Calculations. Rate constants were calculated from the integrated first-order rate equation in the form

$$k_1 t = \ln \frac{\kappa_\infty - \kappa_0}{\kappa_\infty - \kappa_t}$$

where κ_0, κ_t, and κ_∞ are the conductivities at time 0, t, and ∞, respectively. In each case, k_1 was calculated with data extending to one-half life of the reaction. Justification for this procedure was derived from differential plots made for each composition at one temperature, which yielded good straight lines for $\frac{d\kappa_t}{dt}$ *vs.* t covering the reaction to better than 90% completion.

The values of the activation energy, E, and the frequency factor, A, were calculated by a least squares fit of the rate constant to the Arrhenius equation, $k_1 = Ae^{-E/RT}$. The error limits quoted for E are the maximum errors as determined by the method of Purlee *et al.* (*6*). The values of the entropy of activation were calculated from the equation $\Delta S^{\ddagger} = R\ln\left(\frac{Ah}{ekT}\right)$.

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Weathering and Stability of Methylacetylene-Propadiene-Hydrocarbon Mixtures

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When vapor is removed from a vessel containing a liquid hydrocarbon mixture, a simple batch distillation without rectification (called weathering) occurs. The compositions of liquid in equilibrium with vapor for the weathering of a stabilized methylacetylene-propadiene mixture were determined. These measured data agreed well with the composition predicted by the theory of regular solutions. The stability of the vapor compositions was determined by a 100-joule fuse-wire ignition test; the vapor samples were stable throughout depletion due to weathering.

THE POTENTIAL HAZARDS of mixtures containing methylacetylene and propadiene (allene), as well as methods for stabilizing such mixtures, have been reported (*4, 5*). A stabilized mixture of methylacetylene and propadiene (commercially available as MAPP Gas, The Dow Chemical Co., Midland, Mich.) is used for applications such as metal cutting, welding, brazing, flame hardening, heating, and metallizing.

In the course of using the stabilized methylacetylene-propadiene vapor from a cylinder, the composition of the material remaining in the cylinder changes. Essentially, a differential distillation occurs; this is called "weathering."

The present investigation was carried out to measure the change in vapor and liquid composition due to weathering and also to check the stability of the vapor as a cylinder of liquid was depleted.

EXPERIMENTAL APPARATUS AND PROCEDURE

Weathering. Commercial cylinders (about 40 pounds net weight) of a stabilized methylacetylene-propadiene mixture were depleted at 0.5 to 3.0 pounds per hour (typical continuous withdrawal rates for industrial applications) by withdrawing vapor from the top of the cylinders. This weathering was done at ambient temperature; calculations showed that the vapor-liquid equilibrium compositions were very little affected by small changes in temperature.

Stability Measurements. At various levels of depletion of the stabilized methylacetylene-propadiene mixture—0, 20, 30% (weight), etc., depletion—samples of vapor were passed into a 10 1/2-inch i.d. spherical bomb equipped with a 2200-p.s.i.g. frangible safety disk. Previous work using this type of apparatus and testing similar compositions is described by Yoshimine *et al.* (*5*). The vapor in the bomb was taken to a temperature of 68° C. and a pressure of 220 p.s.i.g. Then at least three attempts to ignite the vapor were made by discharging 100 joules of electrical energy across a 1-inch length of 30-gage platinum wire. This amount of energy caused the fuse wire to vaporize with a sharp crack like a fire cracker. If no decomposition of the sample was observed, the sample was considered stable.

It was anticipated that any marked temperature and pressure rise would indicate decomposition. Therefore, it was decided that a sudden pressure rise of at least 50 p.s.i. was sufficient evidence of decomposition. Actually, however, when decomposition occurred, the frangible safety disk was always ruptured. In cases where no pressure rise occurred following ignition, no change in vapor composition was detected by chromatographic analysis.

Care was taken to exclude air from the test bomb. All of the mixtures tested are, of course, flammable in air.

