Stabilization of Methylacetylene and Propadiene Mixtures

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An investigation was conducted to determine the compositions of methylacetylene-propadiene-hydrocarbon mixtures stable to 100 joules of ignition energy in a 10½-inch spherical reactor at extreme storage conditions (68° C., 220 p.s.i.g). The effectiveness of hydrocarbon diluents in stabilization decreased in the following order: isobutane > propane > isobutylene ≥ propylene > butadiene. The low temperature stability of methylacetylene and propadiene, the effect of ignition energy, and the effect of steam as a diluent for methylacetylene-propadiene-hydrocarbon mixtures were also investigated.

LIMITED information is available on the stabilization of the potentially hazardous mixtures of methylacetylene and propadiene (allene) by hydrocarbon diluents at elevated temperatures and pressures. Like acetylene, methylacetylene and propadiene are thermodynamically unstable and decomposition can be induced resulting in the exothermic propagation of a flame in the absence of air. The critical pressure above which a flame is propagated in methylacetylene has been observed by Fitzgerald (*3*) to be 31 p.s.i.g. at 120° C. in a 2-inch diameter bomb and 39 p.s.i.g. by Kuchta, Spolan, and Zabetakis (*6*) under similar conditions. The critical pressure for propadiene has been reported to be 16 p.s.i.g. at 120° C. in a 2-inch diameter bomb (*6*). Methylacetylene and propadiene are more stable than acetylene which undergoes a similar induced decomposition and propagation. The lower pressure limit of acetylene is 6 p.s.i.g. in a 2-inch diameter bomb (*5*).

Similar to acetylene, methylacetylene and propadiene can be stabilized in a given system at a specific temperature and pressure by the use of appropriate diluents. Fitzgerald (*3*) has reported that ethane is more effective than methane or nitrogen in the stabilization of methylacetylene. Kuchta, Spolan, and Zabetakis (*6*) have recently investigated the parameters affecting the stabilization of mixtures of methylacetylene and propadiene by propylene and discovered that stabilization was dependent on temperature, pressure, vessel diameter, and composition.

To secure more information on the safety-stability characteristics of methylacetylene-propadiene-hydrocarbon mixtures (*8*) at extreme storage and shipping conditions (68° C. at 220 p.s.i.g.), the effectiveness of steam and hydrocarbon diluents, the stability of methylacetylene and propadiene, and the effect of ignition energy were investigated.

EXPERIMENTAL APPARATUS AND PROCEDURE

Stability Measurements. The stability of methylacetylene and propadiene was determined in a 1 × 12-inch steel cylindrical bomb equipped with a 5000 p.s.i.g. frangible safety. The effects of diluents on the methylacetylene-propadiene system were studied in a 10½-inch spherical steel bomb equipped with a 2200 p.s.i.g. frangible safety. The supporting equipment for both bombs was similar and that for the 10½-inch reactor will be described.

The asbestos insulated bomb was electrically heated and controlled by a Brown Pyrovane-IC thermocouple system. The static pressure was determined by a Dynisco strain gage transducer system. The dynamic pressure was followed by a Kistler transducer system with a Sanborn recorder, Model 60-1300.

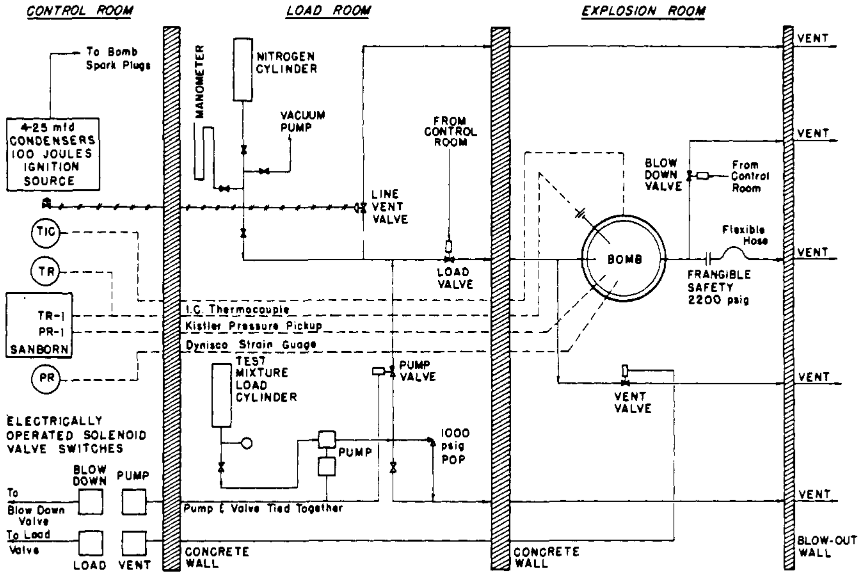
In the experiments where low temperatures were required, the 1 × 12-inch bomb was stripped of the insulation and packed with a water-ice mixture or with a methylene chloride–dry ice mixture. Once the bomb was cooled, it was allowed to warm up to the desired temperature before ignition.

