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CONTRACT NO. DA 18-035-AMC-127(A)

A NEW SMOKE SCREENING CHEMICAL FOR USE
IN AERIAL SMOKE TANKS

FINAL AND SUMMARY REPORT - 448-6512-F

by

William H. McLain

Robert W. Evans

December, 1965

U. S. Army Edgewood Arsenal
CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES
Edgewood Arsenal, Maryland 21010

UNIVERSITY OF DENVER
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FOREWORD

This Final and Summary Report describes the work performed on Contract No. DA 18-035-AMC-127(A) for the U. S. Army Chemical Research and Development Laboratories, Weapons Research Division, Edgewood Arsenal, Maryland. Special technical adviser and program monitors have been Mr. Harold B. Kern and Mr. Howard Carroll, Contract Project Officers, Edgewood.

Notices

This information has not been cleared for release to the general public.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

When this document has served its purpose, DESTROY it.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. William Schmelting, Mr. Philip Keitel, and Mr. Larry Cameron, for their aid in performing this program. Without their assistance much of the reported work could not have been accomplished. We also wish to acknowledge the skilled technical work performed by Dr. Harry Babad who performed the synthesis for most of the phosphorus alkyl derivatives.

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ABSTRACT

A review of the literature for chemical smoke agents is presented. Based on this review an experimental program to evaluate new liquid smoke agents was formulated. The results of this experimental program indicated that liquid agents possessing an obscuring power greater than FS can be developed using selected mixtures, solutions, and compounds of phosphorus. A solution of 33 weight percent methylene iodide in white phosphorus had a TOP of about 2800. A eutectic mixture of phosphorus sesquisulfide and white phosphorus had a TOP of about 2800. The major difficulty of the agents tested was their pyrophoricity which resulted in handling difficulties. Considerable reduction in the rate of oxidation was accomplished using methylene iodide as a flame inhibiting agent. An intimate oil smoke TEA mixture 90622T was tested. This agent has a TOP of 400 and relatively poor persistence. While this agent has many advantages in its handling and corrosive properties, it has a serious drawback in its low TOP and low density particularly for use with restricted volume airborne tankage. A large number of smoke agents were tested and are reported. The results of this program indicate that further work should be performed to develop flame inhibiting agents in order to selectively control the oxidation of phosphorus based liquid smoke agents.

I. INTRODUCTION

This is the Sixth and Final Summary Progress Report describing the accomplishments on Contract No. DA 18-035-AMC-127(A) for U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, Maryland.

The main objective of the research was to find and/or develop a new, non-hazardous, smoke producing chemical for use in existing air-borne dissemination tanks.

The specifications of the improved smoke-producing chemical are as follows:

1. The new agent shall show visual screening properties (obscuration and persistence) equal to or better than FS when compared at the same atmospheric conditions.
2. The liquid shall be capable of being handled in the field without the aid of special protective equipment.
3. The smoke shall be non-toxic to humans at concentrations necessary to produce the required screening effect and for the period of time the smoke persists.
4. The liquid agent shall be non-corrosive and non-reactive to metals such as, but not limited to, low carbon steel, aluminum and its alloys (eg. 60-61), (60-75) and magnesium and its alloys.
5. The smoke shall be non-corrosive and non-reactive to materials, such as, but not limited to, metals, plastics, resins, organic finishes, natural or synthetic fibers and rubber.
6. The liquid density of the agent shall not exceed 1.3.
7. The agent shall show less than ten percent decomposition when stored in a low carbon steel container at 165°F for a period of two weeks and contain less than 1% solids after this period.

8. The liquid shall be free-flowing at temperatures between -40°F and $\pm 165^{\circ}\text{F}$.
9. The liquid agent and disseminated smoke shall have flash points exceeding 125°F .

The approach to this problem consisted of a thorough examination of the literature for possibilities in both existing and new smoke producing chemical agents. This was followed by laboratory synthesis, modifications, and testing to further categorize candidate materials. For selected candidate materials showing considerable promise a field test evaluation was performed to evaluate their suitability for use as smoke agents under simulated field test conditions. These tests included evaluation of TOP in a large smoke tunnel and airborne dissemination from a modified F-80 wing section.

Since World War II relatively little research and development has been directed toward obtaining a new smoke agent with improved characteristics suitable for dissemination from the air. The results obtained under this contract, as well as other recent work, indicates that a smoke producing chemical agent with better characteristics than FS can be obtained. The research and development believed necessary to achieve this are summarized in the next section. A detailed description of the work performed under this contract is presented in the succeeding sections of this report.

II. RECOMMENDATIONS

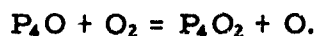
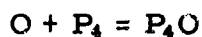
Based on the literature survey and the experimental work performed under this contract, it appears that smokes based on phosphorus containing agents appear to be the most satisfactory - especially if large area smoke screens must be formed. A major disadvantage to their use is the pyrophoricity of the agents that have been evaluated to date. Other smoke agents such as the TEA oil mixture which have many desirable characteristics are simply not as efficient as smoke producing agents.

It is therefore recommended that further research and development should be performed in six major areas of smoke technology. These programs should encompass a technical spectrum ranging from basic research to preliminary hardware development. Some of these research programs should be low level of effort programs designed to determine whether further research efforts would substantially improve the state of the art. The developmental programs would consist primarily of feasibility studies relating to the further evaluation promising smoke agents and serve to provide the necessary technical background for evaluation of hardware design concepts. A brief outline of the recommended programs is contained in the following discussion.

A. Phosphorus Based Smoke Agents

Work on this program has indicated that a white phosphorus-methylene iodide solution and/or a white phosphorus - phosphorus sesquisulfide eutectic mixture have promise as a liquid smoke agent. Field tests have shown that these materials can be handled with a minimum of protective equipment under simulated operational conditions. It is recommended that further work be performed to optimize the physical and handling properties of these solutions. This work should include feasibility demonstrations of the water displacement loading techniques together with preliminary hardware development programs designed to provide adequate field handling and field dissemination equipment. Primary emphasis should be placed on the development of design concepts.

Another area to be investigated is the control of initiation and burning of phosphorus with special emphasis on development of combustion retardants. The oxidation of phosphorus occurs via a chain reaction mechanism. Semenov has shown that the chemical reaction chain consists of two rate limiting oxidation steps described by:



To control the oxidation rate it is sufficient to break the chain by removing oxygen atoms. A number of chemical species capable of doing this are known. Typical species are ethylene, halogens, and metallic carbonyls. A systematic study of the effect of such species on explosion limits would possibly allow the development of agents based on white phosphorus with controlled burning characteristics.

B. Intimate Oil Smoke Agents

While the smoke mixtures containing oil and TEA are not efficient smoke producers, they have many desirable characteristics and appear to be sufficiently efficient smoke producers for some uses. It therefore appears desirable to find out if these mixtures can be used with high performance aircraft. Research and development effort should be expended in attempting to increase the efficiency of these mixtures as smoke producers. (Increase TOP and DOP of the mixtures.)

C. Powdered Smoke Agents

The use of powdered materials to provide military screening smokes has not been fully evaluated. The major difficulty in using powders is associated with the problem of providing adequate dissemination of the agents at ground level. A variety of possible dust particles can be employed to provide smoke dusts. These powders may be completely unreactive e.g. (Microfine) or highly desiccant in nature (metal chlorides). Use of pyrophoric coatings on metal chloride particles to provide the necessary heat of vaporization should be investigated. Such coatings would include phosphorus and metal alkyl derivatives. It is recommended therefore, that a program be initiated to provide further information concerning the smoke producing capabilities of powders. Primary emphasis should be placed on a survey of the smoke properties for a wide range of potential agents together with a concurrent evaluation of the possible methods for effective dissemination at, or near, ground level.

D. Organo-Metallic Smoke Agents

Preliminary studies were made regarding the smoke effectiveness of selected organo metallic compounds as part of this research program. Results of these studies indicated the possibility that

certain organo metallic derivative of titanium could produce a smoke consisting of a mixture of hydrated metal chloride and fog oil. Additional exploratory research evaluating the TOF of isopropyl and isobutyl derivatives of titanium chloride is recommended. A similar research program should be directed toward the synthesis and systematic evaluation of metal phosphorus alkyl derivatives using phosphorus, strontium and calcium. Because both classes of these compounds are not commercially available, a significant portion of this research effort would necessarily consist of the synthesis and physical characterization of these compounds. Emphasis should be placed on outlining the chemical reaction sequences important to the formation of smoke particles during the hydrolysis of these agents.

E. Metal Chloride Based Smoke Agents

Smoke agents based on the hydrolysis of metal chlorides have many advantages in spite of their toxicity. The major problem in using these as military smoke agents is that the metal chlorides which are the strongest desiccants are solids. To supply the necessary heat of vaporization a pyrotechnic mixture must be employed. It is recommended that a program be initiated to investigate the possibility of employing a solution of metal chlorides to provide particulate matter in a finely divided form with a minimum expenditure of energy. Such mixtures and solutions would include but not be limited to solutions of the hygroscopic metal chlorides in boron trichloride and phosphorus trichloride. Primary emphasis should be placed on determining the feasibility of forming stable solutions of the metal chlorides and on evaluating the TOP of these mixtures.

F. Dual Smoke Agent Systems

The effectiveness of using ammonia and amine derivatives to modify the deleterious aspects of the smokes produced via hydrolysis mechanisms has been demonstrated on past programs reported in the literature, and during the present research study. The use of a dual smoke agent imposes additional hardware complexity which becomes a particularly important problem when dissemination of the agents must occur from airborne equipment. The major difficulty in using these agents is to provide adequate mixing of the two components. It is recommended that a design concept program be initiated to outline hardware requirements in this area to determine whether this concept is feasible. Particular emphasis should be placed on the use of FS-Ammonia combination of smoke agents and the effective dissemination of these agents to provide ground level smoke covers.

Of the above recommendations it is believed that A and B are the most promising.

III. SYSTEMS EVALUATION STUDIES

A. Relative Efficiency of Smoke Agents

The efficiency of a smoke can be expressed in terms of relative weight effectiveness (TOP) or relative volume effectiveness (DOP). Figures and charts which list the relative merits of smoke agents in terms of TOP, density TOP, and smoke effectiveness (calculated in two ways described later) for a typical smoke tank, the E39R1, have been developed.

Figure 3 gives the relative coverage of various smoke agents relative to FS for a fixed volume tank (DOP). * A ratio greater than 1 implies a more effective smoke agent than FS for the comparison made. The agents which are better than FS for fixed volume requirements are WP, MIP, WP + P_4S_3 and SO_2 .

In terms of TOP, those agents which are reported in the literature to be better than FS are phosphorus, sulphur trioxide, and dual smoke mixture of titanium tetrachloride and NH_3 . In addition, this research program has demonstrated that a eutectic mixture of white phosphorus and phosphorus sesquisulfide, a solution of white phosphorus in methylene iodide, and a slurry of white phosphorus in carbon disulfide can all be synthesized and all have TOP's greater than FS. It should be noted that in a comparison of DOP and TOP, some of the other agents have had their order of effectiveness inverted. For example, a typical solution of methylene iodide and white phosphorus with a TOP of 2800 as compared to 4600 for WP, but has a DOP of 6700 relative to 8500 for WP. This means that if a comparison is made in terms of TOP, this solution is 61% as effective as WP, whereas, in terms of DOP this solution is 79% as effective.

For a systems requirement in which application is to be made to use existing equipment, the DOP affords a better standard comparison than the standard TOP. A calculation of the volume of smoke produced from a typical smoke tank under "perfect" conditions for a number of smoke agents is given in Table I. These values are normalized to an FS basis by dividing by the equivalent amount of smoke produced by FS. In order to calculate the smoke coverage a standard

* Density Obscuring Power - defined as the TOP multiplied by the specific gravity of the agent.

