A LABORATORY INVESTIGATION OF ARTIFICIAL FOGS PRODUCED UNDER SU--ETC(U)

JAN 80  E J MACK, J T MANLEY

N00019-79-C-0339

UNCLASSIFIED

CALSPAN-6510-M-1
A laboratory investigation of artificial fogs produced under subsaturated conditions

by

E.J. Mack and J.T. Hanley

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A DIVISION OF CALSPAN CORPORATION
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A Laboratory Investigation of Artificial Fogs Produced Under Subsaturated Conditions

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Naval Air Systems Command, Dept. of the Navy
440 Jefferson Plaza, No. 1
Washington, D.C. 20361 (Code AIR-310C)

Calspan is conducting a limited investigation of the efficiency of hygroscopic aerosols in restricting visibility at subsaturated humidity. The artificial fogs are produced by SALTY DOG and phosphorus pentoxide smoke in Calspan's 590 cubic meter chamber at controlled relative humidities of from 40 to 97 percent. Extinction at both visible and IR wavelengths and aerosol size spectra are compared, as functions of humidity, for both types of artificial fogs and with those of simulated natural fogs.

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Section 1
INTRODUCTION AND SUMMARY

Under contract No. N00019-79-C-0339 from the Naval Air Systems Command (AIR-310C), Calspan Corporation continued its experimental investigation of the feasibility of producing stable, optical-obscurant screens (smokes and fogs) with hygroscopic aerosols under conditions of subsaturated relative humidity. The objectives of this limited laboratory investigation were (1) to determine the efficiency of pyrotechnically-generated, hygroscopic aerosols in producing conditions of restricted visibility (at both visible and infrared wavelengths) at relative humidities <100%, and (2) to assess the persistence (lifetime) of the artificial fogs with lowering relative humidity. In the experiments, measurements of aerosol size spectra (0.01 μm to 10 μm diameter) and optical extinction at both visible and infrared wavelengths were obtained as functions of relative humidity to produce "yield-factor" information.

The laboratory investigation is being carried out in Calspan's 590 m³ Chamber. The facility's large size (~9 m diameter by ~9 m high) minimizes wall effects, provides relatively long path lengths for extinction measurements, and provides for a useful aerosol lifetime of many hours. A complete air handling capability permits the removal of virtually all particulate and gaseous contaminants prior to each experiment, the introduction of specified aerosols, and control of humidity from 20 to 98% RH. A cut-away view of the chamber facility and a list of instrumentation pertinent to this investigation are provided in Figure 1 and Table 1, respectively. Specific details of the instrumentation and chamber facility may be found elsewhere (e.g., Mack et al, 1978).

The scope of this effort is limited to an experimental evaluation of the efficiency of "Salty Dog" pyrotechnic aerosols in producing conditions of restricted visibility at subsaturated humidities. In the experiments, fogs (smokes) are generated by burning a prescribed quantity of the pyrotechnic material under prescribed humidity conditions within the Chamber. In this report, results of the experiments, i.e., aerosol size spectra and extinction as functions of relative humidity, are presented and compared with similar data obtained in phosphorus pentoxide smokes and in simulated natural fogs.
Table 1
INSTRUMENTATION

<table>
<thead>
<tr>
<th>VISIBILITY:</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calspan Transmissometer (visible, 0.35-0.55 μm λ) (20 m pathlength)</td>
<td>20-4000 m</td>
</tr>
<tr>
<td>Calspan IR Transmissometer (IR 2.15 μm λ) (10 m pathlength) { (3.7-3.9 μm λ) (7.75-9.8 μm λ) (9.13-10.33 μm λ) (13.5-14.5 μm λ) }</td>
<td>15-3000 m</td>
</tr>
<tr>
<td>MRI Nephelometer (visible λ)</td>
<td>5-80 km</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AEROSOLS:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gardner Small Particle Detector</td>
<td>Total Concentration (&gt;0.0025 μm)</td>
</tr>
<tr>
<td>TSI Electrical Aerosol Analyzer</td>
<td>Size Spectra (.01-.75 μm)</td>
</tr>
<tr>
<td>Royco Optical Particle Counter</td>
<td>Size Spectra (.3-.3. μm)</td>
</tr>
<tr>
<td>Calspan Droplet Sampler (Gelatin Replic.)</td>
<td>Size Spectra (3-.50 μm)</td>
</tr>
<tr>
<td>Lo-Vol Teflon Filter Sampler</td>
<td>Samples for Chemical Analysis</td>
</tr>
<tr>
<td>Casella Cascade Impactor</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Cut-away view of Calspan's 590 m$^3$ chamber facility.

Briefly summarizing, a total of 14 chamber experiments were conducted with the "standard" Salty Dog pyrotechnic on this year's program. In addition, three experiments were conducted with two other alternative Salty Dog formulations, designated NWC-29 and CY85A.* Chemical analysis of aerosol samples

*The Salty Dog pyrotechnics used on this program were supplied by Dr. P. St. Amand of the Naval Weapons Center, China Lake, through the auspices of Dr. L. Ruhnke of the Naval Research Laboratory, and their cooperation with Calspan is gratefully acknowledged.
showed that the primary aerosol from "standard" Salty Dog pyrotechnic is composed principally of KCl. Extinction and aerosol data were consistent with results of the previous year's experiments and with the finding that the active aerosol of "standard" Salty Dog is KCl. The primary aerosol produced by Formulation NWC-29 was found to be composed principally of NaCl, while Formulation CY85A aerosol was composed of a mixture of NaCl and KCl. Results of 10 white phosphorus experiments revealed that, for comparable quantities of material disseminated, phosphorus pentoxide smokes produce greater extinction at all relative humidities than any of the three Salty Dog formulations.
Section 2
EXPERIMENTAL RESULTS