Three ignition systems were utilized. The first igniter was a 1½-inch length of 36-gage platinum wire that projected 6 inches into the 10½-inch reactor. The wire was fused by 110 volts a.c. The second system was similar to the first with a ½-inch length of 36-gage platinum wire. The firing system consisted of four 25-microfarad condensers connected in parallel, which were charged with the appropriate d.c. voltage and discharged through a Thyratron tube (627A) to the platinum wire igniter. In this manner a reproducible amount of energy was fed to the ignition system. For the third system, the spherical bomb was modified to receive six spark plugs with a 1-inch length of 30-gage platinum wire connected across the electrodes. The igniters were fired individually as required by separate discharges from the above described d.c. firing system.

The samples to be tested were formulated and loaded into standard 1-gallon stainless steel Hoke cylinders. The Hoke cylinder was evacuated and the vacuum released with the highest boiling hydrocarbon to be used in the test. The desired amount of hydrocarbon was weighed into the cylinder. Then, the cylinder was cooled with liquid nitrogen and the other hydrocarbon components (from highest boiling to lowest) were added so that the system was held above atmospheric pressure. After weighing into the cylinder all the test components, the cylinder was well mixed by inverting the cylinder 100 times. A liquid sample was taken from the bottom of the cylinder and analyzed by gas-liquid chromatography under the following conditions: instrument, Beckman GC-2; column 30 feet × ¼-inch stainless steel, 15% dimethylsulfolane on 30 to 60 mesh Chromosorb; column temperature, 27° C.; port, 66° C.; sensitivity, 250 milliamperes; and He flow, 70 ml. per minute. Prior to the start of this study the sensitivity factors were determined from pure components. As the apparent sensitivity factors may vary slightly from one GLC system to another, they should be determined for each GLC system.

In Figure 1 the spherical bomb and the loading system are schematically illustrated. The following loading procedure was used for the 10½-inch reactor and was similar to the procedure followed for the 1-inch reactor.

▶ Figure 1. Stability test equipment



TIC - Brown Pyro-Vane Controller, TR - Temperature Recorder, PR - Pressure Recorder.

For a safety precaution the spherical bomb was loaded from a room next to the explosion cubicle. All the remote controls and recorders were placed in a third room. It was not necessary to enter the loading room or the explosion cubicle once the loading of the bomb was started. At the start of each decomposition study, the bomb was first purged and pressure tested with nitrogen. Then, the reactor was evacuated by a Cenco Hyvac 14 pump to approximately 5 mm. of Hg. The liquid test mixture was pumped with a Milton Roy positive displacement pump into the preheated bomb slowly until the desired pressure was obtained. If necessary, small adjustments in the pressure were made with the vent valve. As soon as the desired conditions of temperature and pressure were established the ignition switch was depressed. If no decomposition and propagation occurred as indicated by a pressure and temperature rise, more liquid test mixture was pumped into the bomb until a higher pressure resulted and the ignition procedure was repeated.

After a decomposition occurred the bomb was purged with nitrogen, the frangible safety replaced, if required, and the bomb reloaded. An alternate system of loading the 10½-inch bomb or the 1 × 12-inch reactor was to measure out a predetermined amount of test mixture in a loading cylinder (with a calibrated sight glass). Then the mixture was transferred to the evacuated bomb.

For the water and methylacetylene-propadiene-hydrocarbon mixtures at 220° C., the bomb was rocked to ensure equilibrium mixing. Then the total pressure was adjusted to the desired pressure by venting. Since the mixture was above its critical temperature, the composition of the mixture remained constant on venting.

EXPERIMENTAL RESULTS

Ignition Energies. The effect of ignition energy on the stability of a methylacetylene-propadiene-hydrocarbon mixture was determined in the 10½-inch spherical bomb. In this series of experiments and subsequent testing the 10½-inch diameter bomb was utilized to minimize the heat losses due to radiation. Vessel size from 1 to 10 inches in diameter affected the flammability limits of methylacetylene-propylene mixtures. Above 10 inches the diameter had little effect (*6*). The compositions of the mixtures and the conditions of the tests are listed in Table I.

The decomposition and propagation of the flame were indicated by a pressure rise and bursting of a 2200 p.s.i.g. frangible disk on the reactor. In every test that was considered stable, there was a slight carbon formation around the igniter suggesting a local decomposition. At approximately 51° C. and 190 p.s.i.g., the mixture was stable to 105 and 200 joules of ignition energy. When the temperature was raised to 60° C. with a resulting pressure of 242 p.s.i.g., the mixture was unstable to 100 joules of ignition energy. However, under the same conditions the mixture was stable to 10 joules of ignition energy. When the temperature was raised to 100° C. with a resulting pressure of 310 p.s.i.g., the mixture was unstable to 10 joules of ignition energy.

The results of the experimental data indicate that the stability of a methylacetylene-propadiene-hydrocarbon mixture in a given system at a specific temperature and pressure is dependent upon the ignition energies.