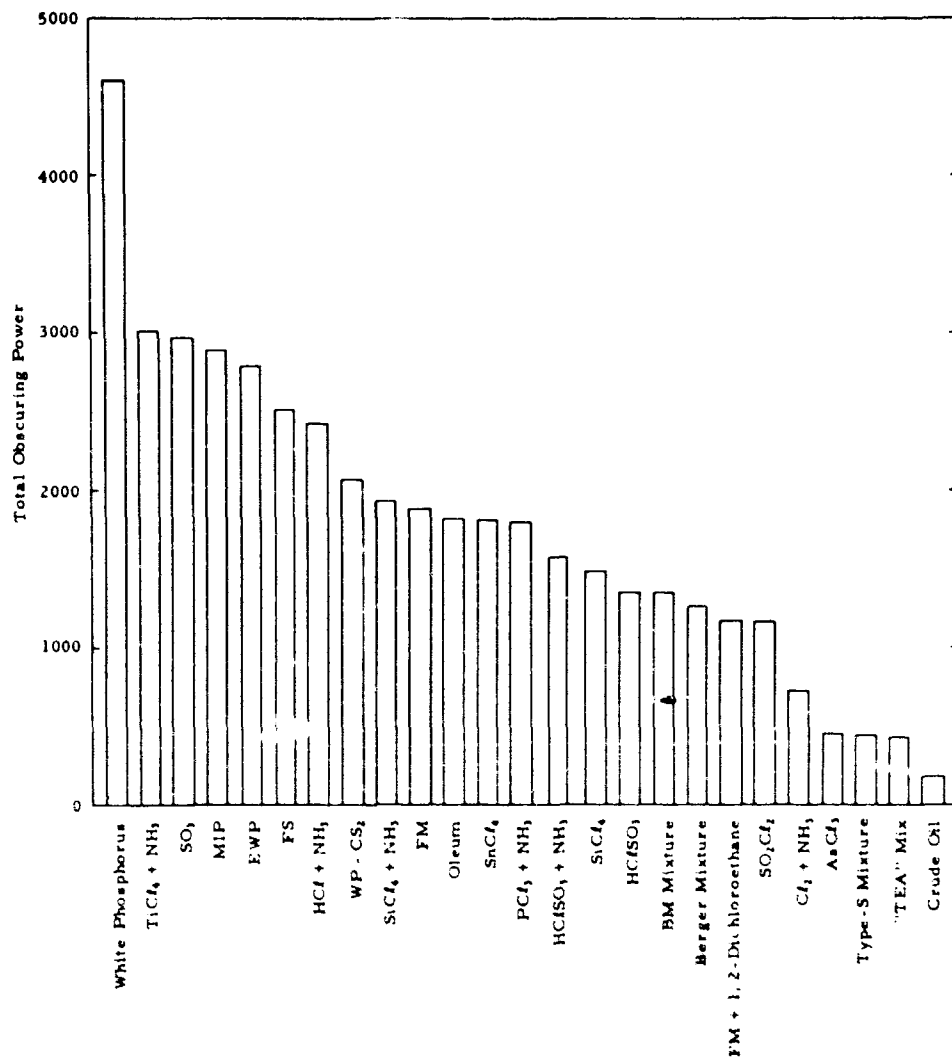


Figure 1. Total Obscuring Power for Selected Liquid Smoke Agents

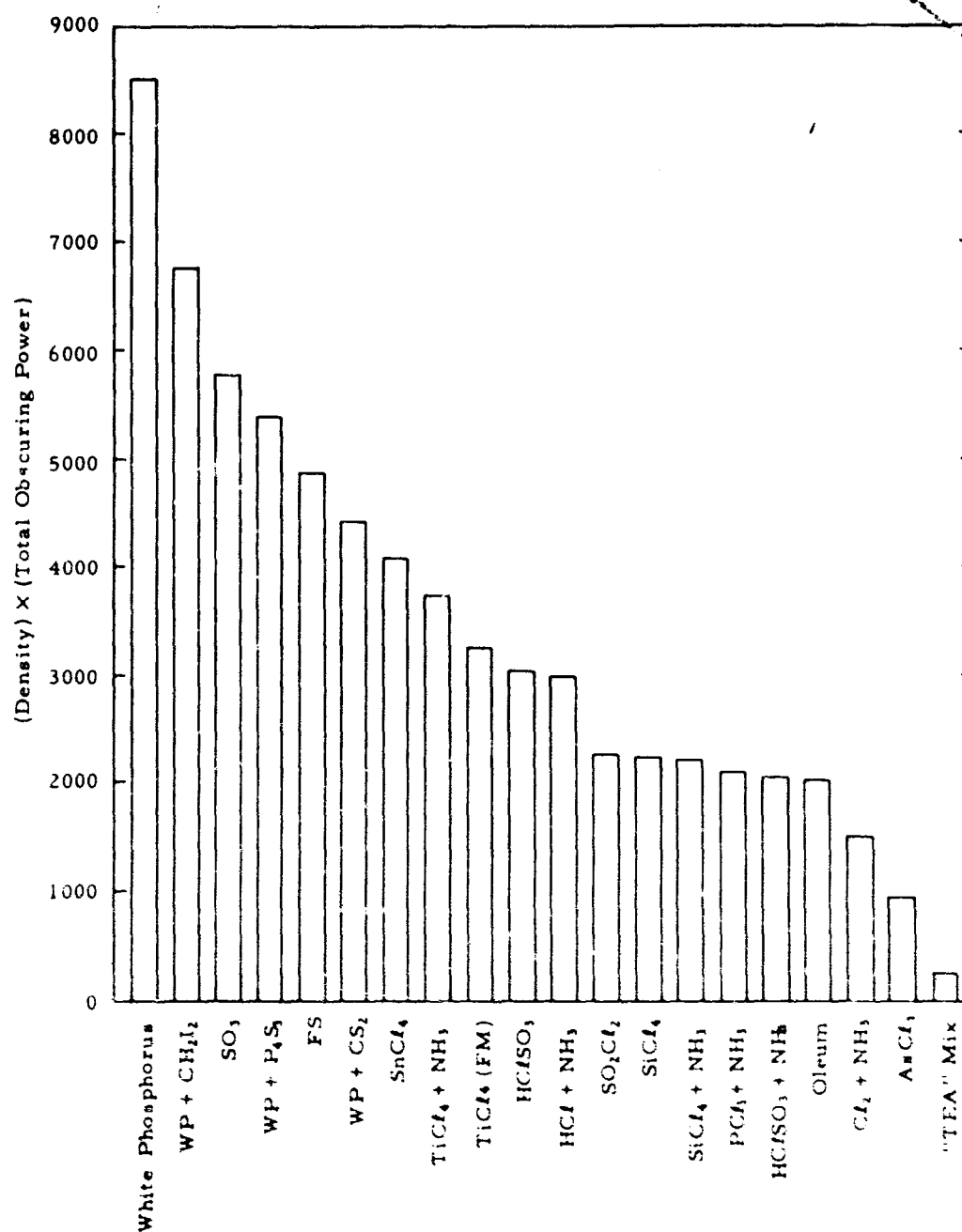


Figure 2. Density Obscuring Power for Selected Liquid Smoke Agents

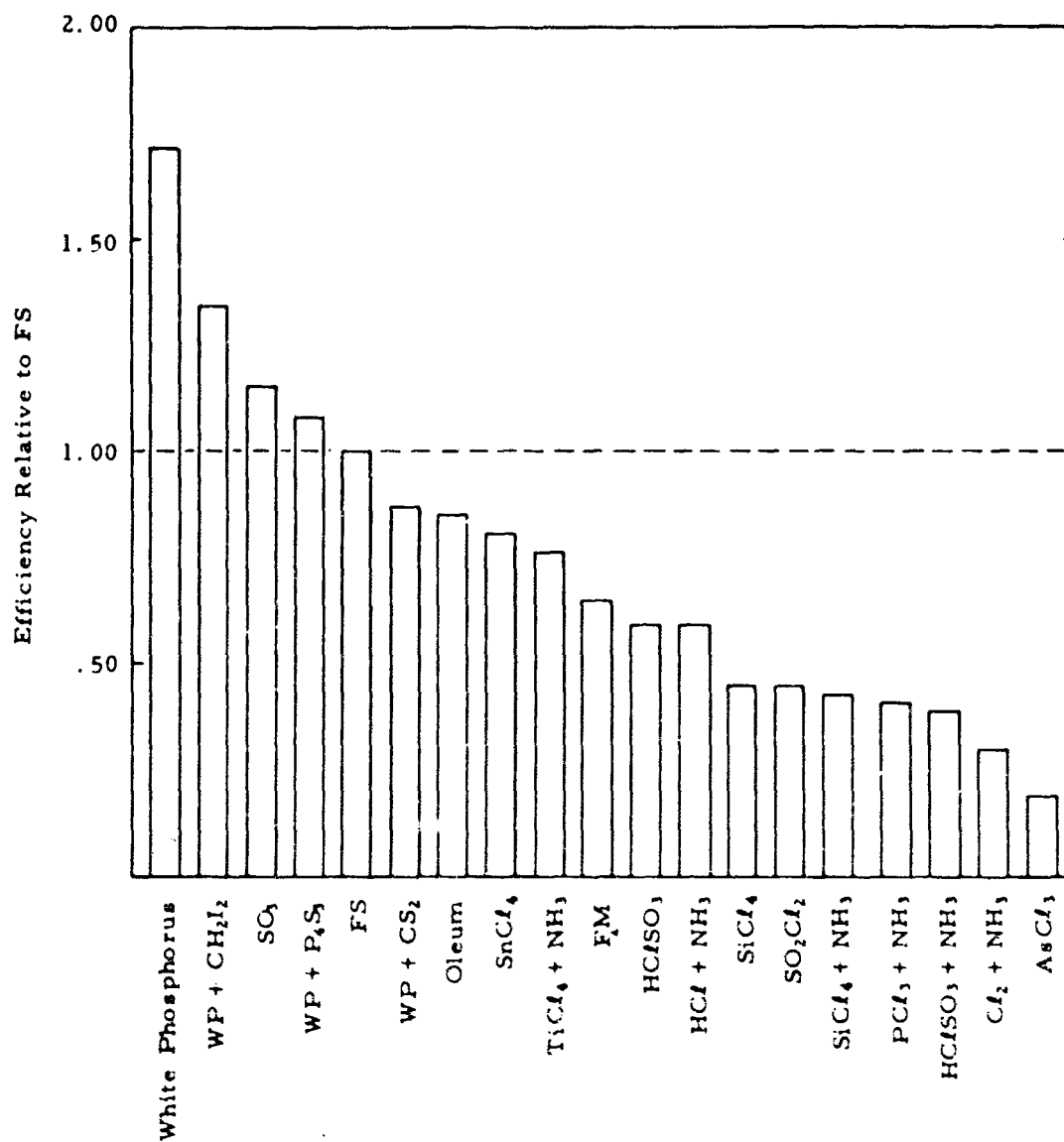


Figure 3. Coverage Capability of Various Smoke Agents Relative to FS

TABLE I
COVERAGE CAPABILITY FOR A NINE GALLON E39R1 TANK

<u>Agent</u>	<u>Cubic Yards $\times 10^6$</u>	<u>Efficiency Relative to FS</u>
White Phosphorus	2.32	1.74
WP-CH ₂ I ₂	1.86	1.39
SO ₃	1.60	1.20
WP-P ₄ S ₃ (EWP)	1.50	1.12
FS	1.34	1.00
WP-CS ₂ (Slurry)	1.22	0.91
Oleum	1.20	0.89
SnCl ₄	1.13	0.85
TiCl ₄ -NH ₃ *	1.04	0.78
FM	0.90	0.67
HClSO ₃	0.83	0.62
HCl + NH ₃	0.83	0.62
SiCl ₄	0.62	0.47
SO ₂ Cl ₂	0.63	0.47
SiCl ₄ + HN ₃	0.62	0.46
PCl ₃ + NH ₃	0.60	0.44
HClSO ₃ + NH ₃	0.57	0.42
Cl ₂ + NH ₃	0.41	0.31
AsCl ₃	0.27	0.20
Mix 90622 T	0.10	0.08

* A 50:50 mixture was assumed for these dual systems unless otherwise specified.

smoke must be defined. For this purpose it was assumed that a standard smoke was a smoke of such density that the light intensity of a 40 watt bulb would be extinguished to 1.25 percent of its value at a distance of 100 feet, and that the volume required included a path width of 100 feet, and, a height of 100 feet.

B. Relative Effectiveness of Smoke Agents

The relative effectiveness of a smoke agent is dependent not only on its obscuring capability but also is a function of all important technical considerations which are involved when it is to be used under operational field conditions. To develop criteria for determining which smoke agents may be effective under given operational conditions, it is useful to perform a preliminary evaluation using analytic weighting functions in which proportional weights are assigned to the various criteria used to evaluate smoke agents. The choice of weighting functions used in this analysis is arbitrary, and depending on the specific mission or type of screening cover required, a complimentary or alternate series of weighting functions should also be developed. There are two methods of assignment which were used in these studies.

Method A

The first method (method A) consists of assigning equal weights to all parameters. This method is the simplest to apply but suffers in its ability to describe with varying levels of accuracy the relative merits of smoke agents for specific operational situations. A major disadvantage in using this method is that it can result in false relative values for systems in which one or two critical parameters must have high values before the system has any merit at all. Thus, for example, if in the analysis under this section it would be possible to have a mythical smoke agent having zero TOP with optimum density and handling characteristics. Such an agent could have a theoretical relative value greater than the best agents even though it would have no intrinsic value as a smoke agent. An example of this effect is demonstrated in Method A where the low TOP of the Ethyl TEA Mixture (400) could severely limit its usefulness as an efficient agent suitable for dispersment from an aircraft.

Calculations Using Method A

A systems engineering study was performed for selected smoke agents. These studies assumed the existence of thirteen important

factors which required evaluation. Each of the factors was assigned a maximum possible individual weight of 100. The system used then rated each of the candidate smoke agents on a relative basis within the category under consideration. The best agent in each area under consideration was assigned a weight of 100. If any other agents were equal then they also were rated the same value. Other agents possessing less favorable characteristics were rated downward. The range varied between zero and one hundred. The basis for assignment of relative values was a combination of literature reports, and experimental experience. Results for this analysis are summarized in Table II. In this method TEA Mixture shows an operational effectiveness capability approximately equal to methylene iodide WP mixtures. White phosphorus, EWP, and EWP-MIP mixtures are somewhat better.

Providing the volume of tankage or weight of material required was not an important factor, under some tactical situation the use of a low TOP smoke agent might result in equal operation effectiveness.

Method B

The second method (method B) consists of weighting the various factors based on a value judgement involving relative importance of parametric values. This is a more flexible method but is also much more difficult to apply.

The principle criterium is the ability to provide a screening cover during a given airborne dispersment run from a typical tank. The important parameter for this purpose is the density TOP which can be correlated with the relative volumes of smoke produced by various agents. A number of other criteria must also be evaluated and their relative weighting values as used in this study are assigned in Table III. It should be noted that this type of rating system is arbitrary and the actual numerical values used should be adjusted to the specific operational mission under consideration. The best that this system can provide is a common basis for comparison which is more or less systematic in outlook, and it is recognized that for any specific smoke agent there may be a unique problem which would tend to rule out its operational usage. A brief detailed description of the above approach is given in the following discussion and a bar chart showing the relative effectiveness of some smoke agents is given in Figure 5.

TABLE II
COMPARISON OF EFFECTIVENESS FACTORS FOR VARIOUS
SMOKE AGENTS - METHOD A

	<u>EWP</u>	<u>WP</u>	<u>MIP</u>	<u>"TEA"</u> <u>Mix</u>	<u>FS</u>	<u>SiCl₄</u>	<u>TiCl₄</u>	<u>SnCl₄</u>
Relative Merit	980	960	945	915	875	855	785	756
DOP	70	100	90	10	50	25	40	46
Optimum Density	80	80	40	75	75	95	90	50
Toxicity of Smoke	90	90	85	100	90	90	40	40
Corrosivity of Smoke	80	80	80	100	20	70	70	70
Irritation of Smoke	85	85	85	100	25	75	65	75
Persistence of Smoke	95	95	100	10	70	15	60	15
Toxicity of Liquid	30	30	30	100	60	60	20	30
Corrosivity of Liquid	80	100	75	100	20	70	60	70
Freezing Point	100	0	50	85	100	100	90	95
Vapor Pressure	100	100	100	100	100	100	100	100
Gumming	100	100	100	65	100	25	10	25
Flash Point	0	0	40	60	100	100	100	100
TOP	70	100	70	10	65	30	40	40

TABLE III
COMPARISON OF EFFECTIVENESS FACTORS FOR VARIOUS
SMOKE AGENTS - METHOD B

	<u>White Phosphorus</u>	<u>WP + P₄S₃</u>	<u>WP + CH₂I₂</u>	<u>FS</u>	<u>TiCl₄</u>	<u>SnCl₄</u>	<u>SiCl₄</u>	<u>TEA (Mix)</u>
Relative Merit	1012	830	868	755	664	658	580	455
Density TOP	537	345	428	310	207	261	143	25
Minimum Density	-45	-65	-105	-55	-38	-88	-13	-45
Toxicity of Smoke	90	90	90	90	90	90	90	90
Corrosivity of Smoke	90	90	90	40	70	70	70	90
Irritation of Smoke	40	30	30	20	30	30	10	40
Persistency of Smoke	70	70	70	70	80	50	80	20
Toxicity of Liquid	20	20	30	20	15	25	30	30
Corrosivity of Liquid	60	60	60	40	50	50	50	60
Freezing Point	0	40	20	40	40	40	40	25
Vapor Pressure	90	90	90	90	90	90	40	90
Gumming	60	60	50	60	0	40	10	30
Flash Point	0	0	15	30	30	30	30	0

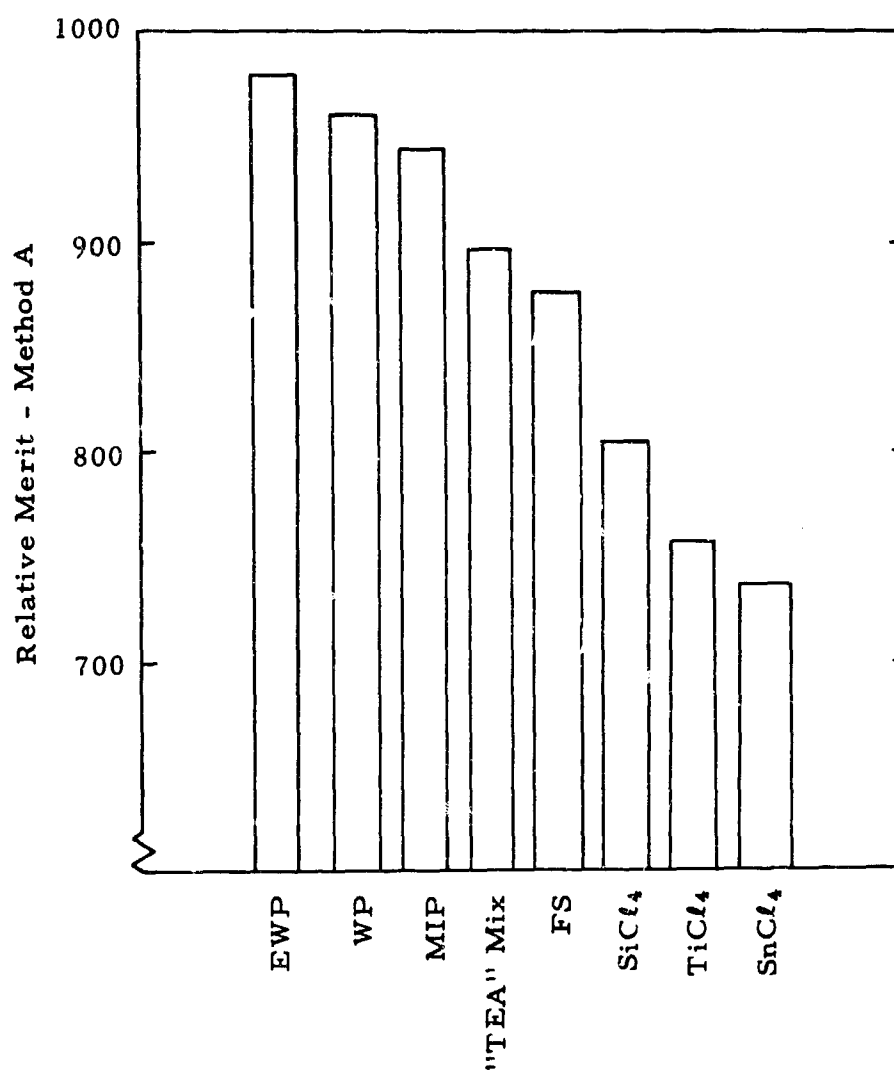


Figure 4. Relative Effectiveness of Various Smoke Agents - Method A

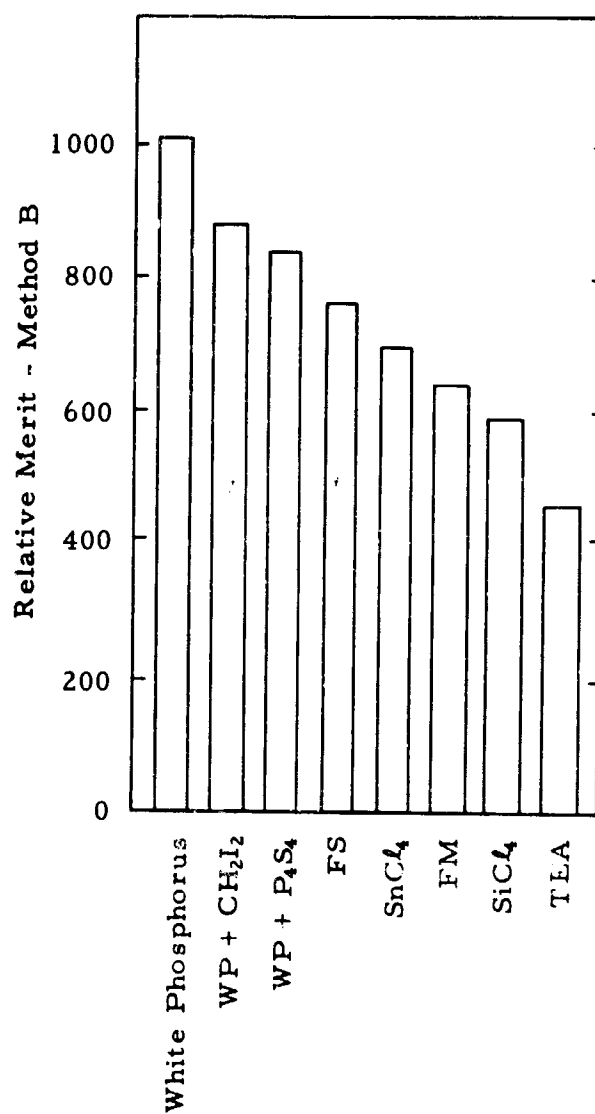


Figure 5. Relative Effectiveness of Various Smoke Agents - Method B

1. Density TOP

The density TOP has been correlated with the smoke producing capability of various smoke agents for use in fixed volume hardware. In our evaluation of the smoke producing capability of selected smoke agents, calculations have been made for possible usage of the E39R1 tank. This tank has a volume of 9 gallons and can be considered as volume limited hardware. A definition of density TOP which has been used in this study is the TOP multiplied by the density of the smoke agent at ambient temperature (70°F). The weight of 310 was assigned to this function for FS as a standard smoke agent based on the assumption that this parameter should be about one third of the total value of the function. In practice this weight makes a high value to density TOP a necessary condition for a high evaluation. To evaluate a given smoke agent the ratio of the Density TOP of the smoke agent to the Density TOP of FS is multiplied by 310. Thus, it is possible to have a weight to this parameter considerably in excess of 310 if the smoke producing capability and density are high. Alternatively, a smoke agent with a high TOP value but low density is given less weight which fact corresponds to the operational requirement that of needing more tankage capacity for a given smoke dispersment operation.