2.1 Salty Dog Smokes

The basic aerosol used for producing conditions of restricted visibility at subsaturated humidities in these experiments was generated by pyrotechnic devices known as "Salty Dogs." The devices, developed at the Naval Weapons Center (Hindman and Heimdahl, 1977), are said to be composed of "18% hydrocarbon binder, 5% magnesium, 10% sodium chloride, 65% potassium perchlorate and 2% lithium carbonate." When burned, the pyrotechnic produces copious quantities of hygroscopic aerosol (~10^{11} particles >0.5 \mu m diameter per gram of material, according to Hindman and Heimdahl).

In the design phase of the laboratory investigation, it was desired that the experiments be conducted with aerosol concentrations ranging from that observed in the natural marine environment (i.e., 1-50 cm^{-3}) to several orders of magnitude greater. Based on the data of Hindman and Heimdahl, it was decided to conduct specific experiments with three different quantities of the pyrotechnic: 0.1 g, 1.0 g, and 6.0 g -- corresponding to aerosol concentrations for particles >0.5 \mu m diameter of ~17 cm^{-3}, ~170 cm^{-3} and 10^5 cm^{-3}, respectively, for our chamber volume. A total of 14 experiments with the "standard" Salty Dog were conducted as part of this year's effort; on last year's program (see Mack et al, 1978), 16 primary Salty Dog experiments were performed. In addition, three experiments were performed this year with two other versions of the Salty Dog pyrotechnic: Formulation NWC-29 and Formulation CY85A. Results of these experiments are summarized in this Section.

For our experimental set-up, the employed ranges of Salty Dog payloads (i.e., 0.1 to 6.0 g) and relative humidities (i.e., RH 40-97%) were required in order to acquire both aerosol and extinction data in resultant smokes. Larger payloads of Salty Dog at higher humidities were necessary to achieve extinction
at IR wavelengths, but, for larger payloads, aerosol concentrations were so great as to saturate aerosol-size instrumentation. To maintain consistent aerosolization in our experiments, the Salty Dog pyrotechnic was aerosolized by "forced burning"--i.e., the flame from a propane torch was directed onto the pyrotechnic, even though it would burn freely, until it was completely consumed.

In a typical experiment, a prescribed quantity of pyrotechnic was burned at a prescribed RH, the resultant aerosol fog was allowed to stabilize and reside in the chamber for ~5-10 min, and then RH was lowered. The visibility (extinction) data* from one such experiment (6 g of Salty Dog burned at 96% RH) are shown as functions of time in Figure 2. Note that, within ~1 min of the 20 s burn (commencing at time = 0), visibilities at all wavelengths stabilized at near minimum values, remaining at those values for the next 10 min while RH was held constant. At visible wavelengths, extinction corresponding to a visibility restriction of ~35 m was achieved. At 2.15, 3.8 and 9-10 μm wavelengths, visibilities were greater than at visible wavelengths by factors of ~8, 20 and 35, respectively. At approximately 12 min, reduction of RH (by heating) was begun, and, within ~20 min, visibilities at shorter wavelengths improved by a factor of ~2 in response to a reduction in RH from 96 to 87%.

The aerosol population generated by Salty Dog is characterized by high concentrations of very small particles. Typically, the pyrotechnic produces $10^{13}$ and $10^{10}$ particles per gram at sizes >0.1 and >1.0 μm diameter, respectively, these values being in good agreement with those reported by Hindman and Heimdahl. Aerosol size spectra from four different (0.1 g) Salty Dog experiments at four different relative humidities are presented in Figure 3. These data show, as expected, that changes in optical transmission through the smoke in response to changes in RH are attributable to the hygroscopic nature of Salty Dog aerosols

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*Extinction data at all wavelengths are presented in terms of visibility (meteorological visual range) because this is a parameter with which one can easily relate. Visibility is defined as the distance required to produce 98% extinction and is related to extinction (B) through the relation $V = 3.912/B$.  

6
AEROSOL SIZE SPECTRA AS FUNCTIONS OF RELATIVE HUMIDITY FOR SALTY DOG SMOKES

LOAD = 0.1 GRAM

A = 45%
B = 59%
C = 81%
D = 97%

FIGURE 3
and hence to changes in the equilibrium sizes of the Salty Dog solution droplets. The data further show that for RH < 90%, nearly all of the particles in Salty Dog smokes are smaller than 5 \( \mu m \) diameter. Appreciable quantities of particles of size > 5 \( \mu m \) diameter are observed only in Salty Dog smokes at RH > 90%. Thus, it is readily seen from the data presented in Figures 2 and 3 that dense fogs (smokes) can be produced from the Salty Dog pyrotechnic and that extinction through such a fog is RH dependent due to the dependence of particle size on relative humidity.

Pertinent parameters for the initial 5-10 minute periods in each of the 17 Salty Dog experiments conducted under this year's contract are provided in Tables 2 and 3. Table 2 presents general information on the quantity of pyrotechnic burned, relative humidity, resultant visibility restriction (visible wavelengths) and aerosol characteristics.* In Table 3, the data from this year's experiments are presented in terms of per-gram yield. As with last year's experiments, aerosol output was in the expected range and in good agreement with the results of Hindman and Heimdahl.