Composition. Samples of both liquid and vapor were taken at the above levels of depletion of the stabilized methylacetylene-propadiene mixture and analyzed by gas-liquid chromatography.

Weathering Calculations. A computer program was developed to calculate vapor-liquid equilibrium compositions at various stages of isothermal depletion and starting with various initial liquid compositions. This program was based on vapor-liquid equilibrium correlations and data reported by Hill *et al.* (*3*). For ethane and *n*-butane, Antoine constants were obtained from Dreisbach (*2*) and solubility parameters from Chao and Seader (*1*).

The mathematical representation of the process of weathering used equilibrium ratios in the form

$$K_i = \frac{P^0_i \gamma^L_i}{P} = f(T, P, x_1, x_2, \cdots x_i, \cdots x_n)$$

Hill *et al.* (*3*) give a full discussion of vapor-liquid equilibrium of C_3 hydrocarbons. Briefly, however, a regular solution is defined as one in which the entropy of mixing is equal to that of an ideal solution throughout the concentration range. For multicomponent regular solutions whose components all have similar molar volumes, the liquid-phase activity coefficient is given by

$$\text{Ln } \gamma_i^L = \frac{V_i (\bar{\delta} - \delta_i)^2}{RT}$$

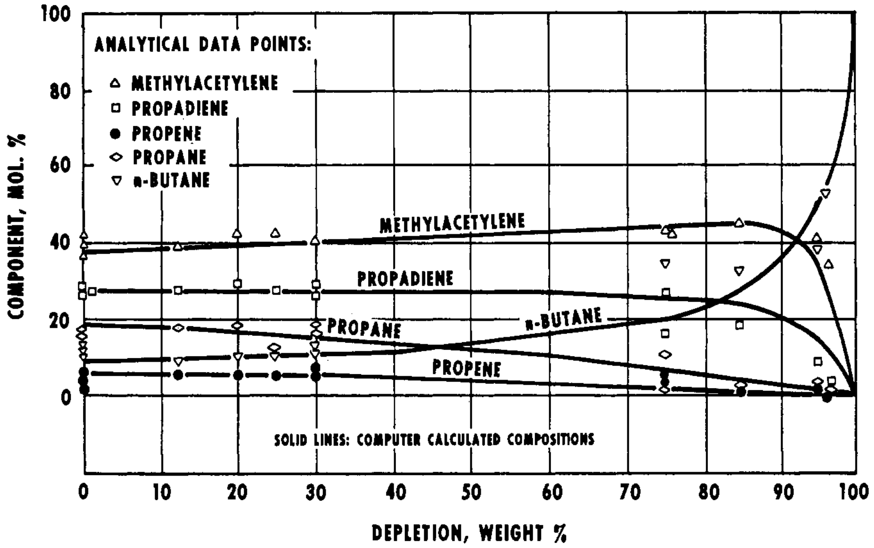

Figure 1. Equilibrium liquid compositions

Weathering of stabilized methylacetylene-propadiene mixture at 25° C.