A similar dependence of decomposition ignition energies on the pressure of a given system has been reported. Line (*7*) has observed that the required ignition energy for the

Table I. Effect of Ignition Energy on the Stability of a Methylacetylene-Propadiene-Hydrocarbon Mixture in a 10½-Inch Diameter Reactor[a]

Charge, 460 grams

Ingition Energy, Joules	Temp., ° C.	Pressure, P.S.I.G.[b]	Propagation
200	50	190	No
105	51	199	No
100	55	220	No
100	55	220	No
100	55	230	No
100	60	242	Yes
100	70	220[c]	Yes
10	60	245	No
10	70	300	No
10	100	310	Yes

[a] Propane, 9.5%; propylene, 13.5%; propadiene, 32.6%; methylacetylene, 40.2%; butadiene, 1.2%; isobutylene, 1.6%; butylene, 0.6%; butane, 0.7%; and cyclopropane, 0.7%. [b] Liquid plus vapor. [c] Vapor only.

decomposition and propagation of a mixture of 70% methylacetylene–30% propadiene at 4 to 7 atm. and 150° C. was 170 to 190 mjoules. Below 3 atm. the energy requirement was reported to increase abruptly. Ivanov and Kogarko (*4*) reported that minimum ignition energy requirements for the decomposition of acetylene were 10 mjoules at 7 atm., 70 mjoules at 4 atm., and 100 joules at 1 atm.

Several important factors are taken into consideration in establishing 100 joules as a standard ignition energy level in the authors' studies. If a source of high energy should develop, the consequence of a methylacetylene-propadiene explosion is very serious. Secondly, an increase of the temperature and pressure of a "stable" system, for example, as a result of a fire, would cause the system to become unstable at much lower ignition energy levels. And, finally, a 100-joule ignition source is reasonable considering the minimum energy requirement for decomposition at 1 atm. of acetylene is also 100 joules (*4*).

Stability of Propadiene and Methylacetylene at Low Temperatures. The results of the stability tests on propadiene and methylacetylene in a 1-inch diameter bomb with a 100-joule ignition source (Pt wire igniter) are described in Tables II and III, respectively.

Approximately 0.1 mole of 97% propadiene was condensed into a 1 × 12-inch evacuated reactor. The decomposition and propagation of propadiene were indicated by a pressure rise, and it was considered unstable under the experimental conditions.

Results of the experiments indicated that the critical pressure above which a flame was propagated by a 100-joule ignition source was less than 12 p.s.i.g. at −11° C. In two cases, runs 5 and 7, there was a violent explosion with over 100-fold increase in pressure, rupturing a 5000 p.s.i.g. frangible safety. As a result of these explosions, the potential explosive capacity of propadiene is being investigated in this laboratory.

Further testing indicated that methylacetylene is more stable than propadiene under conditions of this study. The critical pressure above which the methylacetylene flame was propagated by a 100-joule ignition source was 48 p.s.i.g. at 15° C. in a 1 × 12-inch reactor.

Effect of Hydrocarbon Diluents on the Stabilization of Methylacetylene-Propadiene Mixtures. The stability of various compositions of methylacetylene-propadiene and hydrocarbon diluents was tested in a 10½-inch diameter reactor. The 10½-inch reactor was used for reasons previously discussed.

A stable composition is defined as a mixture at 68° C. and 220 p.s.i.g. (extreme storage conditions) that does not decompose and propagate a flame in the absence of air when subjected to a 100-joule ignition energy (platinum wire igniter) in a 10½-inch spherical bomb. The decomposition of the mixture and propagation of the flame is indicated by an increase in the pressure and temperature of the test system.

Table II. Stability of 97% Propadiene in a 1-Inch Diameter Reactor

Charge, 0.1 mole

Run	Temp., ° C.	Pressure, P.S.I.G.[a]	Propagation
1	11	60	Yes
2	8	56	No
3	8	56	Yes
4	2	30	Yes
5	−6	31	Yes[c]
6	−6	28[b]	No
7	−11	12	Yes[c]
8	−12	25	No
9	−17	20	No
10	−40	$\sim$0	No

[a] Vapor plus liquid. [b] Vapor only. [c] Ruptured 5000 p.s.i.g. frangible safety.

The compositions, test conditions and results of the experiments are listed in Tables IV, V, VI, and VII, in the order of decreasing actives (methylacetylene and/or propadiene) concentration. The range of actives studied was approximately 77 to 50 mole % with the majority of the testing done with 50-50 ratio of actives. In general, test compositions consisted of the actives and isobutane plus the stabilizer to be studied.

To compare better the stability of the compositions investigated, the decomposition data were plotted. An experimental uncertainty of ±1% in the composition of actives was observed in the decomposition of the mixtures. The curve in Figure 2 indicates for any combination of actives (methylacetylene plus propadiene) and the diluents (propane, propylene, isobutylene, isobutane, and butadiene) what compositions are stable under extreme storage conditions of 68° C. and 220 p.s.i.g. In Figure 3 a similar stability curve was obtained for compositions at 200° C. and 160 p.s.i.g.