In Figure 4, measured visibilities (visible wavelength data from stable periods in both last year's and this year's Salty Dog tests) are plotted as functions of relative humidity for each of three Salty Dog payload sizes. (Approximately 30% of the data points in Figure 4 were obtained in the Salty Dog Smokes after relative humidity was lowered by 5-10% RH.) These data illustrate the marked dependence of visibility on both the ambient RH and the quantity of pyrotechnic disseminated. Note that resultant visibilities at a given RH for 1.0 and 6.0 g payloads are \( \approx \)1/10 and \( \approx \)1/60 (i.e., extinction is factors of 10 and 60 greater), respectively, of that for the 0.1 g payload. The data further suggest that the aerosols in these experiments are at equilibrium sizes (i.e., no vapor depletion effects are evident) and that a decrease in the rate of change of equilibrium droplet size with decreasing RH occurs below \( \approx \)65-70% RH.

Data from the three tests involving the two new Salty Dog formulations (Experiments No.s 15-17) are called-out on the "6g" curve shown on Figure 4.

*Aerosol data are not available for high concentration/high RH experiments due to saturation of aerosol sizing instrumentation.
### Table 2
LOG OF PRIMARY SALTY DOG CHAMBER EXPERIMENTS

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Salty Dog Payload</th>
<th>Relative Humidity</th>
<th>Minimum Visibility</th>
<th>Particle Concentration at Sizes &gt; Indicated Diameter</th>
<th>Aerosol Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 g</td>
<td>41%</td>
<td>22.2 km</td>
<td>&gt;0.01 (\mu)m: 1.42x10^4 (\text{cm}^{-3})</td>
<td>44.8 (\mu)m^3/cm^3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;0.10 (\mu)m: 3.46x10^3 (\text{cm}^{-3})</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>50</td>
<td>16.9</td>
<td>&gt;1.2 (\mu)m: 1.6 (\text{cm}^{-3})</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>55</td>
<td>17.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>95</td>
<td>1.750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.01</td>
<td>56</td>
<td>1.670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>60</td>
<td>1.560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.01</td>
<td>70</td>
<td>1.240</td>
<td></td>
<td></td>
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<tr>
<td>8</td>
<td>0.98</td>
<td>79</td>
<td>0.370</td>
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</tr>
<tr>
<td>9</td>
<td>1.00</td>
<td>85</td>
<td>0.340</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td>96</td>
<td>0.180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6.0</td>
<td>42</td>
<td>0.285</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>6.0</td>
<td>69</td>
<td>0.270</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>6.0</td>
<td>77</td>
<td>0.145</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>6.0</td>
<td>93</td>
<td>0.036</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>6.0 (NWC29)</td>
<td>68</td>
<td>0.285</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>6.0 (CY85A)</td>
<td>69</td>
<td>0.210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>6.0 (CY85A)</td>
<td>72</td>
<td>0.175</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Visible wavelength
Table 3
The Yield (per gram) of Aerosol and Extinction in Chamber Experiments with Salty Dog Pyrotechnics

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Relative Humidity</th>
<th>Integrated Extinction Coefficient</th>
<th>Particles/gram At Sizes &gt; Indicated Diameter</th>
<th>Aerosol Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41%</td>
<td>1.04 m²/g</td>
<td>8.4x10¹³/g 2.0x10¹³/g 0.9x10¹⁰/g</td>
<td>0.26cm³/g</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>1.37</td>
<td>6.2x10¹³ 2.3x10¹³ 3.0x10¹⁰</td>
<td>0.40</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>1.30</td>
<td>12.2x10¹³ 2.7x10¹³ 1.6x10¹⁰</td>
<td>0.30</td>
</tr>
<tr>
<td>4</td>
<td>95</td>
<td>15.38</td>
<td>17.2x10¹³ 5.6x10¹³ 134x10¹⁰</td>
<td>8.9</td>
</tr>
<tr>
<td>5</td>
<td>56</td>
<td>1.37</td>
<td>3.0x10¹³ 1.8x10¹³ 6.4x10¹⁰</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>1.48</td>
<td>8.0x10¹³ 2.5x10¹³ 6.5x10¹⁰</td>
<td>0.59</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td></td>
<td></td>
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<td>8</td>
<td>79</td>
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<td>10</td>
<td>96</td>
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<td>11</td>
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<td>12</td>
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<tr>
<td>14</td>
<td>93</td>
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<tr>
<td>15(NWC-29)</td>
<td>68</td>
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<td></td>
</tr>
<tr>
<td>16(CY85A)</td>
<td>69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17(CY85A)</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4

VISIBILITY (VISIBLE WAVELENGTH) AS A FUNCTION OF RELATIVE HUMIDITY AND QUANTITY OF SALTY DOG AEROSOLIZED.
The extinction (visibility restriction) achieved in these three experiments did not differ significantly from that achieved in tests of "standard" Salty Dog.

Of prime concern in this investigation is the stability of the Salty Dog aerosol fogs--i.e., the ability of the cloud to remain an effective screen when exposed to lower relative humidities. The extinction data (visible wavelengths) for the Salty Dog pyrotechnic summarized in Figure 4 show that, for relative humidity changes of 10% in the range between 65 and 97% RH, resultant visibilities change by only a factor of ~2.