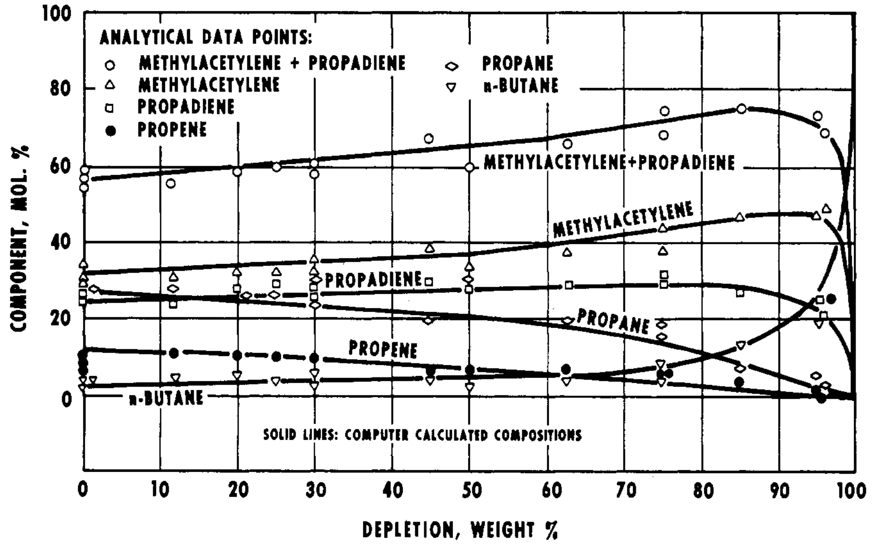

Figure 2. Equilibrium vapor compositions

Weathering of stabilized methylacetylene-propadiene mixture at 25° C.

Vapor pressures for each component were obtained from the Antoine equation:

$$\text{Log}_{10} P_i^0 = A_1 - \frac{A_2}{t + A_3}$$

The computer program used to calculate vapor and liquid compositions as a function of depletion was based on the Rayleigh equation

$$\ln \frac{B}{B_0} = \int_{x_i^0}^{x_i} \frac{dx_i}{K_i x_i - x_i}$$

This was used to calculate the x_i values for each B as B was changed from B_0 to zero in specified decrements. A composition and pressure at the first B was assumed in order to calculate K_i applying between B_0 and B. An arithmetic average K_i was used.

The Rayleigh equation gave x_i values at the first B value. The total pressure at this B was calculated using

$$P = \sum_{i=1}^{n} \gamma_L^i x_i P_i^0$$

New K_i's were then calculated and the program was iterated until the x_i's totaled 1.0.

Table I. Initial Liquid Composition for Calculated Curves, Mole %

	Figs. 1, 2	Fig. 3	Fig. 4	Fig. 5	Fig. 6	Fig. 7
Methylacetylene	38.2	74.0	65.0	65.0	44.5	40.9
Propadiene	26.9	...	...	...	31.5	29.1
Propene	7.8	...	...	...	...	16.0
Propane	18.4	...	35.0	...	9.0	...
n-Butane	8.7	...	...	35.0	15.0	14.0
Ethane	...	26.0	...	...	...	...