The maximum amount of actives that can be stabilized with saturated hydrocarbons appears to be approximately 70 to 71% and the maximum amount of propadiene that can be stabilized by propylene appears to be approximately 50% (see Table IV).

A comparison of the critical pressures above which a mixture can decompose and propagate a flame for a given content of methylacetylene and propadiene gives an indication of the effectiveness of the diluents or the combination of diluents. The authors assumed that there are no synergistic effects operating when combinations of diluents are compared. The critical pressures are determined for a given composition at a given temperature by raising the pressure of the mixture in 5- to 10-p.s.i.g. increments. When the mixture decomposes, the last pressure at which the mixture was stable is taken as the critical pressure. When the pressure increment is greater than 20 p.s.i.g. for decomposition, the critical pressure is listed as greater than the last stable pressure. Repeated tests indicate an uncertainty of ±5 p.s.i. on the determination of the critical pressures.

A few specific comparisons of the critical pressures illustrate the effectiveness of the diluents at similar actives concentrations. Isobutane is the best stabilizer of all the diluents studied. Mixture 10, with a critical pressure greater than 240 p.s.i.g. at 200° C., and mixture 11, with a critical pressure of less than 200 p.s.i.g. at 200° C., indicate that isobutane is a better stabilizer than propane. The experimental fact that propane is a better stabilizer than propylene is well illustrated in mixtures 19 and 20. Mixture 19 has a critical pressure greater than 230 p.s.i.g. at 68° C., and mixture 20 has a critical pressure less than 200 p.s.i.g. at 68° C. The stabilizing effects for isobutylene and propylene appear to be similar at 68° C. The critical pressure

Table III. Stability of 95% Methylacetylene in a 1-Inch Diameter Reactor

Charge, 0.05 mole

Run	Temp., ° C.	Pressure, P.S.I.G.[a]	Propagation
1	8	35	No
2	8	35	No
3	15	48	No
4	17	50	No
5	16	50	Yes

[a] Vapor plus liquid.

Table IV. Stabilization of Methylacetylene-Propadiene Mixtures by Propane, Propylene, and Isobutane

	Component Concentration, Mole %									Intensity of Decomposition		
Experiment	Methylacetylene	Propadiene	Propane	Isobutane	Propylene	Initial Temp., °C.	Initial Press., P.S.I.G.	Critical Press., P.S.I.G.	Propagation	Final temp., °C.	Final press., p.s.i.g.	Final press./Initial press.
1	60.3	16.7	14.5	8.5	...	68	160	>60	Yes	978	2150	13.4
2	61.0	14.0	...	8.7	16.3	68	130	120	Yes	848	1730	13.3
3	37.4	37.3	17.2	8.0	...	68	170	160	Yes	768	820	4.8
4	33.7	41.0	10.6	8.3	6.4	68	140		Yes	814	1940	13.8
5	35.4	38.0	...	9.5	17.0	68	120		Yes	808	595	4.9
6	58.1	15.1	8.9	8.7	9.2	68	150	145	Yes	936	1550	10.3
7	36.0	36.3	19.8	8.0	...	68	220	190	Yes	285	320	1.4
						200	160	140	Yes	360	240	1.5
8	35.9	34.0	9.2	21.9	...	200	200	180	Yes	360	305	1.5
9	35.3	34.4	22.6	7.7	...	68	240	>240	No			
10	37.1	32.2	8.3	22.4	...	68	220	>220	No			
						200	240	>240	No			
11	33.9	35.0	22.0	9.1	...	68	262	>262	No			
						200	200		Yes	580	420	2.1
12	35.3	33.4	15.4	7.8	8.0	68	220	210	Yes	748	555	2.6
						200	140	130	Yes	622	300	2.3
13	35.4	32.3	9.7	22.6	...	200	160	160	Yes			
14	34.2	32.1	13.4	9.6	10.7	68	220	>220	No			
						200	160		Yes	490	245	1.4
15	32.8	33.3	7.0	9.3	17.6	68	240	230	Yes	820	1030	4.3
16	33.3	32.7	25.6	8.3	0.1	150	300		Yes	1070	2880[a]	7.6
17	51.5	13.9	27.4	7.2	...	68	285	>285	No			
18	33.0	31.8	0.1	8.5	26.6	68	220		Yes	733	590	2.6
						200	120	>80	Yes	770	240	2.0
19	51.7	13.1	28.1	7.1	...	68	230	>230	No			
20	52.9	11.8	...	8.2	27.1	68	200	>164	Yes	748	3300[a]	16.5
21	32.7	31.8	5.6	9.4	20.5	68	220	>220	No			
						200	160	140	Yes	655	305	1.9
22	31.2	33.7	13.2	8.3	14.6	68	220	>220	No			
						200	200		Yes	405	310	1.5
23	42.5	21.3	14.0	7.8	14.4	68	305	>305	No			
						200	265	>140	Yes	785	600	2.2
24	49.6	13.1	0.1	8.5	28.7	68	230		Yes	468	2500[a]	10.9
25	30.2	31.4	...	9.5	28.9	68	220	200	Yes	805	600	3.0
						200	140	120	Yes	695	370	2.6
26	29.6	29.6	...	8.2	32.6	68	210	190	Yes	798	635	3.0
						200	160	150	Yes	662	335	2.1
27	28.1	27.7	5.0	5.2	34.1	68	240	>240	No			
						200	200	180	Yes	693	440	2.2
28	27.5	25.3	...	5.4	41.7	68	240	>240	No			
						200	200	>200	No			
29	...	50.5	0.2	...	49.3	68	260	240	Yes	619	550	2.1
						200	160	140	Yes	586	418	2.6