The results of all the Salty Dog tests conducted on this program are summarized in Table 4 and Figure 5. In Table 4, the average per-gram yield of the Salty Dog pyrotechnic in terms of aerosol production and extinction is presented as a function of relative humidity. The extinction data shown in Figure 4 are normalized to a one gram payload and plotted in Figure 5. A scale along the right side of the Figure 5 shows the "integrated" extinction coefficient (m²/g) achieved in the smokes. The integrated extinction coefficient is the measured extinction coefficient (m⁻¹) normalized to the mass loading of aerosolized material (g/m³); hence, the units are m⁻¹/(g/m³)=m²/g.

These values may be used to estimate extinction coefficient (and hence visibility) through a Salty Dog cloud (of any size, assuming uniform aerosol distribution) by multiplying by the amount of material disseminated and dividing by the volume of the cloud. It is clear from these data that Salty Dog pyrotechnics produce increasingly effective screening with increasing relative humidity above 66-68% RH.

2.2 The Chemistry of Salty Dog Smokes

According to Hindman and Hemidahl (1977), the Salty Dog pyrotechnic is composed of "18% hydrocarbon binder, 5% magnesium, 10% sodium chloride, 65% potassium perchlorate and 2% lithium carbonate." When burned, the hydrocarbon and oxygen components are presumably consumed, and the pyrotechnic produces hygroscopic aerosol containing Cl, K, Na, Mg and Li. Stoichiometrically, the expected aerosol would contain Cl, K, Mg, Na and Li in relative concentrations of 45.1, 36.4, 9.9, 7.8 and 0.8%, respectively. No doubt, residual carbon and oxygen would also be found in resultant aerosols.
Figure 5: The per-gram (per 590 m²) extinction (visible wavelength visibility) as a function of relative humidity for Salty Dog smokes.
In a few of the Salty Dog experiments conducted on the current effort, lo-vol samples (~200 l volume) were collected on 47 mm Fluoropore* teflon-membrane filters (0.4 μm pore size). Chemical analysis** of a 1.05 mg sample from Experiment Number 12 (6 g of Salty Dog burned at 69% RH; see Table 2) revealed that the aerosol sample comprised 440 μg of Cl, 285 μg of K, 88 μg of Na, 52 μg of Mg, and 2 μg of Ca, for a total of 0.87 mg or ~83% of the sample. Li was below detectable limits (i.e., <1 μg), while C and O₂ were not analyzed; the remaining 17% (0.18 mg) of the sample was probably C, O₂, water and trace constituents. The origin of the Ca found in the analyzed sample is unknown. Thus, the relative concentrations of Cl, K, Mg, Na, Ca and Li in the Salty Dog aerosol were found to be 50.7, 32.9, 6.0, 10.1, 0.2 and <0.1%, respectively; these values being in fair agreement with the quoted bulk composition of the Salty Dog pyrotechnic material.

In addition to the lo-vol filter samples, Salty Dog aerosols were collected with a 4-stage Casella cascade impactor for scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA). The combination of these two techniques allowed (1) visualization of the impacted particle where size and morphology could be ascertained and (2) determination of elemental

---

Table 4

Average Aerosol and Extinction Yield (per gram)
As Functions of Relative Humidity for Salty Dog Pyrotechnics

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Number of Particles of Size &gt; Indicated Diameter</th>
<th>Aerosol Volume</th>
<th>Integrated Extinction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt;0.01 μm</td>
<td>&gt;0.1 μm</td>
<td>&gt;1.0 μm</td>
</tr>
<tr>
<td>40-58%</td>
<td>7.3x10^{13} g</td>
<td>2.0x10^{13} g</td>
<td>2.3x10^{10} g</td>
</tr>
<tr>
<td>60-69%</td>
<td>8.0x10^{13} g</td>
<td>2.1x10^{13} g</td>
<td>8.4x10^{10}</td>
</tr>
<tr>
<td>70-77%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>79-85%</td>
<td>6.9x10^{13} g</td>
<td>2.4x10^{13} g</td>
<td>19.6x10^{10}</td>
</tr>
<tr>
<td>93-97%</td>
<td>8.1x10^{13} g</td>
<td>3.3x10^{13} g</td>
<td>59.4x10^{10}</td>
</tr>
</tbody>
</table>

* Millipore Corporation, No. FHLP-047-00
** Analysis for K, Mg, Na, Ca and Li was performed by atomic absorption spectroscopy; Cl was analyzed by ion chromatography.
composition of individual particles with specific identification of elements from sodium (atomic number 11) and greater in atomic number. (Data can be obtained only for particles >0.2 μm diameter; maximum observed particle sizes were generally <4 μm.) The samples were collected on cellulose acetate propionate substrates with flow rates of ~14 l/min and sampling times of 0.5 min. (The substrate is a smooth, carbonaceous material devoid of interfering elemental composition.) A typical example of the Salty Dog particle collections is shown by the SEM photographs (Figure 6) of two impactor stages of the sample obtained in Experiment No. 12. (Note the 1.0 μm markers at the bottom of the photomicrographs.) As shown by the photographs, the Salty Dog aerosols ranged in shape from nearly cubic to irregular agglomerates.

After length and width dimensions were measured, the elemental composition of individual particles was determined using energy-dispersive x-ray analysis (EDXA). An example of the x-ray energy spectrum for a single Salty Dog particle is shown at the bottom of Figure 6. For the sample represented by the data in Figure 6 for Salty Dog Experiment No. 12, a total of 25 particles, ranging in size from 0.2 to ~2.0 μm was examined. Each particle exhibited an x-ray energy spectrum* like that shown in the figure, indicating that the primary constituents of the crystalline aerosols were K and Cl. Na was not detected. The obvious conclusion is that the nearly cubic crystals produced by the "standard" Salty Dog pyrotechnic are predominantly KCl.