2. Optimum Density

The optimum density is chosen to be 1.35. Any value different from this optimum downgrades the smoke. The function assumed is given by

$$| 1.35 \pm \rho | \times 100.$$

Thus, for example, if a smoke has a value of (1.85) then $(1.35 - 1.85) \times 100 = 50$ points which is subtracted.

3. Toxicity of Smoke

If the established toxicity per eight hour exposure is greater than that contained in thirty cubic meters of a standard smoke, then the agent was not considered. This quantity of smoke agent corresponds roughly to the amount of air inhaled by a person during a 10 hour day assuming an average inhalation of 1.25 liters per breath and forty breaths per minute. In most cases there is not sufficient data to evaluate those factors in detail. For the cases where insufficient data was available a smoke agent was either assumed to have a toxicity which

is directly related to another similar smoke agent, or, the entire point value of 70 points for this character was subtracted. For cases where minimum values are listed, 70 points were given if the smoke produced by the smoke agent was within operating standards.

4. Corrosivity of Smoke

A corrosivity value for the produced smoke was established by evaluating the sum of corrosivities relative to FS in four categories. The categories which were evaluated are; corrosivity to aluminum alloys (30), corrosivity to iron alloys (30), corrosivity to plastic (30), and others (20). It was assumed that a relative rating system using good, moderate, poor is numerically meaningful. For example, FS smoke is rated as poor in the category of iron corrosion. To have a meaningful approach, a rating of moderate is assigned a numerical value of 20. For a smoke which is good in each of these categories, a rating of 30 for each category is possible. For FS smoke a value of forty was assigned. It is apparent that this system is arbitrary but its principle advantage lies in the ability to numerically assign a weighted value to this characteristic.

5. Irritation of Smoke

To allow an evaluation of this factor, a weighting system using High, Moderate, Mild was used with values assigned of 10, 30, 50 respectively.

6. Persistency of Smoke

Meaningful numerical values of smoke persistency are exceedingly difficult to obtain. To allow an evaluation of this characteristic, a system using good, moderate, poor was established with numerical valuation of 80, 50, 20 for each of these categories.

7. Toxicity of Liquid

Many of the liquid smoke agents in current usage are difficult to handle being subject to rapid degradative hydrolysis. For this reason the necessary storing and loading procedures involve the use of remote handling techniques with limited vapor or liquid contact by personnel. A value of 20 was assigned for FS, and it was assumed that for other agents where a substantially different handling procedure would be required that a value between 0 and 30 would be assigned.

8. Corrosivity of the Liquid

The corrosivity of the liquid is important in two situations. The major difficulty is one of logistics. An operational smoke agent must be stored for long periods of time before use. If the liquid directly attacks common metals used in storage drums and attacks similar drums with a plastic insert, as commonly used in chemical shipments, then a value between 0 and 40 was assumed depending on the anticipated handling problems. FS is somewhat difficult to store, but because it is reasonable to use this agent as a basis for comparison, it was assigned a value of 40. A smoke agent substantially better than FS with regard to liquid corrosion is assumed to have a value of 60.

9. Freezing

An operational smoke agent should be suitable for worldwide usage. For most of these agents a heated storage and/or loading system can be developed without extensive problems to operate at 0°F. Therefore, a value of 40 points was assigned to a smoke agent which had a freezing point -40°F or lower and a value of 20 points assigned to those which had a freezing point between 0° and 15°F. If the melting point was greater than 15°F the smoke agent was not considered to be a liquid under normal operating field conditions.

10. Vapor Pressure Ullage Pressure at 130°F

A smoke agent must be able to be stored in a sealed drum at 130°F without danger of rupture. The most common storage vessel is a 55 gallon drum. This type of drum will withstand positive internal pressures of at least 40 pounds above ambient. To evaluate this parameter it is necessary to choose an ullage volume and then to consider the effect on ullage pressure of the volume compression due to liquid expansion, the increase in vapor pressure of the liquid, and the heating effect on the inert pressurant gas. If the combination of these pressures is between forty and fifty pounds above ambient then a value of 40 is assigned, if below forty a value of 90, and, if above fifty, zero. The total value of this category is assigned a value of roughly 1/3 that of the density TOP relative to FS.

11. Gum Formation

One of the common liquid smoke agents is FM. The major reason this agent has not seen greater use is that upon air or water contact there occurs a polymerization of $TiCl_4$ to form a gum. To

date no effective anticlogging agents have been found. Because of the seriousness of this problem in airborne hardware maintenance, a value of 60 points was subtracted for smoke agents which were known to have a severe gum formation.

12. Flash Point

The flash point of a liquid has importance in the aerial dispersment and loading operations. Because of the remote control used in loading FS, it was assumed that a low flash point could be controlled for most smoke agents utilizing similar loading procedures and keep the smoke agents tightly sealed against air contact. The problem of aerial dispersment is of a different kind. In this case a flash-back to the tank and an air-agent explosion could have serious consequences to the flight vehicle. A value of the 30 points was subtracted for all liquids which had flash points less than that of JP-4. The use of this standard was chosen for the reason that JP-4 is routinely dumped from aircraft without difficulty. FS was assigned 30 points.

IV. LABORATORY EVALUATION AND TESTING

Based on results obtained from a review of the literature, described in Section VI, a program was initiated to synthesize specific chemical compounds which should have promise as smoke agents. A review of smoke chemistry indicated that smoke agents based on phosphorus compounds would be the most promising with titanium derivatives a definite possibility. Therefore, emphasis was placed on making select phosphorus and titanium derivatives. Four major approaches were developed relative to phosphorus based smoke agents. The first was concerned with the development of solutions containing WP in selected solvents. The most promising solvents were carbon bisulphide and methylene iodide. The second approach was the stabilization of slurries of WP in solvents in order to increase the solids loading and desired physical properties. A third approach was the synthesis of typical select phosphorus alkyl derivatives. In this latter area primary emphasis was placed on the testing of alkyl derivatives of diphosphine and phosphorus amides. The fourth general method was to develop eutectic mixtures of WP and phosphorus sesquisulfide. A limited synthetic program was performed in the field of alkyl derivatives of titanium tetrachloride. Because of the survey nature of the program, emphasis was placed on obtaining data of a preliminary nature rather than optimized results for the most efficient solutions, mixtures or compounds. The values of TOP reported are therefore, in general, conservative for solutions of WP in methylene iodide and slurries. A description of the work performed during the programs is given in this section. The work reported included results for several standard military smoke agents such as FS, FM and WP. These agents were used to provide a reference base between work performed on this contract and previous literature results and also aided in the development of measuring techniques and equipment.

Laboratory investigations and tests include the development of two test chambers to aid in the systematic evaluation of new chemicals or combination of chemicals and for a number of standard smoke agents. This work had the following objectives: (1) Development of standard testing procedures to be used in screening each potential smoke-producing chemical, and (2) Comparison of potential smoke agents as regards reproducibility of smoke concentration, obscuration characteristics and persistence.

A. Description of Test Chambers

1. Preliminary Observation Chamber

This chamber consists of a rectangular glass container. The unit was utilized in a fume hood located in the laboratory and is shown in Figure 6. The dimensions of the basic glass chamber were 36 inches long, 16 inches high, 12 inches wide with a volume of 4.25 ft.³. The front of the container consists of a wooden panel provided with two glove-box type access holes for simple manipulation of materials within the chamber when desired. It also had three fittings which could be used for introducing the smoke-producing chemical, purging the chamber and exhausting the smoke subsequent to measurement. When making an obscuration measurement, the glass container was covered with an exterior box equipped at one end with a variable light source and at the other end with cadmium sulfide photocell, power supply and meter. With this unit, initial observations and obscuration measurements were made to determine the best dissemination method and whether a particular compound warrants further study. FS was studied in this unit in order to gain additional information on this mixture and to set up standard procedures to be used on subsequent materials. Results from this chamber were used to design the following laboratory test chambers and to perform selected preliminary work.

2. TOP Chamber Modification A

A stainless steel container was modified for use in making TOP measurements. This chamber is capable of withstanding low interior pressures and has dimensions of 31 inches long, 22 inches in diameter and a volume of 6.37 ft.³. It is shown in Figure 7. One end was equipped with a variable-distance light source. This consisted of a stainless steel tube 36 inches long and one-half inch outside diameter which moves through an O-ring sealed bearing. A 40-watt, frosted, light bulb was mounted on the end of the tube with the electrical leads running through a seal down the interior of the tube. The other end of the tank is supplied with an access plate and O-ring seal. A twelve-inch viewing port in the center of the plate allows for visual observation or mounting of a cadmium sulfide photocell. The plate is also provided with lines for addition of a smoke-producing chemical, water or gas purging, drain line and a mixing unit. This unit was used for approximately six months at which time a modification was made to provide better control over the divergence angle from the light source and an intensity readout onto a chart paper recorder. Substantially the same results were obtained for both detector systems.

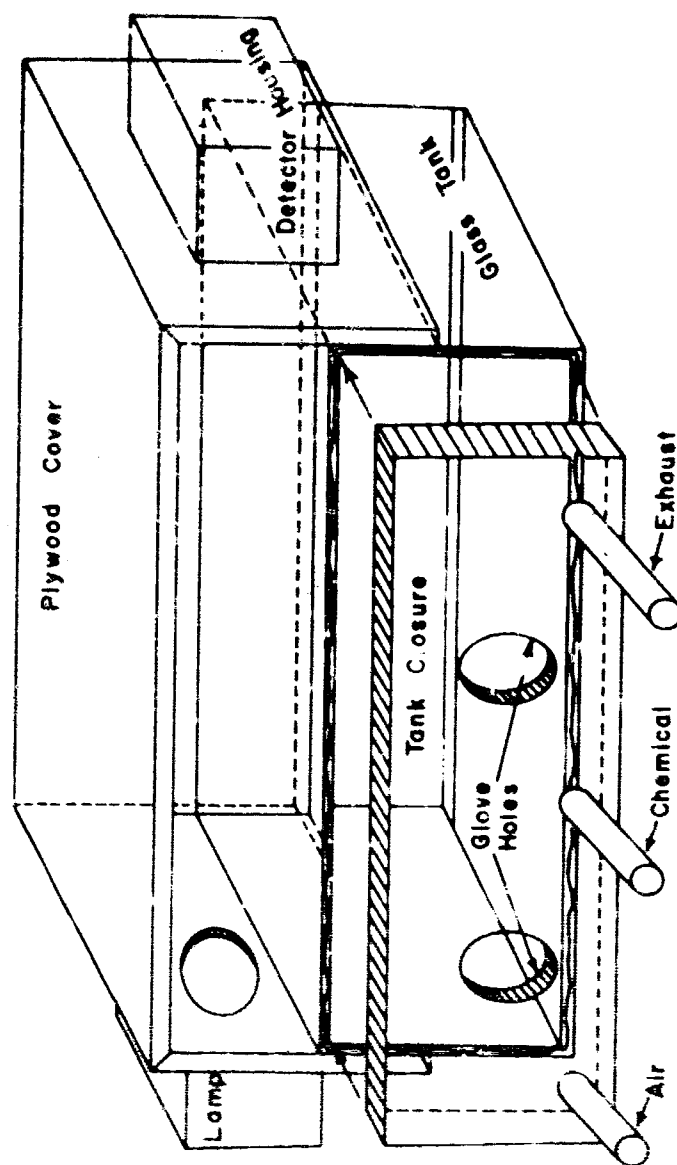


Figure 6. Preliminary Observation Chamber

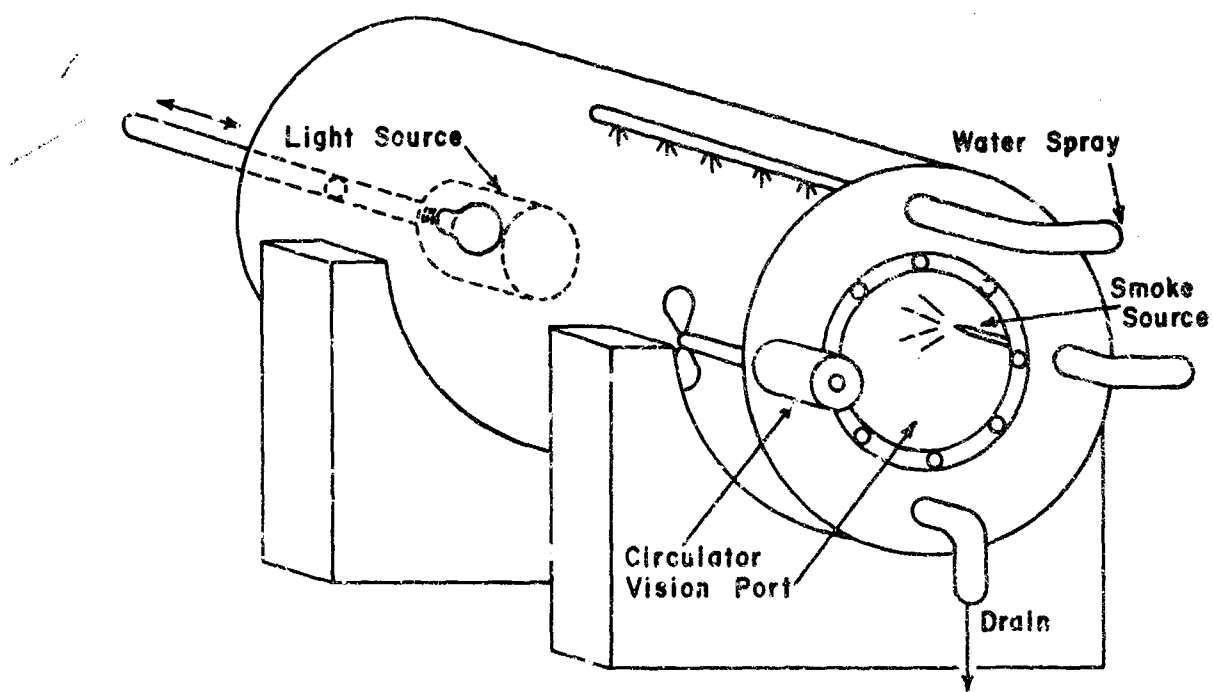
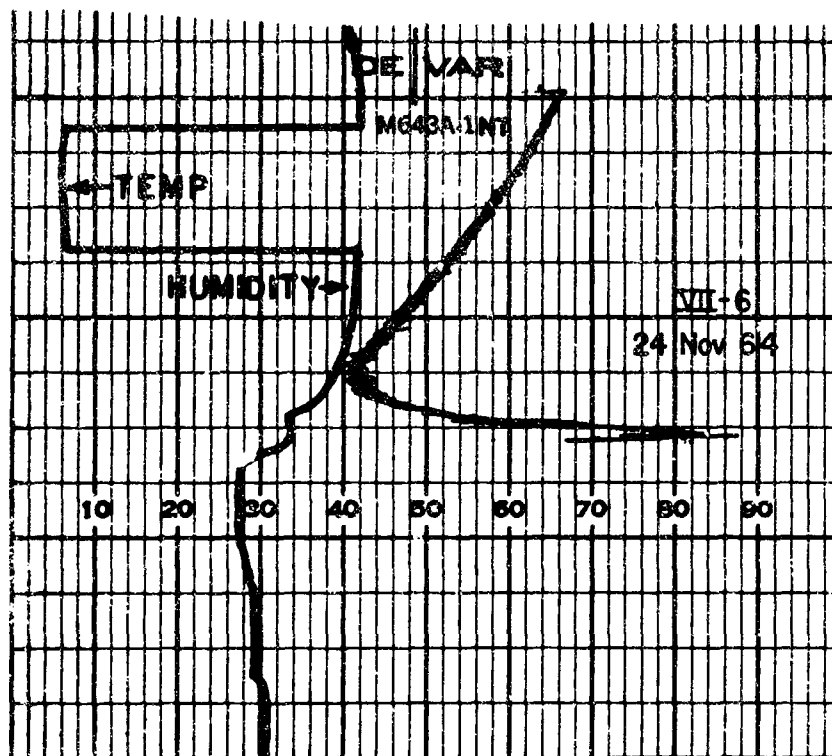