[a] Ruptured 2200 p.s.i.g. frangible safety.

of mixtures 25 and 34 is 200 p.s.i.g. at 68° C. However, at 200° C. mixture 25 has a critical pressure of 120 p.s.i.g. as compared with 160 p.s.i.g. for mixture 34, suggesting at least that isobutylene is a better stabilizer than propylene at higher initial temperatures. Butadiene appears to be the poorest stabilizer tested based on limited experimental data. The comparison of the critical pressure of 180 p.s.i.g. at 68° C. of mixture 36 with the critical pressure of 210 p.s.i.g. of mixture 12 suggests that propylene is a better stabilizer than butadiene. The specific examples cited above plus the stability data plotted in Figures 2 and 3 show that the stabilization of methylacetylene-propadiene mixtures by hydrocarbon diluents decrease in the following order: isobutane > propane > isobutylene ≥ propylene > butadiene.

The authors were able to predict the order of the effectiveness of the stabilizer on the following assumptions: The decomposition is initiated by discharging a concentrated instantaneous source of energy to the system. The success of the initiation leading to propagation depends on the ability of the flame front to generate heat faster than it is lost to the system. Any diluent in an appropriate concentration that can quench the decomposition flame will stabilize the system. Thus, the effectiveness of a stabilizer appears to be related to the ability of the diluent to absorb heat at the decomposition temperature of the diluent. The most effective stabilizers are thermodynamically unstable (large negative ΔF_T° values), decompose endothermically (large positive ΔH_T° values), and absorb heat going to the decomposition temperature (large positive $H_T^\circ - H_{298}^\circ$ values). The less effective stabilizers absorb little heat going to the decomposition temperature (small positive $H_T^\circ - H_{298}^\circ$ values), are thermodynamically stable (large positive ΔF_T° values), or are thermodynamically unstable and decompose exothermally (large negative ΔH_T° values). The decomposition flame temperature for methylacetylene is approximately 1600° K. (*1*), but the hydrocarbon diluents decompose over a 600° to 1000° C. range (*2*) and the thermal properties of the diluents should be compared in this range. Stabilizers tested in this study and others reported in literature (*3*) are listed in Table VIII in the decreasing order of effectiveness as predicted by the thermal properties at 1000° K. While the diluents do not completely decompose to the elements, the correla-

Table V. Stabilization of Methylacetylene-Propadiene Mixtures by Propane and Isobutylene

Experiment	Component Concentration, Mole %					Initial Temp., °C.	Initial Press., P.S.I.G.	Critical Press., P.S.I.G.	Propagation	Intensity of Decomposition		
	Methylacetylene	Propadiene	Propane	Propylene	Isobutylene					Final temp., °C.	Final press., p.s.i.g.	Final press./Initial press.
30	34.2	36.3	9.5	...	20.0	68	220		Yes	497	590	2.7
						200	160		Yes	415	280	1.7
31	32.9	37.3	9.5	0.2	20.2	200	120	115	Yes	380	220	1.8
32	33.5	35.2	23.0	0.3	8.1	200	160		Yes	440	360	2.2
33	34.2	34.0	21.7	...	10.1	68	220		Yes	358	365	1.7
34	30.2	33.9	7.5	...	28.4	68	220	200	Yes	765	2220[c]	10.1
						200	170	160	Yes	655	390	2.3

[c] Ruptured 2200 p.s.i.g. frangible safety.

Table VI. Stabilization of Methylacetylene-Propadiene Mixtures by Propane and Butadiene

Experiment	Component Concentration, Mole %				Initial Temp., °C.	Initial Press., P.S.I.G.	Critical Press., P.S.I.G.	Propagation	Intensity of Decomposition		
	Methylacetylene	Propadiene	Propane	Butadiene					Final temp., °C.	Final press., p.s.i.g.	Final press./Initial press.
35	36.1	34.3	9.6	20.0	68	120		Yes	440	270	2.2
					200	60	40	Yes	295	100	1.6
36	35.0	34.8	21.2	8.9	68	220	>180	Yes	438	1220	5.5

tion of the thermal properties with the experimental results is surprisingly close.