Table II. Butane and Propane as Stabilizers

<table>
<tr><th rowspan="2">Propane-Butane Ratio</th><th colspan="5">Vapor Composition, Mole %</th><th rowspan="2">Ignition at 68° C. and 220 P.S.I.G.</th></tr>
<tr><th>Methyl-acetylene</th><th>Propadiene</th><th>Propene</th><th>Propane</th><th><i>n</i>-Butane</th></tr>
<tr><td>8.1</td><td>52.1</td><td>17.6</td><td>6.5</td><td>21.2</td><td>2.6</td><td>Yes</td></tr>
<tr><td></td><td colspan="2">69.7</td><td></td><td colspan="2">23.8</td><td></td></tr>
<tr><td>7.1</td><td>59.3</td><td>15.0</td><td>5.4</td><td>17.8</td><td>2.5</td><td>Yes</td></tr>
<tr><td></td><td colspan="2">74.3</td><td></td><td colspan="2">20.3</td><td></td></tr>
<tr><td>1.4</td><td>45.1</td><td>29.1</td><td>4.3</td><td>12.5</td><td>9.0</td><td>No</td></tr>
<tr><td></td><td colspan="2">74.2</td><td></td><td colspan="2">21.5</td><td></td></tr>
<tr><td>0.7</td><td>47.7</td><td>27.8</td><td>3.8</td><td>8.3</td><td>12.4</td><td>No</td></tr>
<tr><td></td><td colspan="2">75.5</td><td></td><td colspan="2">20.7</td><td></td></tr>
<tr><td>0.5</td><td>62.2</td><td>14.3</td><td>7.8</td><td>5.1</td><td>10.6</td><td>No</td></tr>
<tr><td></td><td colspan="2">76.5</td><td></td><td colspan="2">15.7</td><td></td></tr>
<tr><td>0.3</td><td>58.2</td><td>15.6</td><td>7.6</td><td>4.7</td><td>13.9</td><td>No</td></tr>
<tr><td></td><td colspan="2">73.8</td><td></td><td colspan="2">18.6</td><td></td></tr>
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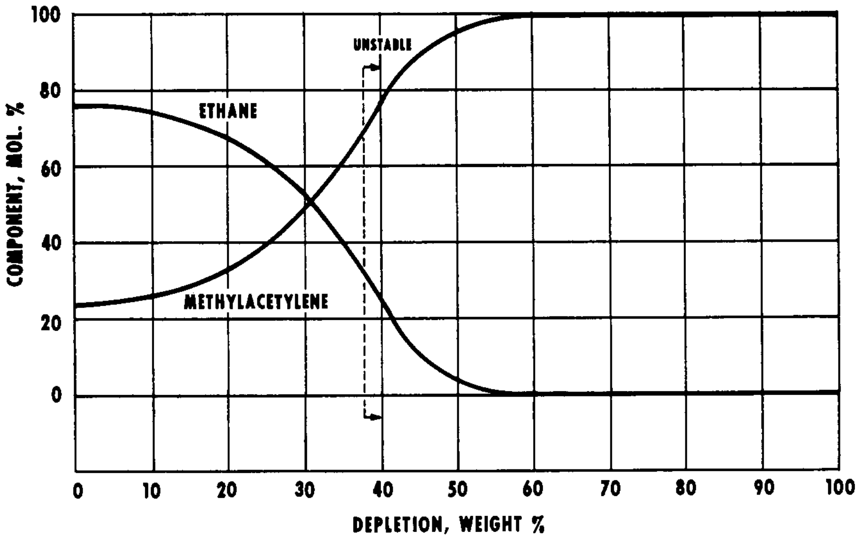

Figure 3. Equilibrium vapor compositions

Calculated weathering of ethane-methylacetylene mixture at 25° C.

The vapor compositions at the first B were then calculated by

$$y_i = K_i x_i$$

The program then decreased B, which corresponds to moving to the right on the abscissa of the figures, and repeated the routine.

RESULTS

Weathering. The results of the depletion tests confirmed that the approach of Hill *et al.* (*3*) was a reliable method of predicting vapor and liquid compositions of the stabilized methylacetylene-propadiene mixture due to weathering. In Figures 1 and 2, the lines represent the calculated compositions due to constant-temperature weathering at 25° C., and the actual sample analyses are shown as points. The initial liquid composition used to develop the calculated curves in Figures 1 and 2 is given in Table I.

Stability. None of the vapor samples shown in Figure 2 ignited under the test conditions, indicating that the stabilized methylacetylene-propadiene mixture was stable throughout depletion.

That all of these compositions were stable might not be expected from the data of Yoshimine *et al.* (*5*). Although they recognized that isobutane (2-methylpropane) is a better stabilizer than propane, the correlation of the data on a triangular plot—where one ordinate is "propane and isobutane"—tends to obscure this point.

The data in Table II illustrate that butane is a much more effective stabilizer than propane. Methylacetylene-plus-propadiene concentration, propene concentration, and propane-plus-butane concentration were held essentially constant, and the relative amounts of propane and butane were the only variable; under these conditions ignition occurred less readily at higher butane (lower propane) concentrations. Thus, as the contents of a cylinder of the stabilized methylacetylene-propadiene