The foregoing conclusion helps to clarify the relationship between extinction and relative humidity observed in the chamber experiments with Salty Dog aerosols. Figure 5 shows an inflection point in the data at a relative humidity of 66-68%, indicating a decrease in the rate of change of equilibrium droplet size with decreasing RH below that point. Figure 7 is reproduced from Winkler and Junge (1972) and shows growth curves, in terms of relative mass increase, for pure salts of KCl, NaCl and MgCl₂ as functions of relative humidity. Winkler and Junge's data show a similar inflection point for KCl aerosols at

* The peak on the far right side of the spectrum is from the chrome plating used to make the slide surface conductive.
Figure 6  Examples of Scanning Electron Photomicrographs and Elemental X-ray Energy Spectra of Salty Dog Pyrotechnic Aerosols (Experiment No. 12).
67-68% RH (denoted by the arrow on the figure) on the dashed curve representing aerosol behavior under conditions of decreasing RH. Thus, the experimental data, which were obtained primarily in experiments during which RH was lowered (to observe fog stability), reflect the well-known hysteresis effect* (for KCl aerosols) exhibited by deliquescent materials.

From Winker and Junge's data, the following conclusions concerning the effectiveness of Salty Dog aerosol as a stable screen are evident: (1) the hysteresis effect is responsible for the observed stability (under conditions of lowering RH) of Salty Dog fog between ~70 and ~83% RH; (2) the Salty Dog fog must be generated at relative humidities >83% in order to take full advantage of the hysteresis effect; and (3) if a higher proportion of the aerosol were composed of NaCl or MgCl₂ instead of KCl (such as might occur if additional Na or Mg were added to the pyrotechnic, for example in the form of a different oxidizer--e.g., sodium perchlorate or magnesium perchlorate), the new artificial fog might exhibit extinction properties at relative humidities much lower than the 67-68% RH minimum characteristic of the Salty Dog pyrotechnic.

2.3 Other Salty Dog Formulations

As previously discussed, two other Salty Dog formulations were tested: Formulation NWC-29 (Experiment No. 15) and Formulation CY85A (Experiment No.s 16 and 17). These three experiments were conducted at 68, 69 and 72% RH, respectively, and did not produce integrated extinction coefficients (yields) which were significantly different from that expected for "regular" Salty Dog.

In Experiment No.s 15 and 16, cascade impactor samples were acquired, and examples of SEM and EDXA analyses for these experiments are presented in Figures 8 and 9, respectively. Again, a total of 25 particles in the size range 0.2 to 4.0 µm was analyzed for each experiment, and all examined particles in the respective experiments exhibited x-ray energy spectra such as shown in Figures 8 and 9. Formulation NWC-29 apparently was composed primarily of Na

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*The hysteresis effect arises as a result of nucleation phenomena in the super-saturated (with respect to the dissolved salt) solution produced in an evaporating droplet.
and Cl, while detectable concentrations of both Na and K were found along with Cl in Formulation CY85A.

Based on Winkler and Junge's data, for comparable particle sizes and concentrations, both Formulation NWC-29 and Formulation CY85A would be expected to produce larger droplets and hence greater extinction than does "standard" Salty Dog at all relative humidities above the deliquescence point. Relatively, the greatest differences would be expected at an RH of ~65% in a condition in which RH was lowered from >84%. However, for this limited experiment set, differences in particle sizes may mask differences in the deliquescence and hysteresis characteristics of the respective aerosols. The photomicrographs in Figures 6, 8 and 9 indicate, at least qualitatively, that the particle size distributions in the three experiments may have been different from each other. The relative contributions of particle size, concentration and composition to the observed extinction are unknown.
Figure 8 Examples of Scanning Electron Photomicrographs and Elemental X-ray Energy Spectra of Salty Dog Pyrotechnic (Formulation NMC-29) Aerosols (Experiment No. 15).
Figure 9  Examples of Scanning Electron Photomicrographs and Elemental X-ray Energy Spectra of Salty Dog Pyrotechnic (Formulation CY85A) Aerosols (Experiment No. 164).
2.4 Comparison of Salty Dog and Phosphorus Pentoxide Smokes

For comparison of the relative effectiveness of Salty Dog in producing conditions of restricted visibility at subsaturated humidities, a limited number of experiments was conducted with white phosphorus. Upon burning, phosphorus reacts with oxygen to produce phosphorus pentoxide which immediately hydrates to form phosphoric acid. Phosphoric acid is extremely hygroscopic, deliquescing at relative humidities as low as 10%. A total of 10 primary white phosphorus experiments* were conducted, and the pertinent parameters for these experiments are presented in Tables 5 and 6. Data at the bottom of Table 6 may be compared with the averaged Salty Dog yields presented in Table 4.

In Figure 10, visibility data at both visible and IR wavelengths are compared for 6 g phosphorus and 6 g Salty Dog smokes, both produced at 95-96% RH. At all wavelengths, extinction (visibility restriction) in the phosphorus smoke is much greater than that of Salty Dog, being a factor of ~2 greater (except at ~10 μm λ) in the phosphorus smoke. Apparently, some absorption effects occur at near 10 μm wavelengths in the phosphorus smoke.