Figure 7. Stainless Steel Laboratory TOP Measurement Chamber

3. TOP Chamber Modification B

Modifications that were made to the stainless steel test chamber consisted of improvements in the light source and related parts, and in the incorporation of a thermocouple to monitor chamber temperatures. The light source was modified to use a 250 watt General Electric photo enlarger No. 213 light bulb. To reduce heat output and increase the stability of the light source this bulb was operated at 70 volts through a Variac backed by a constant voltage transformer. This type of bulb has the marked advantage of an exceedingly uniform light output over the exposed surface. A substantial heat flux was emitted from the lamp source. To reduce this heat to minimum, a stainless steel shield surrounding the light bulb was used to support a closely wound copper tube cooling coil. The coolant used was the available tap water supply in the laboratory. It was observed that the heat absorbed in the path of the light beam was quite noticeable, and therefore, a glass cover-plate was placed over the front end of the cooling coil. This cover consists of a three-inch pyrex watch glass taped to the supporting shield. Using these shields, the heat output of the lamp to the smoke chamber is reduced to a point where it is not possible to detect any significant change by a thermocouple detector placed in the closed chamber over a period of 15-20 minutes. A second modification was to feed the output of the photocell directly into a two pen, two channel recorder. A cadmium sulfide photoresistor with a spectral response close to that of the human eye was used to monitor light intensities. This recorder is used to monitor smoke obscuration and chamber temperature. A thermocouple was placed about two inches above the optical path. This allows a monitoring of changes in chamber temperature with a sensitivity of about one-half degree Centigrade. The entire interior of the smoke chamber was blackened to reduce reflected light and a careful alignment was made of the photocell slits to allow observation of a closely controlled area on the surface of the lamp. Because of the changes in the lamp system, the data previously obtained must be related to the present values by a factor which accounts for the differences in light intensity. The percent transmission versus weight curves for phosphorus have been experimentally rerun and a small correction factor to account for this effect on TOP was experimentally obtained. This laboratory test chamber was adequate for testing the relative values of new smoke agents under simulated static wind conditions.



FM RUN - HIGH HUMIDITY

Figure 8. Typical Output Record for Smoke Chambers

4. TOP Measurements

A critical analysis of the experimental data indicates that the small smoke chamber is capable of producing valid relative TOP (total obscuring power) values.

The theory of a TOP measurement is based on the validity of the form of Beer-Lambert relationship:

$$I = I_0 e^{-\epsilon c l}$$

here:

I is the observed light intensity

I_0 is the initial intensity without smoke

c is a concentration

l is path length

ϵ is the scattering or extinction coefficient

The form of this relationship indicates* that the slope of a plot of $\ln \frac{I}{I_0}$ versus weight concentration would be a means of evaluating the TOP. As long as this slope is linear, the Beer-Lambert relationship is valid and a value for TOP can be obtained with some assurance of significance.

For phosphorus, a linear relation existed for all smoke concentrations. However, for some of the other systems studied, it was apparent that considerable curvature exists at higher concentration. The physical reason for this curvature is not simply derived and is a function of several parameters. The most probable cause for curvature is a decrease in the number of particles per unit volume through collisional coalescence and particle growth. The results for phosphorus indicate that the present apparatus can be used to evaluate the relative smoke producing capability of different smoke agents if the "scattering parameter," is a constant in the region studied. This means that care must be exercised to obtain data only in the region of linearity which can then be extrapolated to a value of $\frac{I}{I_0}$ of approximately 1.25%. The basis for using 1.25% transmission for $\frac{I}{I_0}$ is obtained by reference to psychological studies concerned with the discrimination capability of the human eye.

* See following discussion.

A comment should also be made regarding the TOP values reported in this work. The reported literature TOP value for WP was 4600. This value is defined in terms of the distance at which the extinguishment of a 40 watt light bulb occurs for smokes of known concentration. The relation governing this definition is:

$$\begin{aligned} \text{TOP} &= \frac{1}{(\text{Distance to Obscuration}) (\text{Concentration of Agent})} \\ &= \frac{\text{Cubic feet}}{(\text{Distance to Obscuration}) (\text{lbs.})} \end{aligned}$$

which has dimensions of:

$$\text{TOP} = \frac{\text{ft}^2}{\text{lb}}$$

To provide a relation which does not require a movable light source and to allow use of a small chamber having relatively low concentrations of smoke agents, use was made of Beers Law. Beers Law states that:

$$\frac{I}{I_0} = e^{-cl}$$

where these parameters have been previously defined.

Then,

$$\ln \frac{I}{I_0} = -cl$$

and

$$\frac{1}{-c} \ln \frac{I}{I_0} = l$$

TOP is defined as

$$\text{TOP} = \frac{1}{cl}$$

where l is the distance to obscuration of a 40 watt light bulb and c is concentration of the agent. Clearly,

$$\text{TOP} = -c \ln \frac{I}{I_0}$$

If one observes that the proper value to choose for $\ln \frac{I}{I_0}$ for extinguishment is between 1% and 2%, say 1.25%, corresponding to the sensitivity of the eye to distinguish between a signal and noise, then

$$TOP = (\epsilon) (\ln 0.0125)$$

where ϵ is now given by

$$\epsilon = \frac{\ln \frac{I}{I_0}}{c * l^*}$$

in which c^* is the concentration corresponding to a value of $\frac{I}{I_0}$ of 0.0125 and l^* is the distance of observation. ϵ now is identical to TOP multiplied by $\ln 0.0125$ and a value can be obtained in this manner using low concentrations of smoke agent even though experimental data is not available at total extinguishment. To do this, a plot of $\ln \frac{I}{I_0}$ (minimum

light transmission) is made versus weight of agent used. In general, $\frac{I}{I_0}$

for an actual smoke run is greater than 0.0125 criteria used and an extrapolation of the data to this concentration must be made. Thus, a plot of $\ln \frac{I}{I_0}$ versus weight of agent used allows experimental data for relatively dilute concentrations to be extrapolated to find what concentration (c^*) should be used to correspond to total extinguishment. This is particularly useful for laboratory measurements involving short optical path lengths. This extrapolated value is much more accurate than actual measurements under these conditions. The reason for this is that to attain minimum light transmission values in the region of 1 to 2 percent, very high concentrations of agents must be used. Smokes formed from articles at these high concentrations may have substantially different persistence and scattering characteristics than those at low concentrations. One reason for these differences is caused by increased collisional coalescence. In some of the experimental work reported, pronounced curvature was observed. In these situations, the data was taken only from the straight line portion of the curve.

The $\log \frac{I}{I_0}$ versus concentration is plotted for WP and is extrapolated to a value of transmission of 1.25%. A TOP value is thus obtained which lies between 4500 and 4800 for the small chamber. There were no arbitrary factors in this calculation using a 40 watt bulb. In

latter work in order to increase the degree of reproducibility a 120 volt 250 watt enlarger bulb operated at 70 volts was used. For this setup it was necessary to incorporate a constant multiplicative factor in the calculation in order to back correct to the intensity of a 40 watt light bulb. Based on this analysis our data can be related to the older literature values within 100 TOP units and our experimental accuracy is of about this magnitude.

The values of TOP obtained in this smoke chamber have closely corresponded to the reported literature values for WP but have been significantly lower for FM and for low TOP smoke agents in general. The values of TOP obtained in this research program for FM are approximately 1000-1100. The older literature reports a value of 1860. This is a significant difference and particularly important to a survey type evaluation of new smoke agents if a systematic error exists because of the small size of the DRI apparatus or other effects in our procedures. Support for our smoke values is obtained from a recent report (Mahoney et al.). Figure 9 shows this data for FM, obtained in a smoke chamber, together with data for FM in the DRI laboratory chamber. Within experimental error these two sets of measurements agree. Both sets of measurements were made with either photovoltaic or photo-resistor cells with approximately similar frequency response. A major difference in these experiments is associated with the light source. M, K, & K used a carbon arc lamp whereas the present work has used a commercial photolamp.

Another factor which deserves major consideration in the comparison of these two experiments is the scale on which each was performed. The smoke chamber* experiment was conducted in a quonset building cell which had a volume of about 18,000 cubic feet, whereas the DRI laboratory chamber was on the order of 6.4 cubic feet in volume. The significant difference in volume of smoke tested tends to suggest that the data obtained from each experiment might not correlate too closely due to wall effects, maintaining consistent density of smoke, light intensity in M, K, & K experiment and other inherent factors. Because the data from Picatinny does correlate within experimental error with that obtained at Denver Research Institute, it is believed that this laboratory testing technique is valid.

* Mahoney, Jerry J., Douglas D. Keough, David T. Kilminster, "Thermal Attenuation by Chemical Smokes," U. S. Army Chemical Warfare Laboratories Technical Report, CWLR 2353, January, 1960.

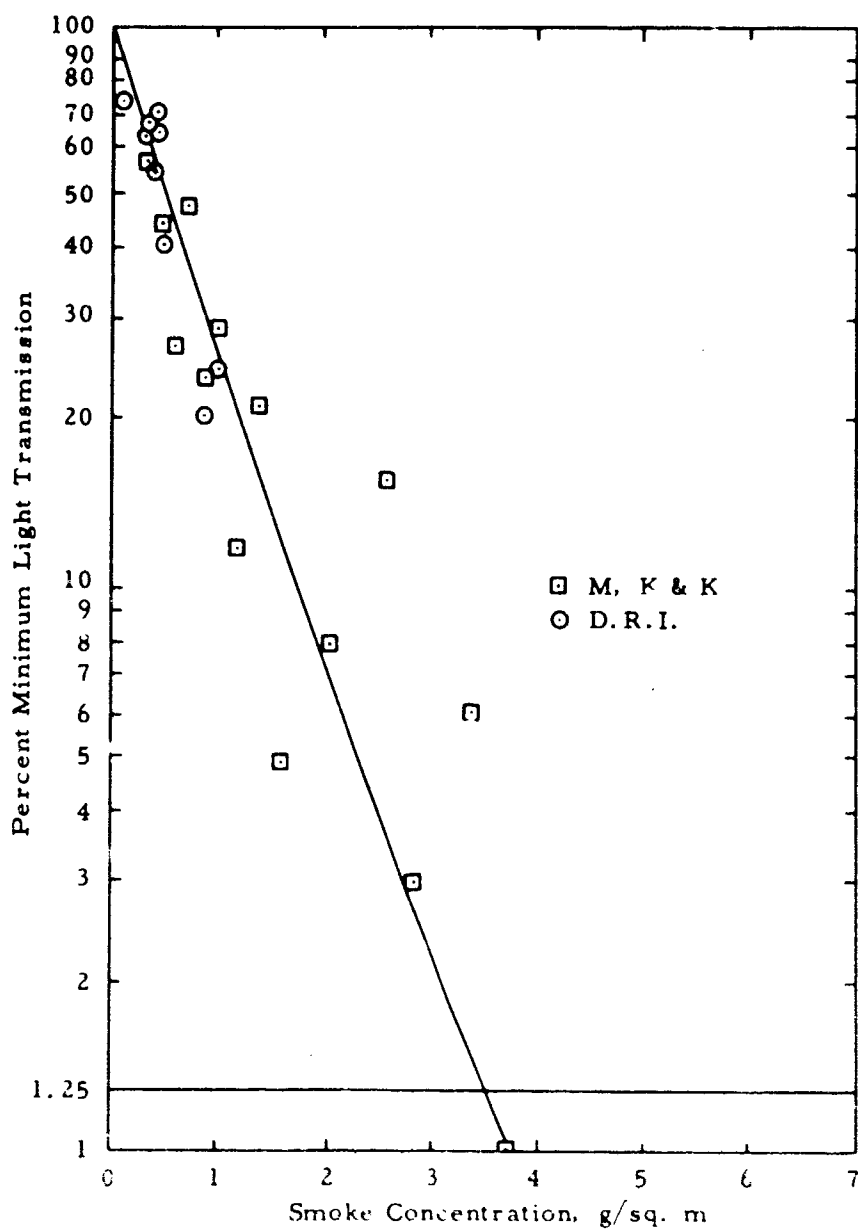


Figure 9. Correlation of 6.4 Cubic Foot Test Chamber Results with 18,000 Cubic Foot Chamber at Picatinny Arsenal for FM Smokes

5. Particle Size Determination

A critical parameter in both the effectiveness and persistency of a smoke agent is the particle size distribution of the smoke particles. In order to determine whether changes in this parameter were occurring as a function of changes in experimental condition, a Cascade impactor was used to determine particle size distribution in conjunction with a high power microscope. A problem in obtaining reproducible results for the standard smoke agents negated some of the early results and extensive use of this technique to characterize the smoke particle size for a wide range of smokes was not pursued. A significant observation was that under certain conditions the TEA Mix 60922T produced a solid Al_2O_3 species.

6. Large Smoke Tunnel Test Facility

A large smoke tunnel was completed and fully instrumented. This tunnel consists of a concrete walled tunnel containing a volume of approximately 2300 cubic feet. The physical dimensions of the smoke tunnel are 6 feet wide, 7 feet high and 54.75 feet long. The tunnel construction, including the ceiling, is of 8 inch reinforced concrete and was originally designed for use as an experimental ordnance test facility. The general layout of the smoke tunnel is presented in Figure 13. An angle iron track which runs full length, was installed to facilitate mobility of the source lamp. The track was leveled to a tolerance of ± 0.1 inch over the 50 foot span, thereby providing for accurate alignment of the source lamp with the photo detector at any desired distance. The source lamp used is designated as a G. E. 4554 Aviation Landing Lamp rated at 500,000 candlepower. The source is installed in a light and smoke tight enclosure which is adjustable in the horizontal and vertical directions in relationship to the carriage base upon which the enclosure is mounted. The opening of the source enclosure is fitted with a photographic diaphragm coupled with a lens system which enables the source to be focused on the detector unit. At a distance of 45 feet, the detector is centered in an intensely illuminated area of approximately 450 square inches. The photo detector unit that was selected is designated as a G. E. A35 cadmium sulfide photoresistor. This unit was selected because its wavelength sensitivity response corresponds closely to the human eye. The detector unit is mounted at the end of a 36 inch aluminum tube which is $1\frac{1}{2}$ inches in diameter and painted a flat black on the interior to minimize reflections which might enter from the smoke tunnel. This detector unit is mounted on a former gun mount in the instrument room at the east end of the tunnel.

(Figure 10). A detailed drawing of the detector unit is presented in (Figure 11). The port, through which the detector unit is sighted, contains a one inch thick plate glass window. The effect of the window upon incident radiation seen by the photoresistor unit is nulled through the instrumentation prior to a test run. A De Var 2 channel recording instrument is used to record the photoresistor output, as well as monitor the internal temperature of the smoke tunnel during a test run. The temperature is read from ten copper copper-constantan thermocouples located at alternately high and low positions throughout the tunnel at equidistant stations as indicated. The tunnel temperature was read immediately prior to a test run. An Abbeon Relative Humidity and Temperature Indicator Model M2A4 was utilized for read out of relative humidity contained in the smoke tunnel prior to each test. Two squirrel-cage type fan units were located in the test tunnel to insure homogeneous mixing of smoke and air in the chamber. These mixing fans are operated throughout the entire test run. A Variac operated tungsten coil was incorporated in the test tunnel for utilization as an ignition system when ignition of the test material was required. After a test run had been completed, the smoke was exhausted by a 36 inch fan located in the west end of the tunnel. The complete interior of the tunnel is painted a flat white (Figure 13).

The amount of energy reaching the detection unit that is produced by reflecting light was found to be negligible in comparison to the energy received from the aligned source. For convenience, a source lamp-detector distance of 45 feet was established as a standard testing distance and the majority of tests have been conducted at this distance. Source lamp voltage was standardized to 25 volts for test runs in order to minimize color temperature effects. It has been found that the effects of color temperature greatly influence the transmission of the emitted light through the smoke screening materials.

Evaluation of a number of potential smoke agents was performed in this large-scale smoke test tunnel.