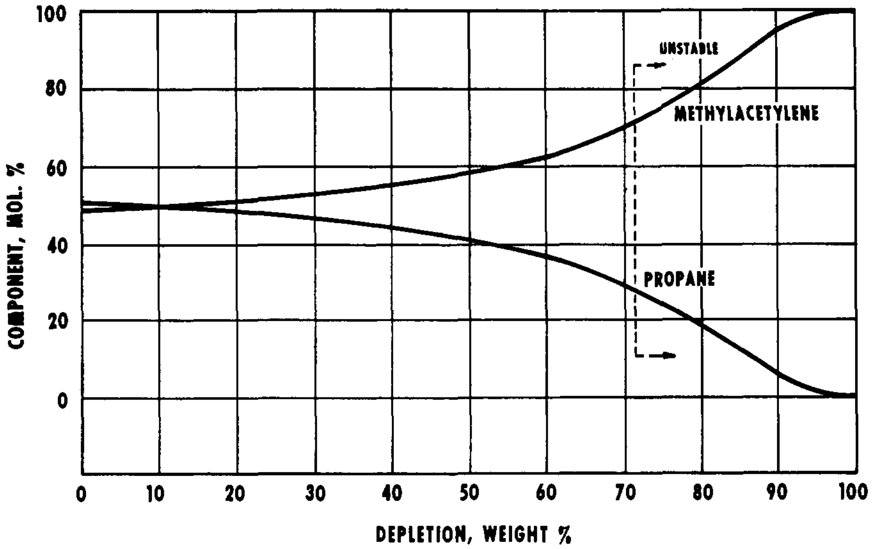

Figure 4. Equilibrium vapor compositions

Calculated weathering of propane-methylacetylene mixture at 25° C.

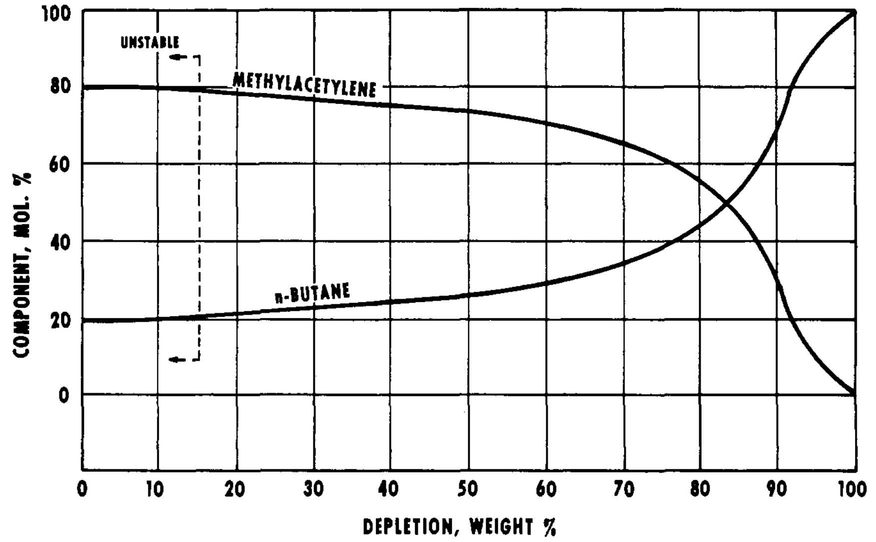

Figure 5. Equilibrium vapor compositions

Calculated weathering of n-butone–methylacetylene mixture at 25° C.

mixture were depleted, even though the per cent of methylacetylene-plus-propadiene in the vapor increased slightly, the vapor remained stable, since the propane-butane ratio decreased.

Some Unstable Methylacetylene-Propadiene-Hydrocarbon Mixtures. Several other methylacetylene-propadiene-hydrocarbon mixtures were examined to illustrate the effect of the type and amount of the stabilizing hydrocarbons on the composition of the mixture and on the stability during weathering. These additional compositions listed in Table I were weathered using the computer program. Although both liquid and vapor compositions were calculated, only the vapor compositions during the course of weathering are shown in Figures 3, 4, 5, 6, and 7. All of the initial liquid compositions are stable, but, as weathering proceeds, the systems shown in the figures reach a vapor composition considered unstable.