Since water or nitrogen has little or no tendency to decompose in the temperature range up to the flame decomposition temperature, the thermal properties are compared at 1600° K. Water and nitrogen are known to be poor diluents and any heat-absorbing capacity is most likely due to the increase in the heat content of the diluent.

The intensity of decomposition is a measure of the instability of a mixture at a given temperature and at a given pressure and is reflected in the ratio of final pressure and initial pressure, *FP/IP*. Although there is an uncertainty of ±5 p.s.i. on the determination of the critical pressures, a qualitative comparison of the *FP/IP* of various mixtures at 5 to 10 p.s.i.g. above the critical pressure of the mixture gives an indication of the relative instability of the composition at a given temperature, 68° and 200° C. in this study. Above the critical pressure the intensity of decomposition, *FP/IP*, appears to increase and probably reaches a maximum as the pressure is increased. In general, mixtures containing more than 72% actives (methylacetylene plus propadiene) with propane, isobutane, and propylene diluents yielded *FP/IP* ratios above 10. For mixtures with active concentration between 72 and 50% with propane, propylene, and isobutane diluents, the *FP/IP* ratios were generally less than 3. The two exceptions with *FP/IP* ratios above 10 were mixtures with high propylene content at pressures much higher than the critical pressures. For mixtures with propane and isobutylene diluents and with active concentration in the range of 70.5 to 64.1%, the *FP/IP* ratios were below 2. The one exception was a mixture containing 28.3% of isobutylene with a *FP/IP* ratio of 10.1. The *FP/IP* ratios indicate that the intensity of decomposition near the critical pressure appears to be dependent largely on the concentration of actives.

The order of the effectiveness of the stabilizer does not help predict the intensity of decomposition of mixtures near the critical pressure. A case in point is the use of butadiene as a stabilizer. From the large negative heat of decomposition, one would expect a high intensity of decomposition. The observed *FP/IP* ratio near the critical pressure was 1.6 (Table VI). It is possible that the large increase in the heat content of butadiene and possible reactions of butadiene with methylacetylene and propadiene moderated the decomposition.

Whenever conditions were such that a composition supported a flame, after an induction period of 1 to 10 seconds, there was a sudden rise in pressure and temperature. The time to maximum pressure after the induction period for mixtures containing 77 to 72.2% actives was in the order of 1.4 to 10 seconds and at lower active concentrations was much longer.

Effect on Stability of Varying Methylacetylene to Propadiene Ratio. A number of compositions were tested to determine

Table VII. Stability of Methylacetylene-Propadiene-Hydrocarbon Mixtures

Experiment	Component Concentration, Mole %							Initial Temp., °C.	Initial Press., P.S.I.G.	Propagation
	Methylacetylene	Propadiene	Propane	Isobutane	Propylene	Isobutylene[a]	Butadiene			
37	37.8	29.4	13.5	1.2	13.7	2.5	1.9	69	218	No
38	28.1	41.4	10.5	0.7	14.6	2.6	1.6	69	204	Yes[b]
39	36.5	31.3	11.9	1.0	13.8	3.0	1.8	69	238	No
								100	249	Yes[b]
40	37.8	28.8	12.2	0.8	12.2	2.4	1.7	70	211	No
41	34.2	32.1	13.4	9.0	10.0	0.7	0.6	68	220	No[c]

[a] Isobutylene plus butylene. [b] Ruptured 2200 p.s.i.g. frangible safety. [c] No increase in pressure or temperature.