The greater extinction achievable in phosphorus smokes (relative to that of Salty Dog) is due primarily to the apparently larger equilibrium droplet sizes exhibited by phosphoric acid. Photomicrographs of gelatin replicas of phosphoric acid droplets collected by impaction in Experiment No.s 1, 5 and 10 (at 51, 62 and 95% RH, respectively) are presented in Figure 11. For comparable payload sizes, such collections cannot be obtained in Salty Dog smokes at relative humidities <~90% owing to the small sizes and low concentrations of droplets produced by Salty Dog aerosols at lower relative humidity. In

*In these experiments, the white phosphorus payload was placed in a crucible, ignited with a propane torch and allowed to burn freely until the flame died. Typically, a 6 g payload burned for ~3 min, and some unburned residue remained in the crucible.
Table 5
Log of White Phosphorus Experiments

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Phosphorus Payload</th>
<th>Relative Humidity</th>
<th>Minimum Visibility</th>
<th>Particle Concentration at Sizes &gt; Indicated Diameter</th>
<th>Aerosol Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;0.01 μm</td>
<td>&gt;0.10 μm</td>
</tr>
<tr>
<td>1</td>
<td>0.10 g</td>
<td>51%</td>
<td>2.88 km</td>
<td>1.03x10^4 cm^-3</td>
<td>5.18x10^3 cm^-3</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>94</td>
<td>0.74</td>
<td>5.22x10^4</td>
<td>21.83x10^3</td>
</tr>
<tr>
<td>3</td>
<td>1.02</td>
<td>43</td>
<td>0.22</td>
<td>15.76x10^4</td>
<td>43.05x10^3</td>
</tr>
<tr>
<td>4</td>
<td>1.02</td>
<td>56</td>
<td>0.34</td>
<td>11.98x10^4</td>
<td>51.80x10^3</td>
</tr>
<tr>
<td>5</td>
<td>1.03</td>
<td>62</td>
<td>0.27</td>
<td>16.29x10^4</td>
<td>57.20x10^3</td>
</tr>
<tr>
<td>6</td>
<td>1.06</td>
<td>74</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.90</td>
<td>85</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.00</td>
<td>95</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6.04</td>
<td>46</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6.00</td>
<td>95</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Visible Wavelength
Table 6
The Yield (per gram) of Aerosol and Extinction in Chamber Experiments with White Phosphorus

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Phosphorus Payload</th>
<th>Relative Humidity</th>
<th>Integrated Extinction Coefficient</th>
<th>Particles/gram at Sizes &gt; Indicated Diameter</th>
<th>Aerosol Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;0.01 μm</td>
<td>&gt;0.1 μm</td>
</tr>
<tr>
<td>1</td>
<td>0.10 g</td>
<td>51%</td>
<td>8.01 m²/g</td>
<td>6.1x10^{13} /g</td>
<td>3.1x10^{13} /g</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>94</td>
<td>25.99</td>
<td>25.7x10^{13}</td>
<td>10.7x10^{13}</td>
</tr>
<tr>
<td>3</td>
<td>1.02</td>
<td>43</td>
<td>10.29</td>
<td>9.1x10^{13}</td>
<td>2.5x10^{13}</td>
</tr>
<tr>
<td>4</td>
<td>1.02</td>
<td>56</td>
<td>6.66</td>
<td>6.9x10^{13}</td>
<td>3.0x10^{13}</td>
</tr>
<tr>
<td>5</td>
<td>1.03</td>
<td>62</td>
<td>8.30</td>
<td>9.5x10^{13}</td>
<td>3.3x10^{13}</td>
</tr>
<tr>
<td>6</td>
<td>1.06</td>
<td>74</td>
<td>19.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.90</td>
<td>85</td>
<td>17.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.00</td>
<td>95</td>
<td>20.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6.04</td>
<td>46</td>
<td>13.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6.00</td>
<td>95</td>
<td>19.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average/gram</td>
<td>43-62</td>
<td></td>
<td></td>
<td>7.9x10^{13}</td>
<td>3.0x10^{13}</td>
</tr>
<tr>
<td>Average/gram</td>
<td>93-95</td>
<td></td>
<td></td>
<td>25.7x10^{13}</td>
<td>10.7x10^{13}</td>
</tr>
</tbody>
</table>
FIGURE 10

COMPARISON OF EXTINCTION (VISIBILITY) IN FOGS PRODUCED BY BURNING, RESPECTIVELY,
6 G PHOSPHORUS AND 6 G SALTY DOG @ 95-96% RH
Figure 11: Aerosol samples from phosphorus pentoxide smokes

- 6.0 g P @ 95% RH
- 1.0 g P @ 62% RH
- 0.1 g P @ 51% RH
Figure 12, complete aerosol spectra* (0.01 to >10.0 μm diameter) are shown for individual 0.1 g phosphorus and 0.1 g Salty Dog smokes generated at 95% RH. Close inspection of the spectra shows aerosol concentrations at sizes <0.5 μm diameter to be a factor of ~2 higher in the phosphorus smoke and, at sizes >~3.0 μm diameter, concentrations are a factor of ~5 greater in the phosphorus smoke than in Salty Dog smoke. At 95% RH, both materials produce droplets of >10.0 μm diameter, but considerably greater concentrations are generated (per gram of material burned) by white phosphorus.