As expected, when a mixture of ethane and methylacetylene is weathered (Figure 3) the ethane flashes off rather quickly, so that the vapor is almost entirely methylacetylene during the last half of depletion. By the ignition stability test, a mixture containing 31% ethane and 69% methylacetylene was stable. Mixtures containing more methylacetylene were unstable.

A similar situation occurs if a mixture of propane and methylacetylene is weathered (Figure 4). However, since the propane is somewhat less volatile, it does not flash off as rapidly as the ethane. Again, by the ignition stability test, mixtures containing more than 70% methylacetylene were unstable.

In both cases the vapor obviously becomes unstable well before depletion is complete. Actually, all samples that contained more than 78% methylacetylene-plus-propadiene failed the previously described ignition test for stability.

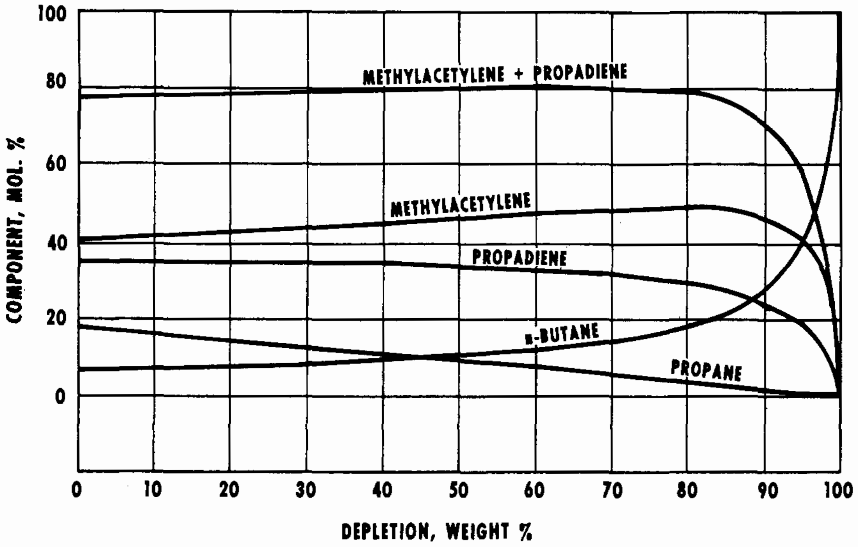

Figure 6. Equilibrium vapor compositions

Calculated weathering of propane-butane-methylacetylene-propadiene mixture at 25° C.

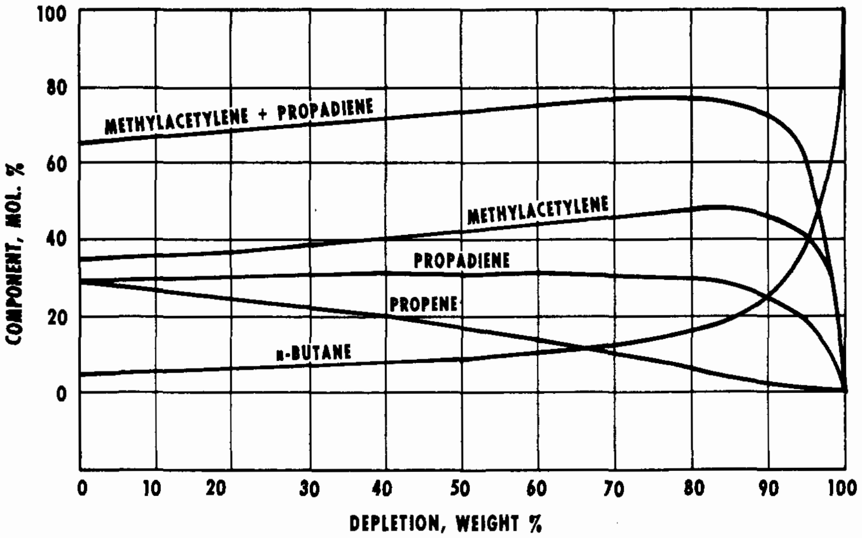

Figure 7. Equilibrium vapor compositions

Calculated weathering of propene-butane-methylacetylene-propadiene mixture at 25° C.