In comparison to TOP values obtained from agents tested under small chamber conditions, it was noted that in the large chamber, FM yielded values which were numerically 500 TOP points greater than the value obtained from the smaller test chamber B; whereas FS and WP + methylene iodide yield somewhat smaller values in the large scale test. Two effects which are probably important are: (a) a different color temperature characteristic influences the analysis of data taken from these two test situations, as the points in the upper region of the curves tend to support the influence of the color-temperature characteristic of

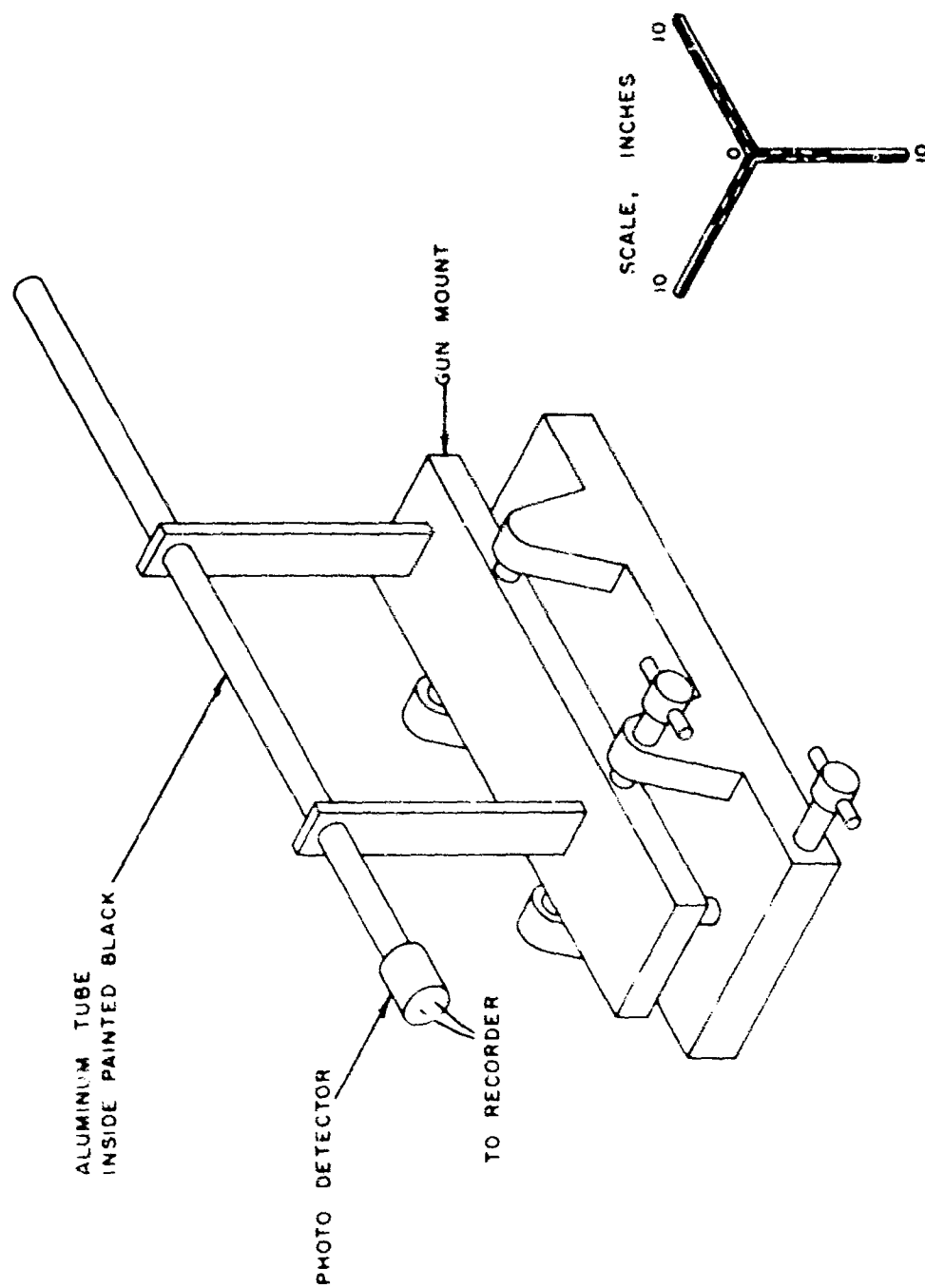


Figure 10. Photo Detector and Mount Assembly

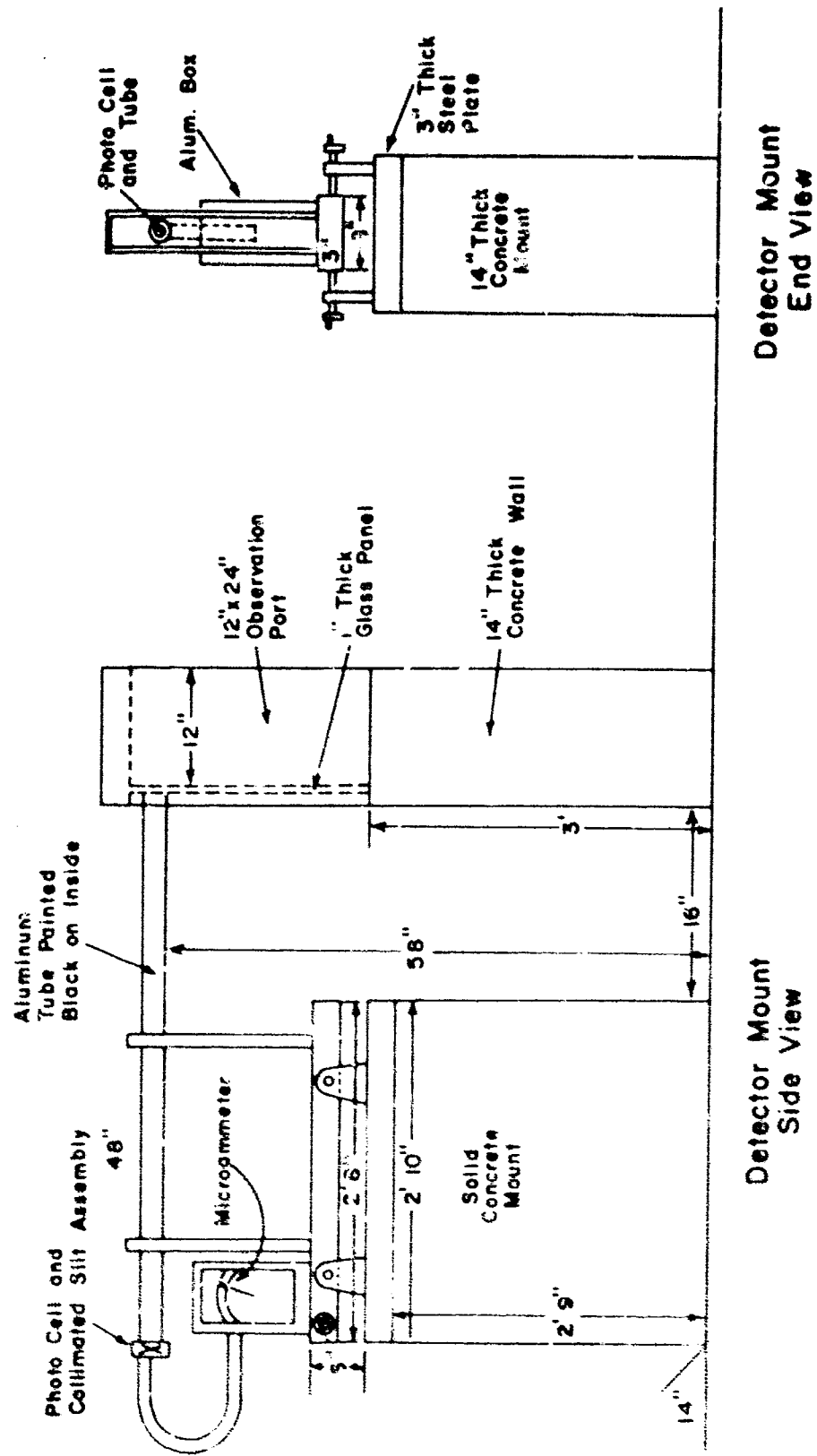


Figure 11. Detailed Views of Photo Detector Assembly

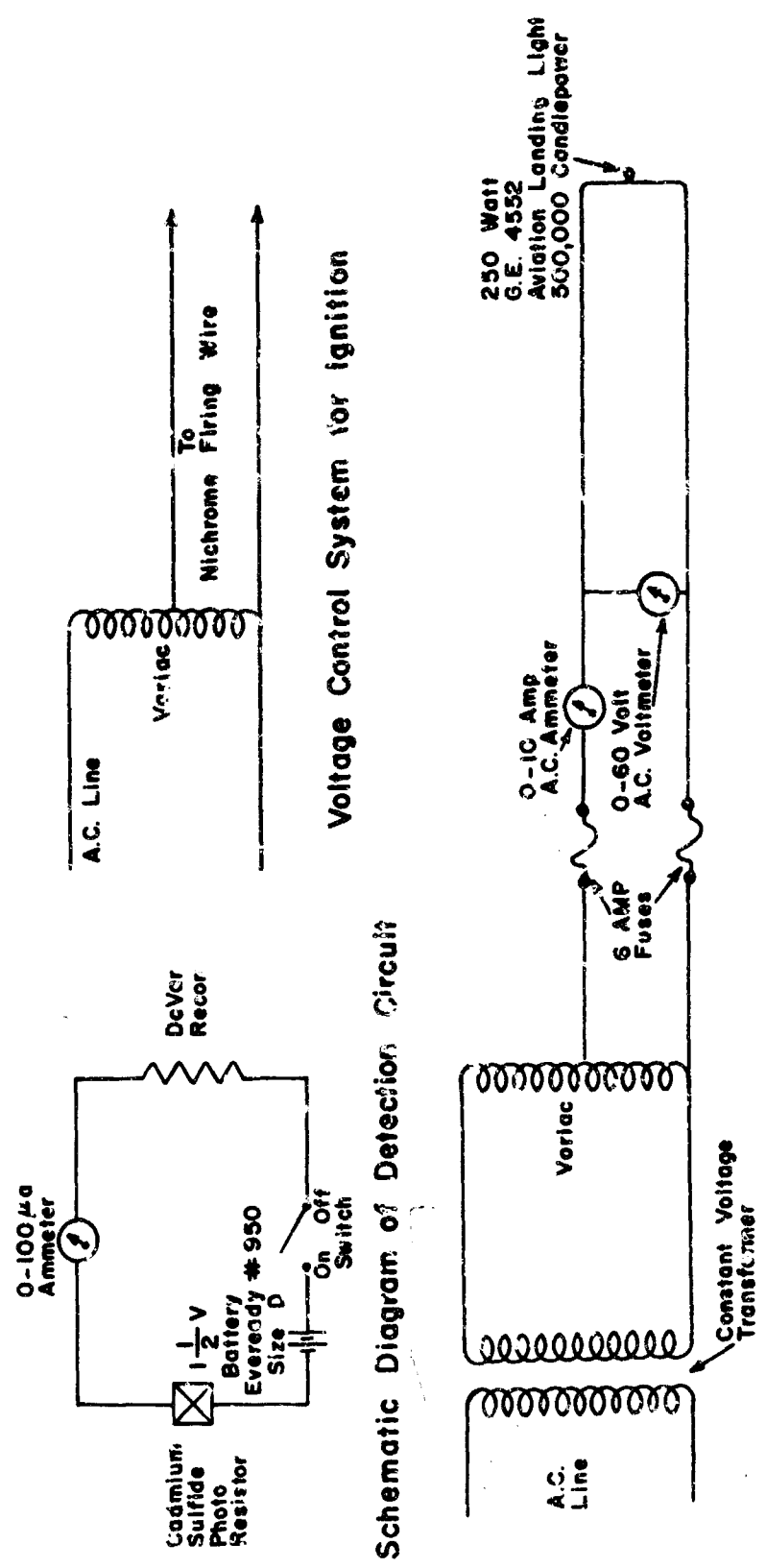


Figure 12. Schematic Diagram of Electrical Circuitry for Smoke Attenuation Tests

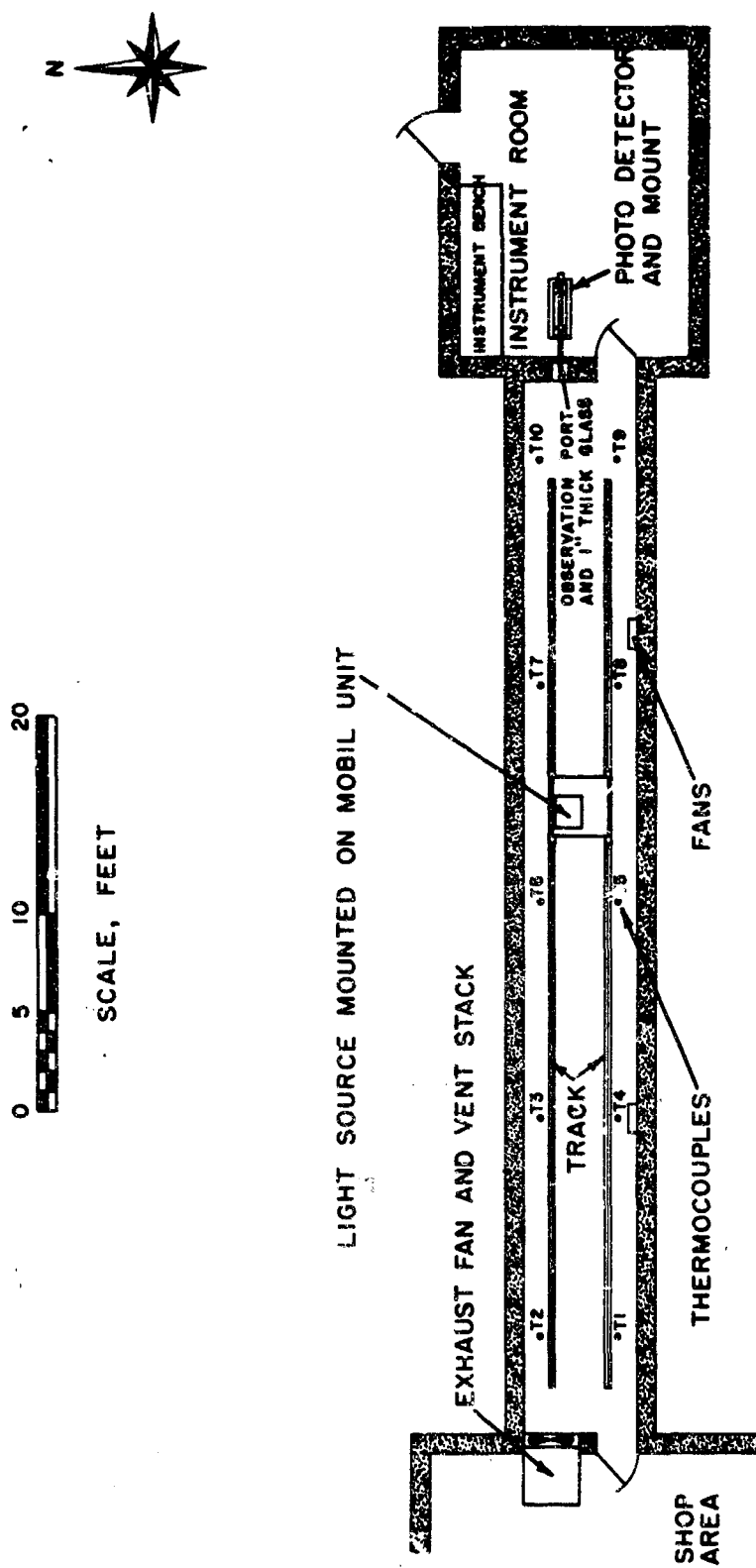


Figure 13. Schematic Diagram of Smoke Tunnel Test Facility

the source, and (b) the effects of humidity conditions which were not fully correlated between the two test setups. Since the small chamber results are substantially in correlation with the large tunnel data, it is believed that the testing techniques employed to obtain the small scale data are satisfactory at least with respect to relative ordering of TOP values and with the results of previous workers.

Similar results occurred in operation of the small test chamber for FS runs as evidenced by a pronounced curvature in the high concentration regions. Since the small chamber results are substantially correlated with the large tunnel data, it is believed that the testing techniques employed to obtain the small scale data are satisfactory at least with respect to relative ordering of TOP values and with the results of previous workers.

7. Discussion of Source Lamp Color Temperature Effects

One of the factors affecting the value of TOP is the influence of source lamp color temperature. An analysis was made of data generated in both the small test chamber and the large scale smoke testing tunnel. Initial investigation of this problem proved to be quite informative. Using the present instrumentation setup incorporating the G. E. A35 photoresistor and the G. E. 4552 Aviation Landing Lamp, a series of runs were made to determine the influence of the color temperature characteristic of the source lamp. The procedure followed was to simply obtain the $\frac{I}{I_0}$ value which evolved as various voltages were applied to the source lamp under no smoke and smoke filled tunnel conditions. See table below:

COLOR TEMPERATURE EFFECTS

<u>Voltage Applied to Source Lamp</u>	<u>I_0</u>	<u>I</u>	<u>$\frac{I}{I_0}$</u>
28.1	100	70	.70
23.8	80	50	.62
20.0	60	33	.55
17.0	40	22	.55
13.7	20	12	.60

It is apparent from the $\frac{I}{I_0}$ values in the chart that the effect of the color temperature of the source lamp significantly influences the resulting TOP value. As an example, the above data for WP could

produce a range of TOP values varying from 4000 to 6000 as a result of the color temperature involved. A possible reason for having higher TOP values could be explained by the fact that the technique currently being used employs a light source of a higher color temperature, therefore a different average wavelength, than the source that was used to establish TOP values found in the literature.