Comparison of the relative effectiveness of Salty Dog and white phosphorus hygroscopic smokes is perhaps best illustrated by the data presented in Figure 13. In the figure, the per-gram yield (per 590 m³) data from all of the Salty Dog and phosphorus experiments in terms of visible wavelength visibility restriction (m) or extinction (km⁻¹) are shown as functions of RH. (Figure 13 is a reproduction of Figure 5 with the phosphorus data added.) The scale along the right side of the figure shows the "integrated" extinction coefficient (m²/g) achieved in both smokes. These values may be used to estimate extinction coefficient (and hence visibility) through a cloud (of any size, assuming uniform aerosol distribution) of either of these two materials by multiplying by the amount of material disseminated and dividing by the volume of the cloud. It is clear from these data that phosphorus pentoxide smokes provide much better screens than do Salty Dog smokes (at least at visible wavelengths), particularly at lower, more commonly-occurring relative humidities. Further, the increase in yield (extinction) from 40% RH to 90% RH for the phosphorus pentoxide smokes (dashed line) is a factor of approximately three, in good agreement with theoretical values derived by Rubel (1978). These data

*The spectra shown in Figure 12 are drawn from data obtained with 3 different instruments: a TSI Electrical Aerosol Analyzer (EAA), a Royco Optical Particle Counter and a Calspan Drop Sampler (gelatin replication of aqueous aerosols). Ignoring the first and last size intervals of each of the instruments, the data indicate fair agreement for the three instruments. (Royco data have not been corrected from factory calibration.)
FIGURE 12

COMPARISON OF AEROSOL SIZE SPECTRA FOR 0.1 g (1.7x10^{-4} g/m^3) SALTY DOG AND PHOSPHORUS SMOKES PRODUCED AT 95% RH
Figure 13  Comparison of the Per-gram (per 590 m$^3$) Extinction (visible wavelength visibility) as a Function of Relative Humidity for Salty Dog and Phosphorus Smokes.
show that, for comparable quantities of Salty Dog and white phosphorus*, the extinction produced by white phosphorus smoke is always greater than that produced by Salty Dog smoke. At 95% RH, extinction is a factor of ~2 greater for phosphorus smokes, and, at RH <70%, extinction is a factor of ~10 greater for phosphorus than for comparable Salty Dog smokes.

In terms of aerosol production, the per-gram yields for Salty Dog and white phosphorus smokes as functions of relative humidity may be found in Tables 4 and 6, respectively. For the Salty Dog pyrotechnic, total aerosol output is consistently ~8x10^{13} particles per gram; at higher humidities the aerosols deliquesce, and greater numbers of larger aerosols (i.e., >1.0 \mu m dia) are observed, giving rise to increases in extinction in Salty Dog smokes. Similar data for phosphorus pentoxide smokes show that, per gram of material burned, the phosphorus smokes exhibit considerably greater numbers of particles of size >1.0 \mu m diameter, thus accounting for the substantially greater extinction achieved in these smokes.

2.5 Extinction at IR Wavelengths in Simulated Natural Fog

To put observed extinction (particularly at IR wavelengths) in the Salty Dog and phosphorus smokes into perspective, we obtained similar measurements in simulated natural fogs. In Figure 14, visibility and drop spectra data are shown for both marine and continental fog types simulated in our 590 m^3 chamber. At the top of the figure, visibility data at visible and IR wavelengths are shown as functions of time for the two fogs. At the bottom of the figure, photomicrographs of gelatin replicas of the fog droplets and the droplet size distributions** derived from those gelatin-replica droplet samples are shown for

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* The scatter in the phosphorus pentoxide smoke data is presently attributed to unburned residue and to difficulties in weighing minute quantities of phosphorus under water.

** The droplet spectra in Figure 14 are annotated as follows: \(T=\)time, \(R=\)mean radius in microns, \(N=\)number concentration per cm^3, \(W=\)liquid water content in g/m^3, and \(V=\)measured visibility in meters.
Figure 14  COMPARISON OF EXTINCTION AND DROPLET SIZE SPECTRA IN SIMULATED MARINE AND CONTINENTAL FOGS PRODUCED IN CALSPAN'S 590 m$^3$ CHAMBER

MARINE FOG

CONTINENTAL FOG

DISTANCE (M) TO ACHIEVE 90% EXTINCTION (VISIBILITY)

T = 9:00
R = 5.9
N = 192
W = 0.187
V = 90

DISTANCE (M) TO ACHIEVE 90% EXTINCTION (VISIBILITY)

T = 8:00
R = 2.6
N = 1632
W = 0.159
V = 54

10$^4$

10$^3$

10$^2$

10

1

10$^{-1}$

0 5 10 15

RADIUS (microns)

10$^4$

10$^3$

10$^2$

10

10$^{-1}$

0 5 10 15

RADIUS (microns)
the 8-minute time in the respective fogs. As seen in the data, the simulated fogs mimicked natural fogs in that they were composed of relatively high concentrations of large (i.e., >5 μm dia) water droplets, liquid water contents of ~0.17 g m⁻³ and visibilities (visible wavelengths) of 50-100 m.

The dependence of extinction at IR wavelengths on particle size is graphically illustrated, and distinguished from that observed in the pyrotechnic aerosol fogs, by the data presented in Figure 14. Mean droplet sizes (at T=8 min) in the marine and continental fogs are ~12 and 5 μm diameter, respectively, while liquid water contents are comparable for the two fogs. Note that for the "large droplet" marine fog, extinction (visibility) at all wavelengths (0.5-15.0 μm) is comparable. For the continental fog with smaller droplets, the difference in extinction between visible and far IR wavelengths is much greater, being a factor of ~2-3. As discussed earlier (Figures 2 and 10), the differences in extinction from visible to far IR wavelengths in the pyrotechnic smokes can be as great as factors of from 10 to 40.