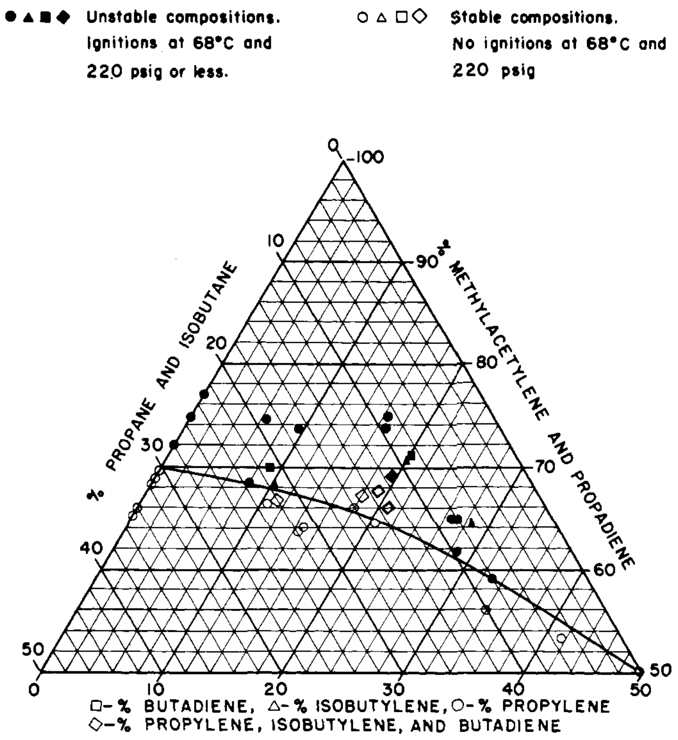


Figure 2. Stability studies of methylacetylene-propadiene-hydrocarbon mixtures

10.5-inch reactor; 100-joule ignition source

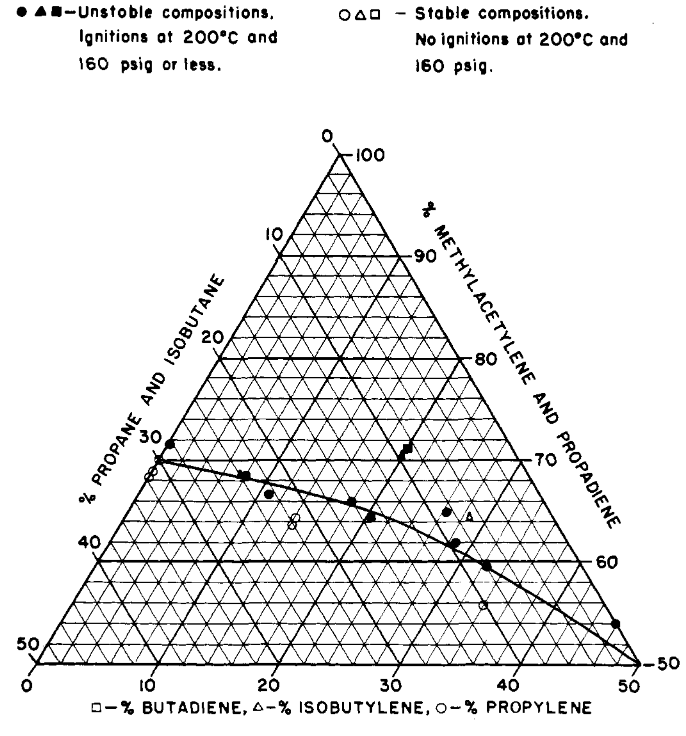


Figure 3. Stability studies of methylacetylene-propadiene-hydrocarbon mixtures

10.5-inch reactor; 100-joule ignition source

Table VIII. Thermal Properties of Methylacetylene-Propadiene Stabilizers at 100° K.[a]

	Decomposition to Elements		Heat Content[b]
	ΔH°_{1000}, kcal./mole	ΔF°_{1000}, kcal./mole	$H^\circ_{1000} - H^\circ_{298}$, kcal./mole
Isobutane	39.1	−66.1	29.0
Propane	30.9	−45.7	22.2
Ethane	25.3	−26.1	15.4
Isobutylene	9.8	−61.7	25.3
Methane	21.4	−4.6	9.1
Propylene	−0.03	−43.4	18.4
Butadiene	−22.8	−62.4	22.5
		At 1600° K.[c]	
	ΔH°_{1600}	ΔF°_{1600}	$H^\circ_{1600} - H^\circ_{298}$
Water	59.9	37.9	12.6
Nitrogen	0	0	10.0

[a] Reference (*9*). [b] Heat content calculated from 298° K. [c] Reference (*10*)

the effect on stability of varying the methylacetylene to propadiene ratio from 80/20 to 50/50. Although propadiene has been shown to be more unstable than methylacetylene, the decomposition data showed little difference between the 80/20 and 50/50 mixtures. For this reason, most of the compositions tested were 50/50 mixtures.

Stability of Methylacetylene-Propadiene-Hydrocarbon Mixtures. The stability of methylacetylene-propadiene-hydrocarbon mixtures (*8*) was tested at 69° C. and approximately 220 p.s.i.g. with a 100-joule ignition source (Table VII). The mixture was considered stable if three successive tests did not indicate a decomposition and propagation (rupturing of the 2200 p.s.i.g. frangible safety). These conditions are slightly different from the previous test conditions where propagation of the flame was determined by temperature and pressure rise. The concentration of the unsaturated hydrocarbons, saturated hydrocarbons, and methylacetylene plus propadiene was plotted in Figure 2. The experimental results indicated that the mixtures were stable in the same range as the test mixtures studied earlier.

Effect of Steam on Decomposition of a Methylacetylene-Propadiene-Hydrocarbon Mixture. A methylacetylene-propadiene-hydrocarbon mixture, which was unstable at 220 p.s.i.g. at 68° C., was tested for stability in the presence of steam at various pressures with a 1-inch platinum wire igniter energized by a 110-volt a.c. source. The experimental conditions and the results are listed in Table IX. The mixture was considered stable if three successive tests did not indicate a decomposition (bursting of the 2200 p.s.i.g. frangible safety). At 220° C. the hydrocarbon-steam mixture with a total pressure of 540 p.s.i.g. and a partial pressure of 222 p.s.i.a. of the hydrocarbon mixture was stable. At a total pressure of 570 p.s.i.g. at 220° C. and a partial pressure of 250 p.s.i.a. of the hydrocarbon mixture, the mixture was unstable, rupturing the frangible safety. Water is a poor diluent in this system as in the case for acetylene stabilization (*5*). The critical pressure above which a flame is propagated appears to be related to the partial pressure of the hydrocarbon mixture and is 222 p.s.i.a. at 200° to 220° C. To check this assumption, the hydrocarbon-steam mixture with a total pressure of 540 p.s.i.g. at 200° C. with a partial pressure of 330 p.s.i.a. for the hydrocarbon mixture was ignited and did propagate a flame as expected. Since the pressure of steam changes rapidly with temperatures near 200° C., it is important to check the partial pressure of the hydrocarbon mixture rather than the total pressure of the system for safe operation of equipment.