The effect on weathering of adding a less volatile component, *n*-butane, to methylacetylene is shown in Figure 5. The initial methylacetylene concentration in the vapor is high and falls off rapidly as depletion progresses. Thus, in contrast to the two previously described systems, the initial vapor is unstable in this case.

Two other systems are shown in Figures 6 and 7. In Figure 6, the initial composition is high in methylacetylene-plus-propadiene. In Figure 7, the stabilizing hydrocarbon is propene. In both cases the amount of methylacetylene-plus-propadiene in the vapor remains fairly constant on weathering. Nevertheless, the vapor composition in Figure 6 becomes unstable in the range of 30 to 80% depletion because of the high initial methylacetylene-plus-propadiene concentration.

Although the content of methylacetylene-plus-propadiene in the vapor does not exceed 78% in Figure 7, testing indicates that the composition in the range of 70 to 80% depletion is unstable. This confirms, as previously noted (*5*), that propene is a less effective stabilizer than propane.

Since it is important for purposes of commercial use to maintain stability over the entire range of weathering—and at the same time maintain a relatively high methylacetylene-propadiene content—the initial liquid composition must be kept fairly close to the composition shown in Table I for Figures 1 and 2.

High Severity Tests. Tests were run to determine the stability of a stabilized methylacetylene-propadiene mixture under the severe conditions of 375 p.s.i.g. and 80° C. These test conditions were chosen because the pressure relief valve setting on cylinders containing a commercially available stabilized methylacetylene-propadiene mixture is 375 p.s.i.g.; 80° C. is the boiling point of the mixture at 375 p.s.i.g. The vapor mixture tested contained 39.5% (mole) methylacetylene, 27.4% propadiene, 7.0% propene, 17.1% propane, and 9.0% *n*-butane. No ignition (no decomposition) occurred when the mixture was subjected even to 170 joules electrical discharge in the 10 1/2-inch spherical bomb. The standard vapor ignition test conditions were 220 p.s.i.g., 68° C., and an energy level of 100 joules.

CONCLUSIONS

A stabilized methylacetylene-propadiene mixture was stable during all stages of weathering (vaporization of gas from a cylinder).

Single-component stabilizer mixtures did not maintain stability of the vapor on weathering (Figures 3, 4, and 5).

Initially stable mixtures may become unstable on weathering because of high initial methylacetylene-plus-propadiene levels (Figure 6) or less effective stabilizers (Figure 7).

NOMENCLATURE

A_1, A_2, A_3 = Antoine constants
B = total amount of liquid in cylinder, pound mole
B_0 = initial amount of liquid in cylinder, pound mole
K = ratio of mole fraction in vapor to mole fraction in liquid of a component at equilibrium
P = equilibrium total pressure of system, mm. Hg abs.
P° = vapor pressure of a pure component, mm. Hg abs.
R = gas constant, 1.987 cal./g. mole, ° K.
T = temperature, ° K.
t = temperature, ° C.
V = molar volume of a component, ml./g. mole
x = mole fraction in liquid of component at equilibrium
y = mole fraction in vapor of component at equilibrium
γ^L = liquid phase activity coefficient for a component
$\bar{\delta}$ = volume average solubility parameter for the liquid solution, $(\text{cal./ml.})^{1/2}$
δ = solubility parameter for a component, $(\text{cal./mole})^{1/2}$

Subscripts

$1, 2, 3, i$ = components 1, 2, 3, *i*, etc.
n = total number of components

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