To further evaluate this effect twenty-five additional runs were made in the smoke tunnel using WP as the smoke agent. After the maximum amount of smoke had been generated from each test sample, the light source was stepped down in voltage through five different voltages and the minimum light transmission were recorded. This is the same procedure that was followed previously. These data are documented in Figure 14. It can be seen from the graph that as the concentration of smoke increases, the influence of color temperature becomes increasingly prominent.

8. Obscuration Capability of WP, FS, FM, MIP and EWP Smoke Agents in Large Smoke Tunnel

Several large scale smoke tests were conducted at the smoke tunnel facility. The smoke agents which were evaluated include WP + Methylene Iodide, Eutectic White Phosphorus, WP, FM and FS. Typical data generated by this experimentation are documented in Figures 15 and 16. Figure 15 compares WP and WP + Methylene Iodide to FS and Figure 16 compares EWP and FM to the standard FS. The TOP values are indicated as those obtained from raw data and those which have been normalized. The raw TOP value obtained from the experimental data of WP is somewhat higher than the published value for this material, whereas the TOP for FM and FS is approximately the same as reported values. A possible explanation is that the source lamp used in the DRI testing facility has a substantially different color temperature emission than the lamps used to obtain literature values. A second possibility is that the condition of ambient humidity is substantially lower in our tests. Therefore, the TOP value for WP has been normalized to the more familiar literature value of 4600. To be consistent, the values of other smoke agents are normalized to the established value of WP in a similar manner, and, both "raw TOP" and "normalized TOP" values are presented.

Smoke agents which were tested yielded the following values for total obacuring power:

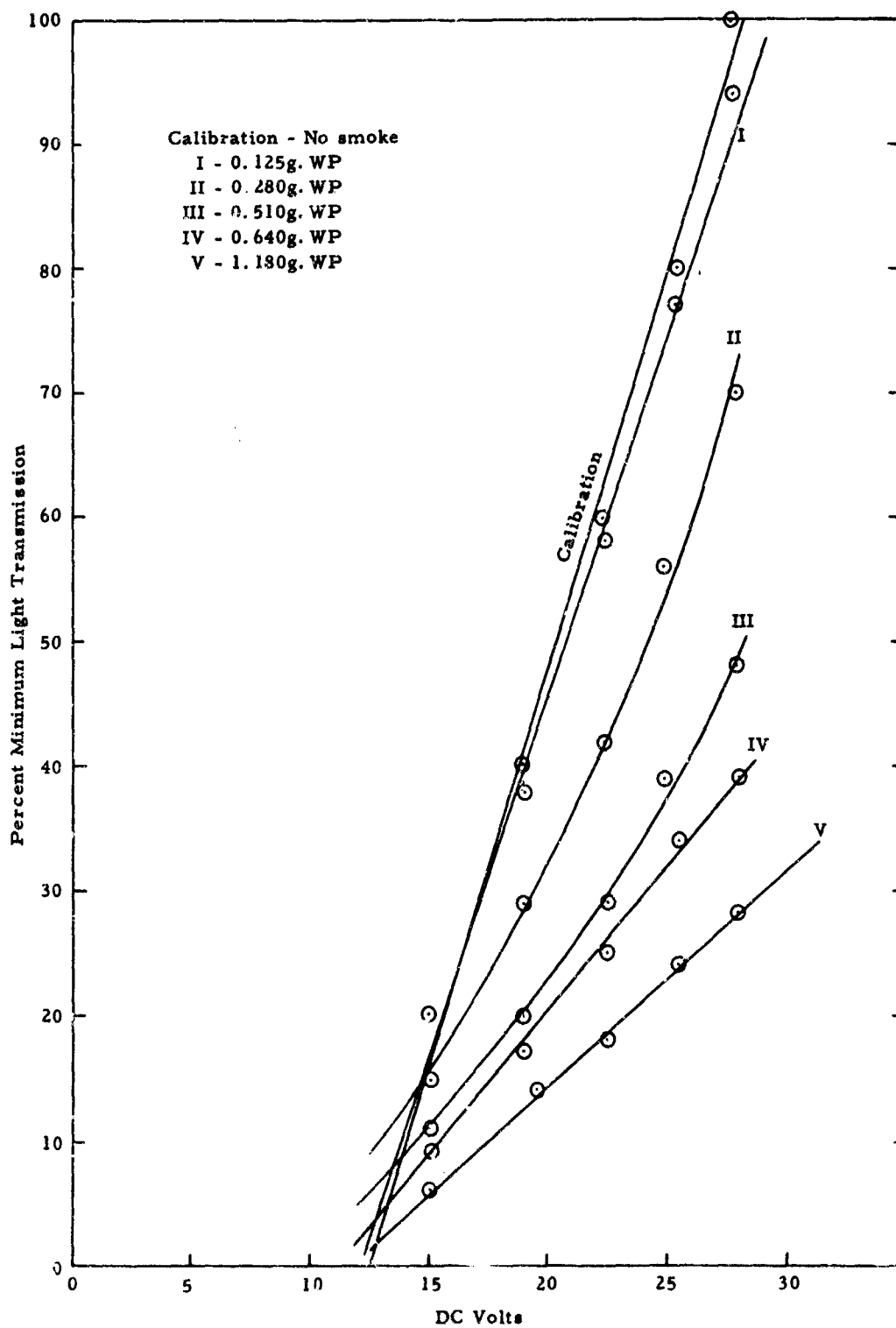


Figure 14. Color Temperature Effects for Tunnel Facility

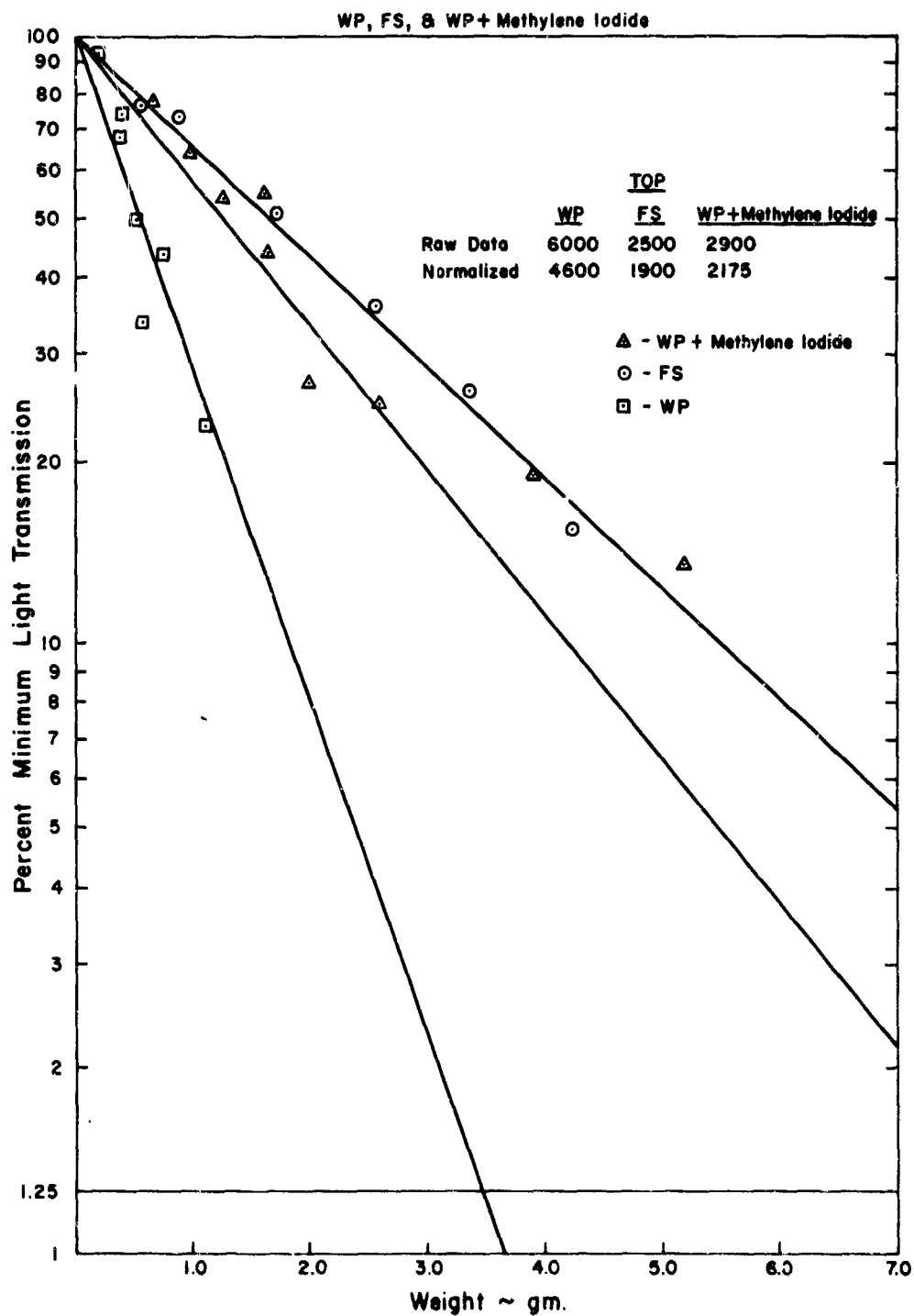


Figure 15. Comparison of WP, FS, and WP + Methylene Iodide Smokes

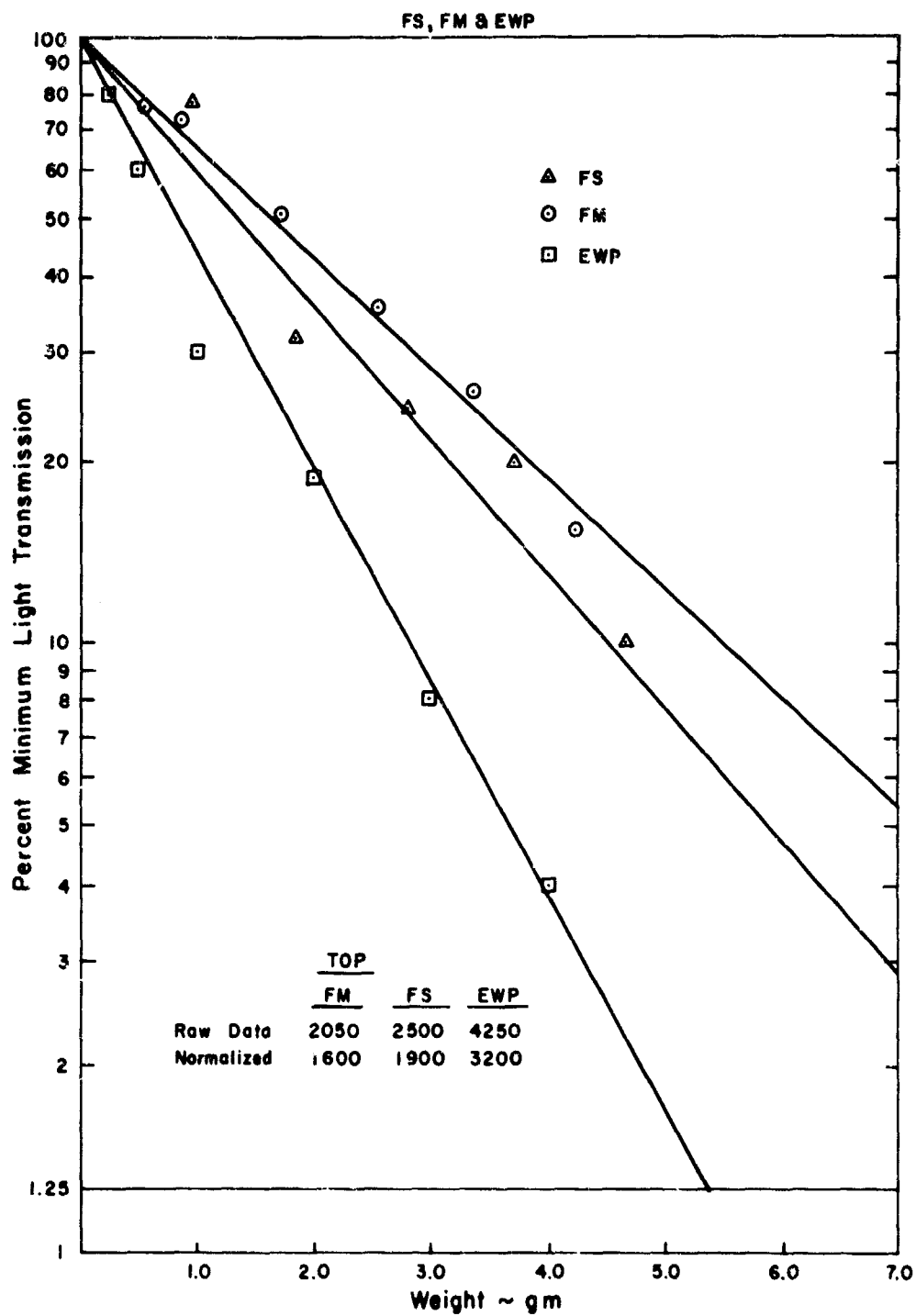


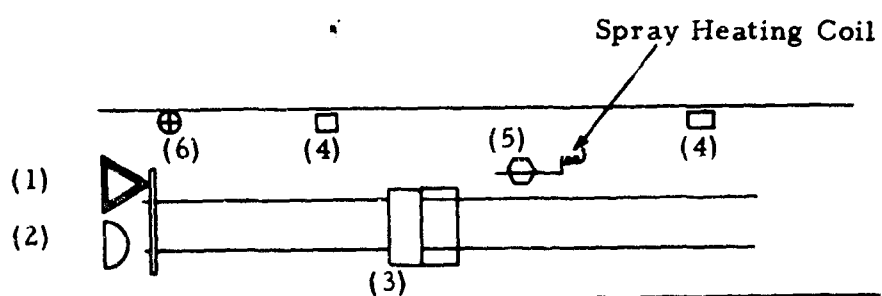
Figure 16. Comparison of FM, EWP and FS Smokes

<u>Smoke Agent</u>	<u>Raw</u>	<u>TOP Literature</u>	<u>Normalized to (WP = 4600)</u>
1. WP	6000	4800	4600
2. EWP	4250		3200
3. WP + Methylene Iodide	2900		2175
4. FS	2500	2500	1900
5. FM	2050	1900	1600

9. Light Reflectance Smoke Tunnel Test Facilities

An alternate technique for evaluating the relative obscuration power of smokes was developed. The method is similar to that used by early workers in the field and consists of determining the distance at which a black-white interface becomes indistinguishable when it is lighted from a point close to the observers location. A schematic diagram of the experimental arrangement is given in Figure 17. The work was performed in the large smoke tunnel using the optical cart and track assembly described previously. An electronic null photodetector circuit was developed in which two optical sensing systems similar to those used in light attenuation studies were focused onto separate black and white placards.

A bridge circuit was used to null the photodetectors. In practice, the procedure was to focus the optical sensors onto two identical white placards at several distances and balance the circuit to a null condition. One of the cards was then replaced by a flat black panel. A measured quantity of smoke agent was inserted into a dish on a hot plate or other vaporization device. Circulation mixing fans were turned on until a uniform smoke mixture was obtained. The cart was pulled forward until the photodetector indicated a signal and the distance noted. Similar experiments were performed using technical workers as observers with similar results achieved. A series of runs made using the reflected light technique are documented in Table IV. Relative obscuration capabilities are documented on both a weight and volume basis. These values are consistent with the results of light attenuation previously reported in terms of the relative effectiveness of smoke agents. For example, if the literature value of 2500 is taken for FS, the TOP of FM is 1830, Methylene Iodide-White Phosphorus mixture 1960 and Ethyl Corporation - Fog Oil Mix 90622T is 425. These values correlate with those previously reported for use with the large smoke tunnel and the laboratory smoke chamber. On a volume basis, a volume of two-and-one-half ($2\frac{1}{2}$) ml of FS is equivalent to thirty (30) ml of the Ethyl TEA Mixture, an order of magnitude differential. These



- (1) Observer or Null Circuit Photodetector Unit
- (2) Light Illuminating Target
- (3) Movable Black-White Targets
- (4) Circulation Fans
- (5) Dissemination Apparatus
- (6) Humidity - Temperature Detector

Figure 17. Schematic Diagram for Obscuration Measurements by Reflected Light

TABLE IV
RESULTS OF REFLECTANCE OBSCURATION TESTS

A. Results of Reflectance Obscuration Tests

<u>Smoke Material</u>	<u>Amount Used</u>	<u>Specific Weight</u>	<u>Distance to Total Obscuration</u>
FS	2.5 cc	1.89 gr/cc	26'
MIP*	2.5 cc	2.37 gr/cc	25' 6"
EWP**	2.5 cc	2.09 gr/cc	15'
FM	2.5 cc	1.86 gr/cc	35' 6"
Ethyl TEA	30.0 cc	.905 gr/cc	24' 6"

B. Relative Effectiveness (FS = 2500)

<u>Weight Basis</u>		<u>Volumetric Basis</u>		<u>Normalized TOP(FS-2500)</u>
EWP**	1.500	EWP	1.77	3750
FS	1.000	MIP	1.04	2500
MIP*	0.784	FS	1.00	1960
FM	0.731	FM	0.75	1830
TEA Mix	0.170	TEA Mix	0.09	425

* Methylene Iodide-White Phosphorus Mix (Sixty-six percent white phosphorus by weight)

** Phosphorus Sesquisulfide-White Phosphorus Eutectic (Sixty percent white phosphorus by weight)

tests provided an independent measurement of the obscuration of effectiveness of smoke agents which more nearly simulate field operational conditions and support the technical procedures previously employed.

