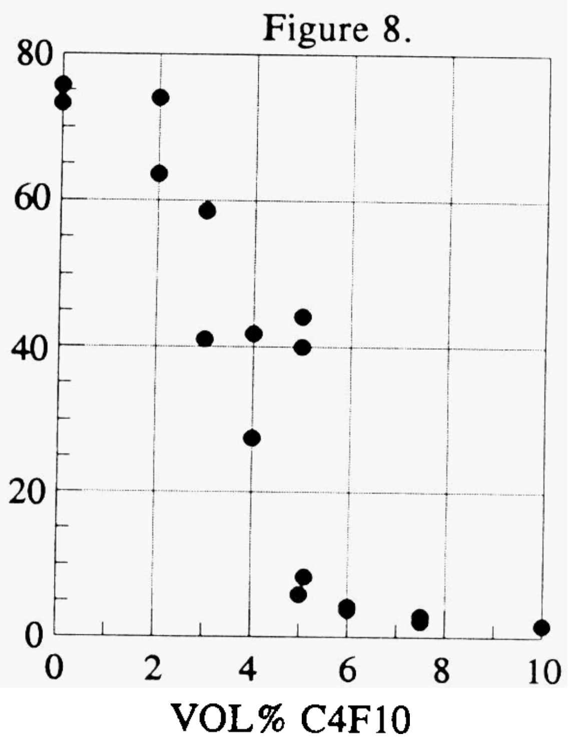
Figure 8.