2.6 Modification of Simulated Natural Fog by Salty Dog Aerosols to Improve Transmission at IR Wavelengths

In view of the differences in IR extinction through the simulated marine and continental fogs, it became evident that it might be possible to modify a "marine" fog (by changing the drop size distribution) to improve transmission at IR wavelengths. Such an experiment is illustrated in Figure 15, which shows the time history of transmission (visibility) at both visible and IR wavelengths throughout the lifecycles of both a control (untreated) fog and a modified fog.

The fogs were formed through adiabatic expansion of nearly saturated air, as were the fogs of Figure 14. During the initial stages of the fog forming process (i.e., up to time=6 min), the time history of transmission through both fogs was nearly identical, with droplet sizes increasing to mode values of ~7 μm diameter by t=6 min. At 6 minutes into the modified fog, it was "seeded" by the forced burning of 1.01 g of a "Salty Dog" pyrotechnic, providing ~70,000 particles/cm³ and 1.8 x 10⁻³ g/m³ of seeding material in our chamber. The effect on visibility in the seeded fog is obvious from the data shown in Figure 15. Note that while visibility degraded at all wavelengths shorter than ~4 μm, visibility improved dramatically at wavelengths between 8 and 11 μm.
Figure 15 MODIFICATION OF SIMULATED NATURAL FOG TO PRODUCE VISIBILITY IMPROVEMENT AT IR WAVELENGTHS

CONTROL FOG

SEEDED FOG

TIME (min)

DISTANCE (m) TO ACHIEVE 98% EXTINCTION (VISIBILITY)

○ VISIBLE

× 2.15 μm

□ 3.7–3.9 μm

△ 7.75–8.8 μm

● 9.13–10.33 μm

▲ 13.6–14.5 μm

TIME (min)

DISTANCE (m) TO ACHIEVE 98% EXTINCTION (VISIBILITY)

T = 11:00

R = 2.8

N = 2528

W = 0.455

V = 25

T = 12:00

R = 4.8

N = 380

W = 0.221

V = 68

RADIUS (microns)

RADIUS (microns)

60 μm

60 μm

10^{-1}

10^0

10^1

10^2

10^3

10^4

DROPS PER CC/RADIUS INT.

50 μm
The premise for the experiment was as follows: high concentrations of tiny (<0.5 μm dia) hygroscopic particles are expected to extract water vapor from the saturated (100% RH) foggy air and grow to some equilibrium size ~2-5 times dry particle size; with the lowered RH, the fog droplets are expected to evaporate to smaller sizes. Hence, an improvement in visibility at longer wavelengths would be expected due to a shift of the mean fog droplet population to smaller sizes. A degradation of visibility at shorter wavelengths would be expected due to an increase in particle concentrations at sizes <~2 μm diameter. The experimental data show that at time=12, mode droplet size was ~12 μm diameter in the Control Fog and ~5 μm diameter in the modified fog. Obviously, the required "over-seeding" was not achieved in this single experiment, but the results validate the premise of the experiment. No attempt was made to optimize these procedures.

Obviously at IR wavelengths, absorption may represent a significant contribution to the total extinction by "natural" fogs. These results, however, demonstrate the potential extinction of IR possible in artificial fogs (screens) through judicious choices of aerosol size, concentration and composition.
Section 3
CONCLUSIONS

The results of these experiments have shown that the Salty Dog aerosol fog can be an extremely dense screen at visible wavelengths and particularly at higher relative humidities, exhibiting good stability for relative humidity changes of the order of 10%. The principal findings of this laboratory investigation are as follows:

1. Yield from the pyrotechnic in terms of aerosols of >0.01 μm diameter is ~$8 \times 10^{13}$/gram, of which ~30% are greater than 0.1 μm in size.

2. The output of particles >1.0 μm diameter is relative humidity dependent, with ~$5 \times 10^{10}$ particles being produced at RH <70% and ~$5 \times 10^{11}$ being produced at 93-97% RH; relatively few particles >5 μm diameter are observed.

3. Likewise, the integrated extinction coefficient (visible wavelengths) for Salty Dog aerosol fogs is also RH dependent, average values being ~1.4, 5.1 and 15.0 m$^2$/g for RH of <70, 79-85 and 93-97%, respectively.

4. Extinction due to Salty Dog aerosol fogs at wavelengths longer than the visible is only a fraction of that observed at visible wavelengths; at 2.15 μm wavelength, extinction is only 10% of that for visible; at 9-10 μm wavelength, extinction is only 2-4% of that for visible wavelengths. In contrast, extinction in natural fogs (with droplets of 5-20 μm diameter) is comparable in the range of wavelength from visible to far IR.

5. The Salty Dog smokes (fogs) are very stable; visibility improvement factors of ~2 are typical for relative humidity reductions of ~10%, hence, evaporation retardants (stabilizers) are probably not necessary.

6. Chemical analysis of aerosol samples from the "standard" Salty Dog smokes for which the above conclusions were drawn show that the primary aerosol in these smokes is KCl. Similar analyses of aerosol samples from two other Salty Dog formulations show that the resultant aerosol from Formulation NWC-29 is primarily NaCl and from Formulation CY85A is a mixture of NaCl and KCl. Both alternative formulations are expected to provide better screening effects than does "standard" Salty Dog at relative humidities below ~80% RH.
7. Apparently because of its greater hygroscopicity and hence larger equilibrium droplet sizes, phosphorus pentoxide smokes exhibit greater extinction at all relative humidities, particularly at RH <70% where extinction/gram is a factor of 10 greater than that of "standard" Salty Dog smokes. It is also expected that phosphorus smokes will exhibit greater extinction than either of the alternative Salty Dog formulations at all relative humidities.
REFERENCES