Table IX. Stability Tests for Methylacetylene-Propadiene-Hydrocarbon Steam Mixture in the 10½-Inch Diameter Reactor[a]

Initial Pressure, P.S.I.G.	Partial Pressure of Hydrocarbon Mixture, P.S.I.A.	Temp., °C.	Propagation
675	355	218	Yes
670	350	219	Yes
650	328	220	No
620	300	220	Yes
570	250	220	No
570	250	220	No
570	250	220	Yes
541	222	222	No
541	222	220	No
541	222	220	No
540	330	200	Yes

[a] Methylacetylene, 39.0%; propadiene, 32.1%; propane, 6.1%; propylene, 17.2%; isobutylene, 3.9%; and butadiene, 2.4%.

CONCLUSIONS

Methylacetylene and propadiene are potentially hazardous materials that can be stabilized with appropriate diluents. Composition of methylacetylene-propadiene-hydrocarbon mixtures stable to 100 joules of ignition energy in a 10½-inch spherical bomb at extreme storage conditions (68° C. and 220 p.s.i.g.) were determined. The effectiveness of the hydrocarbon diluents decreased in the following order: isobutane > propane > isobutylene ≧ propylene > butadiene. The stability of methylacetylene-propadiene-hydrocarbon mixtures was dependent on the ignition energy.

The intensity of decomposition of the mixture appears to be dependent upon the concentration of the actives (methylacetylene and/or propadiene) near the critical pressure (lower limit). Steam is a poor diluent and the stabilization of a steam-methylacetylene-propadiene-hydrocarbon mixture appears to be dependent on the partial pressure of the methylacetylene-propadiene-hydrocarbon mixture.

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LITERATURE CITED

(1) Cummings, G.A. McD., Hall, A.R., Straker, R.A.M., *Symp. Combust., 8th, Pasadena, Calif.* **1960**, 503, Williams and Wilkins Co., Baltimore, Md., 1962.
(2) Ellis, C., "The Chemistry of Petroleum Derivatives," p. 49, Reinhold, New York, 1937.
(3) Fitzgerald, F., *Nature* **186**, 386 (1960).
(4) Ivanov, B.A., Kogarko, S.M., *Intern. Chem. Eng.* **4**, 670 (1964).
(5) Jones, G.W., Kennedy, R.E., Spolan, I., Huff, W.J., *Bur. Mines Rept. Invest.* **3826** (1945).
(6) Kuchta, F.M., Spolan, I., Zabetakis, M.G., J. CHEM. ENG. DATA **9**, 467 (1964).
(7) Line, L.E., "Some Safety and Handling Characteristics of a Mixture of 70% Propyne and 30% Allene," Texaco Experiment, Inc., TM-1104, p. 6, July 14, 1959.
(8) Nelson, R.A., Belfit, R.W., Jr. (to Dow Chemical Co.), U. S. Patent **3,226,213** (Dec. 28, 1965).
(9) Rossini, F.D., Pitzer, K.S., Arnett, R.L., Braun, R.M., Pimentel, G.C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbon and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
(10) Stull, D.R., Dow Chemical Co., Midland, Mich., unpublished data.

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Alterations in Structure and Physical Properties of Green River Oil Shale by Thermal Treatment

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Experimental data are presented showing changes in physical structure and physical properties that occur when oil shales of widely different organic content from the Green River formation are heated under controlled conditions to 950° and to 1500° F. in a stress-free environment. Seven oil shales were investigated yielding from 1 to about 60 gallons of oil per ton of oil shale. Physical properties evaluated, before and after heating, were compressive strength, structural alterations, permeability, porosity, weight loss, and bulk density. These data serve as engineering guidelines for in situ combustion or other retorting processes.

OIL SHALE, a major potential source of both liquid fuels and chemicals, is a stratified or varved, highly consolidated, and nearly impervious organic-inorganic complex. The practically insoluble organic matter is distributed within the interstitial pores of the varve's mineral matrix. Each varve representing seasonal deposition consists of two laminae, one of which is richer in organic matter than the other. Bradley (*1*) reports that the thickness of the varves differs considerably, 0.014 mm. in the richest oil shale to 9.8 mm. in the fine-grained sandstone, and that the average thickness of the varves, weighted according to the quantity of each type of rock in the formation, is about 0.18 mm. The proportion of organic to mineral matter is not uniform throughout the formation, but the composition of each phase is relatively uniform. The changes in organic matter between varves may be gradual or they