B. Documentation of Smoke Agents

Using the facilities described in the previous section, a series of evaluatory tests were performed. The objectives of these tests were; (1) to confirm the literature values for standard smoke agents in order to provide a standard reference basis; and (2) to document smoke values for a number of possible smoke agents for which data was not available in the literature. Some of these tests have been discussed in the preceding section and reference to this data should be made where appropriate (FM, FS, WP, MIP and EWP). The tests performed concentrated on two principle factors, TOP and corrosion. Emphasis on TOP was necessary in order to identify the classes of compounds which are potential smoke agents. The point of view was that if a class of chemical compounds has intrinsic smoke value then further work to develop specific agents may be warranted. Because of the large number of possible candidates, it was not possible to consider all agents, or mixtures thereof, and therefore, much systematic work remains to be performed in this field. Where a class of chemical smoke agents appeared to have promise, further work was carried out to determine corrosion effects of these agents on common materials and to provide a rough characterization of physical properties where necessary. The work reported is divided into six categories. A discussion of each follows.

1. FS and FS + Ammonia

Studies using FS were performed to provide a standard reference. Since the addition of ammonia to an FS smoke would substantially reduce problems of corrosion and irritation, studies using a dual FS-NH₃ were implemented. A discussion of the results for these tests follows.

a. FS Smoke Agent Studies

Using an evaporative method, transmission versus time readings were taken using several different concentrations of FS. Measurements were taken on different days with a probable variance in humidity (not recorded). This relationship is shown in Figure 19. An attempt was

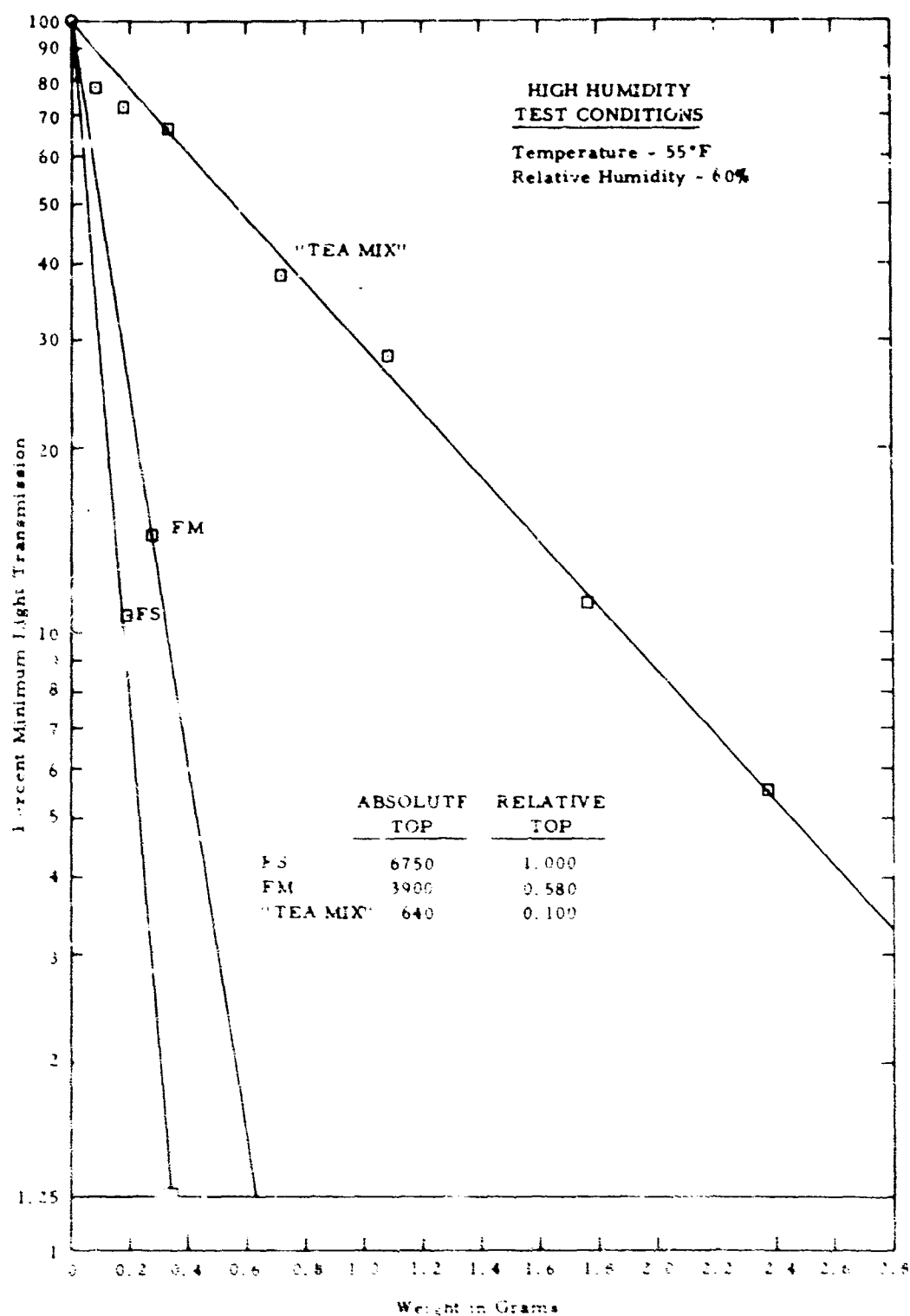


Figure 18. High Humidity Test Condition for FS, FM and TEA Mix

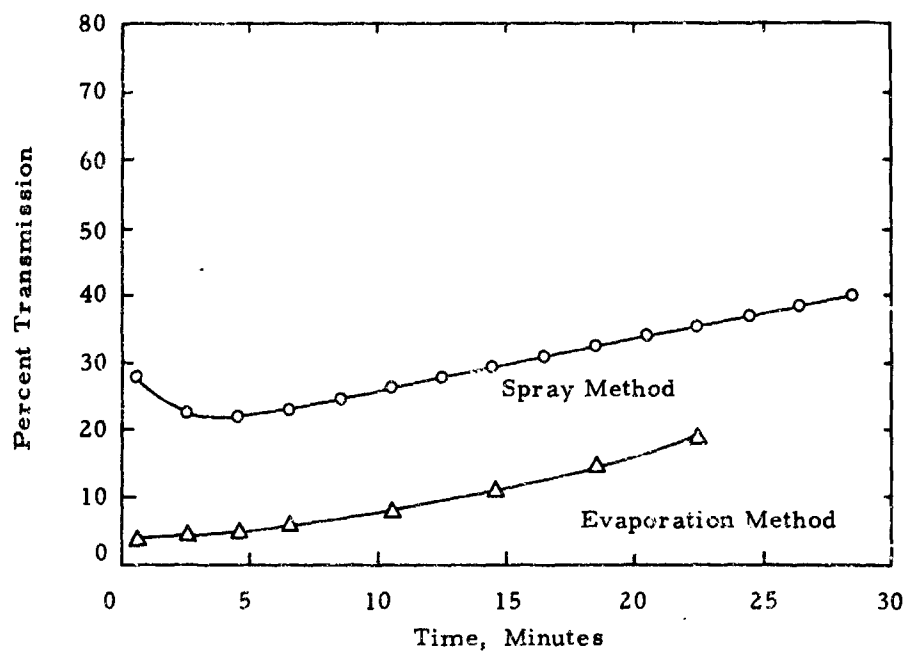


Figure 19. Percent Transmission vs. Time for Spray and Evaporative Dissemination Techniques Using FS

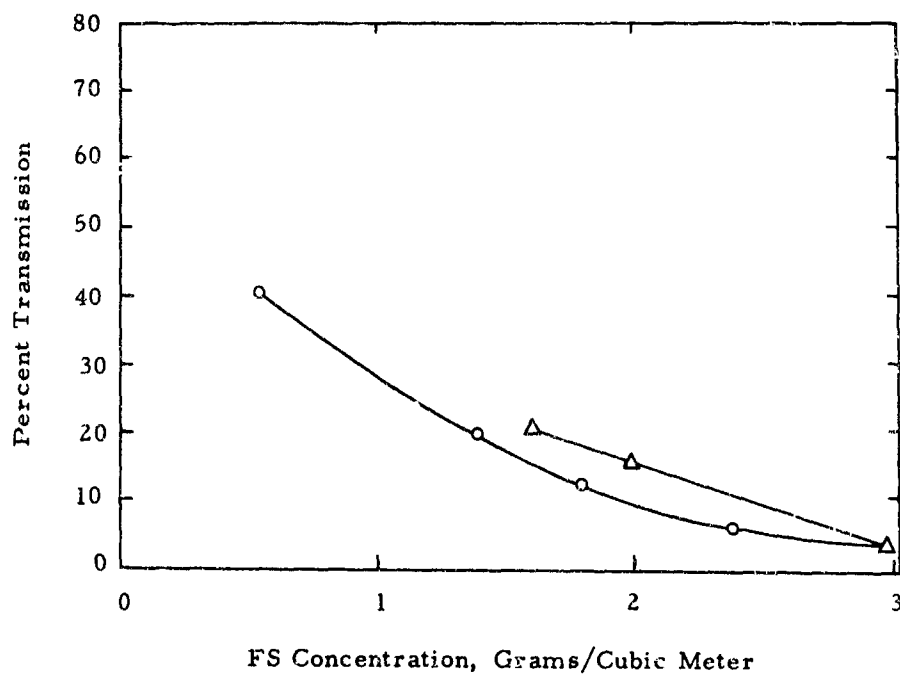


Figure 20. Percent Transmission vs. Concentration for FS - (Model A Laboratory Chamber)

made to obtain transmission-humidity correlations; however, considerable difficulty was encountered. Figure 19 shows transmission-time curves for two different injection techniques. TOP measurements in the large smoke tunnel are reported in other sections. Figure 21 shows transmission-time curves for three different humidity conditions in the small chamber (A). It should be noted that there are initial humidity conditions and that no completely satisfactory method was found to provide a constant humidity environment. Studies were made of the corrosive character of FS on selected materials and are described at length in the corrosion section. In general, the data obtained was similar to that available in the literature and reference is made thereto. Throughout the program FS was used to provide a reference standard for comparison. FS drop tests were made using the air drop test facility and were documented on film. The combination of corrosivity, handling and irritation factors made FS much more difficult to test than any of the other agents used in large quantities.

b. FS-NH₃ Mixtures

One possible method for improving the corrosive smoke produced by FS is to neutralize the sulphuric acid with a weak base. To evaluate the smoke characteristics of the FS-NH₃ system, a series of "TOP" measurements and corrosion tests were performed. The work consists of detailed white light transmission curves and photographs of Aluminum, Magnesium and Steel metal slabs. It was found that the FS-NH₃ smoke had a weight-transmission curve which closely matched that of unmodified FS. However, marked improvements were observed in persistency and the corrosive characteristics of the smoke. Figures 22 and 23 show the minimum percent transmission versus time and weight percent of NH₃ for this system. Three different concentrations of ammonia were used while the amount of FS was held constant. Known amounts of ammonia were introduced to the chamber from a calibrated gas sampling bottle. This involved evacuation of the bottle and filling with ammonia to a known pressure, then diluting with air. Additional air was used to force the contents into the chamber. There appeared to be a marked difference in the quality of the resulting smoke and the persistence was improved considerably.

The lowest percent transmission corresponds to the weight required to reach the neutralization point of the acid base system. The NH₃-FS system has considerable advantages in terms of corrosivity but would require the use of multiple tanks and a mixing system for airborne dissemination.

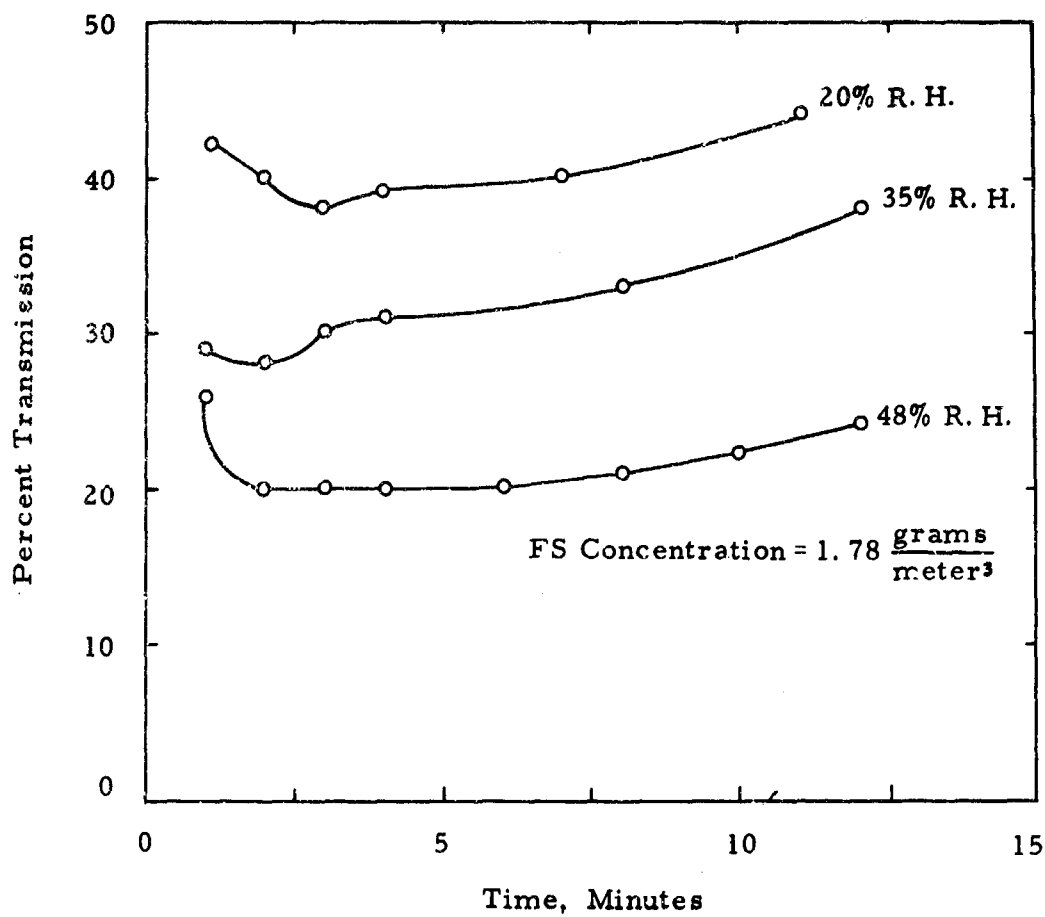


Figure 21. Comparison of FS Smoke Runs at Selected Relative Humidity Conditions

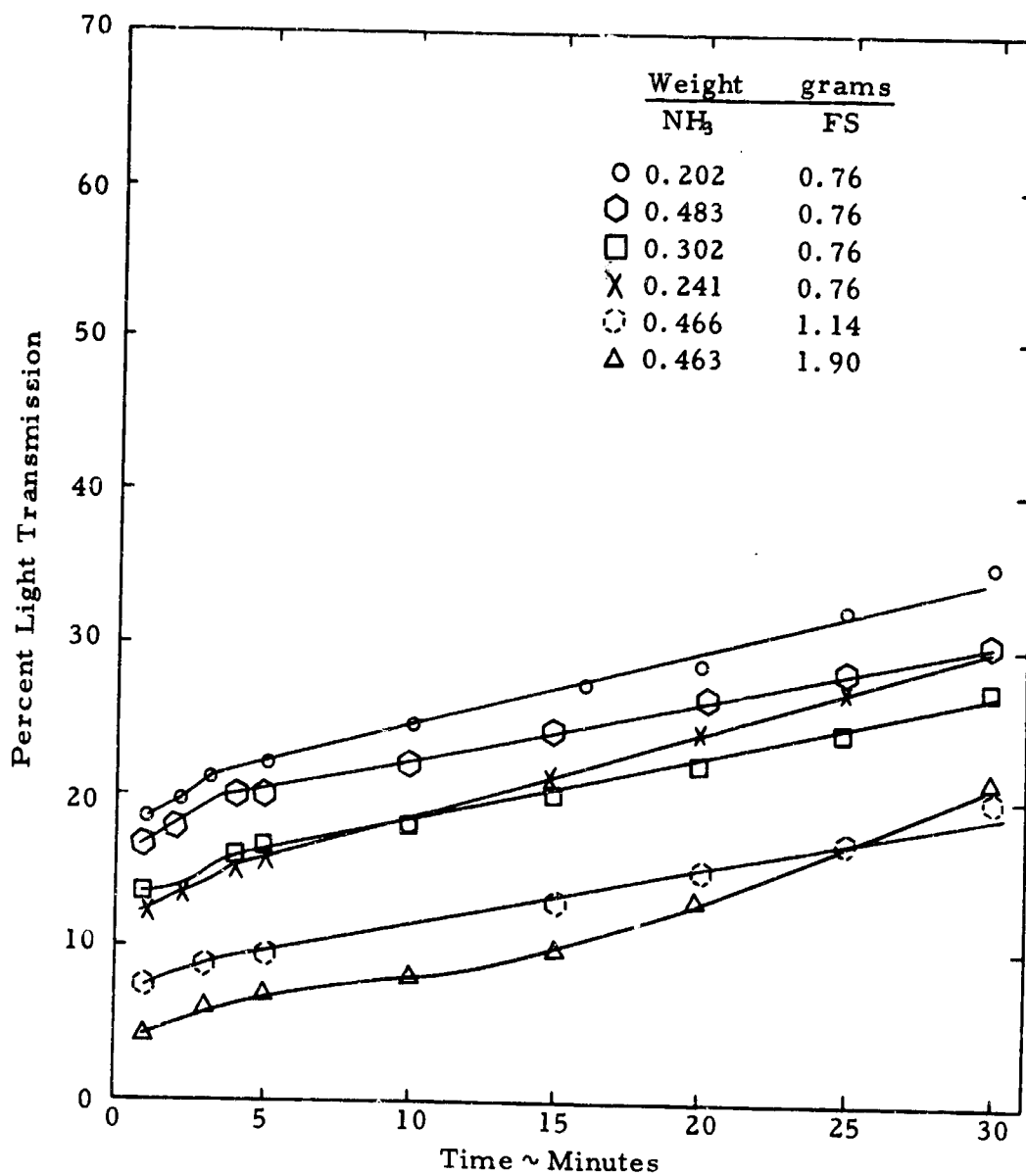


Figure 22. Minimum Percent Light Transmission vs. Time for Ammonia-FS Smoke Mixture

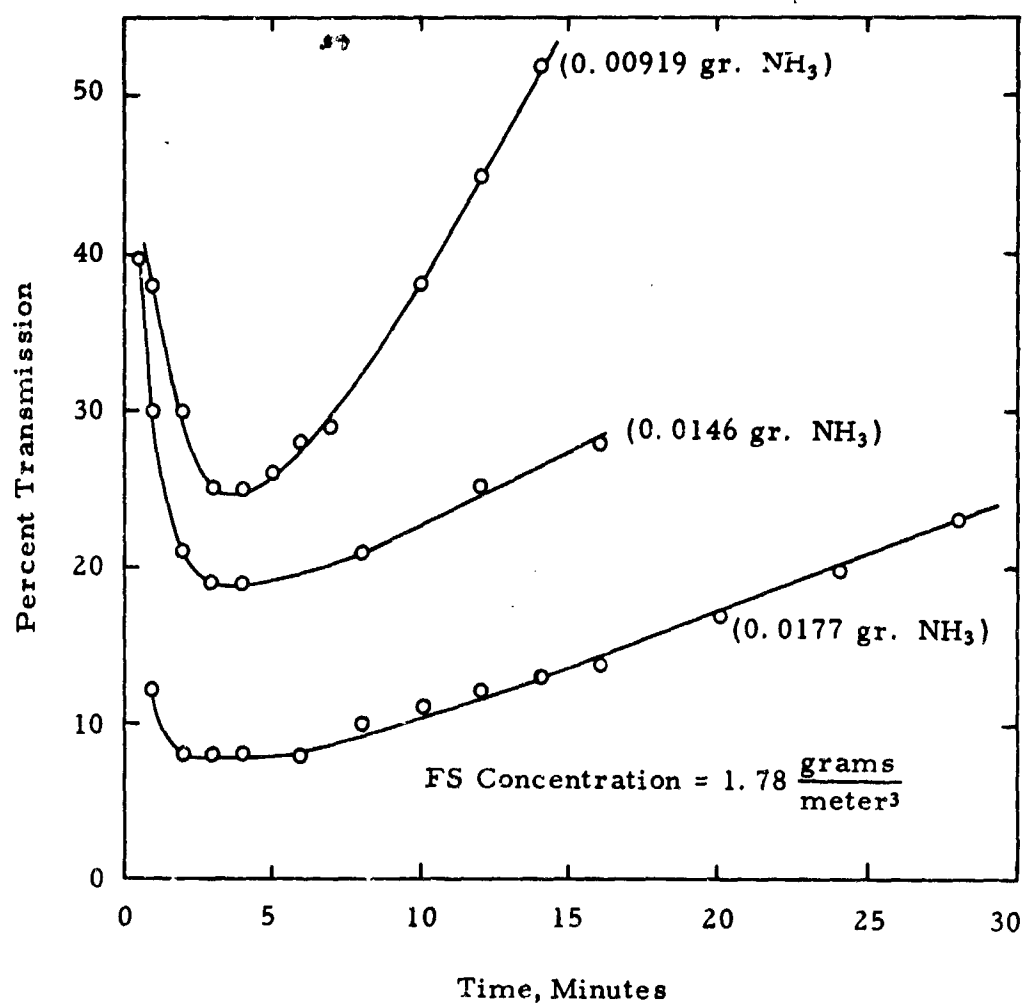


Figure 23. Percent Transmission vs. Time for FS-Ammonia Mixture

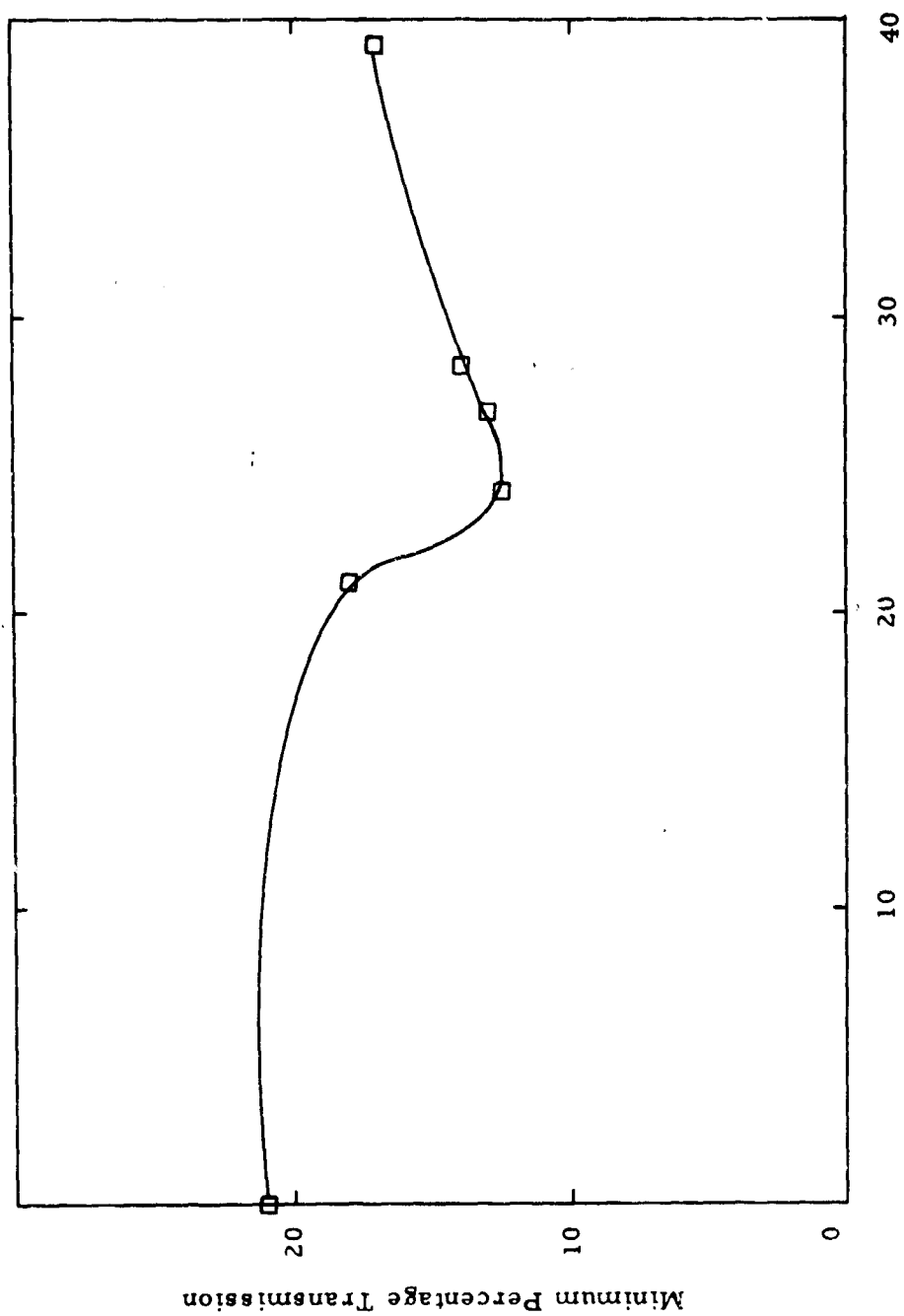


Figure 24. Effect of Ammonia Concentration on Obscuring Power of FS

For a dual smoke agent of this type a number of tankage problems arise. Because of the incompatibility of ammonia and FS the agents would necessarily be carried separately. In a dispersement run, it is probable that a manifold system could be used to ensure partial mixing of the agents immediately aft of the vehicle. However, this would require either conjugate tankage or a manifold system. A possible simple technique would be a spray of ammonia into a normally dispersing FS smoke at the altitude of flight. In this case a systematic study of the dispersement of a mixed aerosol would be necessary to properly design an efficient mixing system.

In addition, it is possible that an arrangement similar to that presently used involving aluminum hemispheres could be used directly. If this were possible, aluminum hemispheres containing ammonia which would be released at ground level would probably diffuse upward through a standard FS smoke with a resultant neutralization and corrosion reduction. If the smoke screen was to be set for a relatively long time, this technique could be rather easily implemented using existing tankage for FS and using similar tankage for ammonia on either the same or following dispersement run. Although specific design studies on the requirements for an ammonia airborne tankage system have not been performed, it is expected that these major changes would involve (1) a stronger reinforcement of the rib structure, (2) component changes in the gaskets and exposed parts, and (3) a separate fill system for ammonia smoke agent loading.

2. Metal Chloride Smokes

The hydrolysis reaction of a metal chloride forms the basis for a number of standard chemical smoke agents. A series of tests were performed to evaluate these agents. These tests are outlined in the following sections.

a. Titanium Tetrachloride - FM

Tests were performed in the laboratory smoke chamber evaluating the obscuration power of titanium tetrachloride. The value obtained (1200) is considerably lower than that reported in the literature (1900). Some of these tests were performed in a chamber in which the chamber walls were lined with water soaked cotton batting. No significant difference due to the change in relative humidity was found. Because of severe plugging in our fog nozzles, it was necessary to go to an evaporative dissemination technique. It may be that the low values

of TOP are caused by this mode of dissemination. Results obtained in the large chamber correlated well with the results in the literature reports. A discussion of these results has been given in previous sections. A brief experimental program was undertaken to determine whether a mixture of phosphorus in carbon disulfide would reduce the gumming which is present in FM handling. The basis for this work was a patent granted to A. J. Ritchie, U. S. P. 2, 407, 384 (1946). Preliminary results indicate that this mixture does result in a small reduction in gum formation. The chemical mechanism which is assumed operative for this agent is that of an internal desiccant action of phosphorus.

As far as can be determined, there are apparently no detailed gas phase investigations concerning the mechanism of these reactions and precisely which of the above postulated intermediates are effective is not known. For this reason, the hypothesis is generally made that the produced smoke consists of particles which are primarily mixed hydroxychlorides, hydrated titanium oxide in rough accordance with the above reaction series. It should be noted that the basis for postulating this reaction series is the assumption that the gas phase hydrolysis duplicates the known solution chemistry. However, even though the above intermediates have been isolated from solution, important differences in the fundamental mechanism of hydrolysis would not be unexpected in view of the change in phase.

An understanding of the mechanistic details of the gas phase reaction would be useful in evaluating possible changes to the TiCl_4 smoke agent. If, for example, the hydrolysis reactions do not go to completion it would be expected that changes in the molecular structure which result in an overall lower molecular weight would result in a more efficient smoke agent. One method of reducing the weight in this manner is to replace a chlorine atom which would not be important in the hydrolysis reactions with lighter alkyl groups. Assuming other reactions are unchanged, the percentage gain in TOP would be predicted to be that which corresponds to the percent weight reduction in the smoke agent. Thus, replacement of one chlorine atom would result in ten percent improvement in TOP, and replacement of two chlorine atoms in about twenty percent. Assuming that the TOP of FM is 1900, a smoke agent consisting of dimethyl dichloro titanium would be expected to yield a TOP value of approximately 2300. (The laboratory synthesis of a methylated TiCl_4 molecule is described in the discussion of metal alkyl derivatives together with experimental smoke evaluation of TDP.)

The above argument is based on the hypothesis that the effective smoke producing reactions in the hydrolysis of titanium tetrachloride do not proceed to completion. The evidence for this hypothesis is (1) that the reactions in the gas phase are expected to be different from those observed in solution chemistry for the reason that from a collision probability basis, TiCl_4 molecules will encounter water molecules on a relatively infrequent basis. The mechanism of solution hydrolysis can be expected to be modified in favor of the initial formation of a lower hydrate, for example, $\text{TiCl}_4 \cdot 2\text{H}_2\text{O}$ which will then proceed via a first order disproportionation reaction to form $\text{TiCl}_2(\text{OH})_2$ and hydrochloric acid. In the gas phase, recent spectroscopic studies indicate that this intermediate has a half-life of two hours. Additional evidence for supporting this hypothesis is that similar solution reactions using an alcoholysis rather than hydrolysis do not readily proceed past the $\text{Ti}(\text{OCH}_3)_3\text{Cl}$ intermediate. Also, the gums produced by moisture contact with FM have been reported to be in part $\text{Ti}(\text{OH})_2\text{Cl}_2$. This latter situation corresponds to a water limited condition similar to that of atmospheric gas phase hydrolysis.

The above arguments tend to support the thesis that improved smoke agents based on the hydrolysis of a modified FM system may be developed. Specific agents of interest are trimethyl titanium chloride, dimethyl titanium dichloride and methyl titanium trichloride. As has been stated previously, the analogues of these agents in other chemical families, eg., silicon and tin should also be considered.

b. Silicon Tetrachloride

It is reported in the literature that silicon tetrachloride smoke produces a TOP of approximately 1500. An investigation was carried out to verify this value. The approach taken was to place a small quantity of SiCl_4 in a large test tube and stop it with water soaked, loose glass wool. The test tube was then placed in a beaker of boiling water, and the SiCl_4 was allowed to vaporize. The SiCl_4 vapor passed through the wet glass wool and escaped. This arrangement is believed to roughly simulate the situation where SiCl_4 was introduced into the smoke stack of warships to produce smoke. The result of this experiment was negative, with little smoke produced. Further search of the literature revealed that probably NH_3 was introduced simultaneously with the SiCl_4 . This fact was not apparent from the tables as published in the literature.

c. Tin Tetrachloride, and Germanium Tetrachloride

Other compounds tested for their smoke producing capabilities were tin tetrachloride and germanium tetrachloride. Tin tetrachloride was investigated using the standard testing procedure. Data resulting from these tests yielded a TOP value of 200 and are documented in Figure 25. The investigation of germanium tetrachloride was quite brief as an ignition problem existed. After utilization of several ignition techniques, the same negative result occurred and no smoke was produced.

d. Antimony Pentachloride

Antimony chloride was suggested as a possible smoke candidate. An antimony pentachloride was tested and experimental results indicate a TOP value of 220.

e. Chromous Chloride

CrCl_3 was evaluated. By itself the agent produced no smoke. A combination of a dual agent using tetrahexyl silane and chromous chloride produced copious quantities of smoke. No TOP values were taken but visual observations would indicate a TOP of the order of 1200. Similar smokes were produced using other silane derivatives.

3. Selected Metal Alkyl Derivatives

The use of metal alkyl derivatives as possible smoke agents was previously discussed in the review of the literature. A series of tests were performed for selected metal alkyls, metal chloro alkyls and for an intimate oil smoke based on the oxidation of triethyl aluminum. The experimental work performed under this contract in this area is outlined in the following sections.

a. Selected Tin and Zinc Metal-Organic Smoke Agents

Several metal-organic compounds were subjected to a series of tests. Based on visual observations, three compounds tetraethyltin, tetrabutyltin and diethyl zinc were considered for further testing. The results of smoke chamber testing indicated a TOP value of about 650 for tetrabutyltin and 140 for the tetraethyltin. These results are documented in Figure 26. It would appear that in this case the production of tin dioxide is relatively unimportant to the light scattering process.

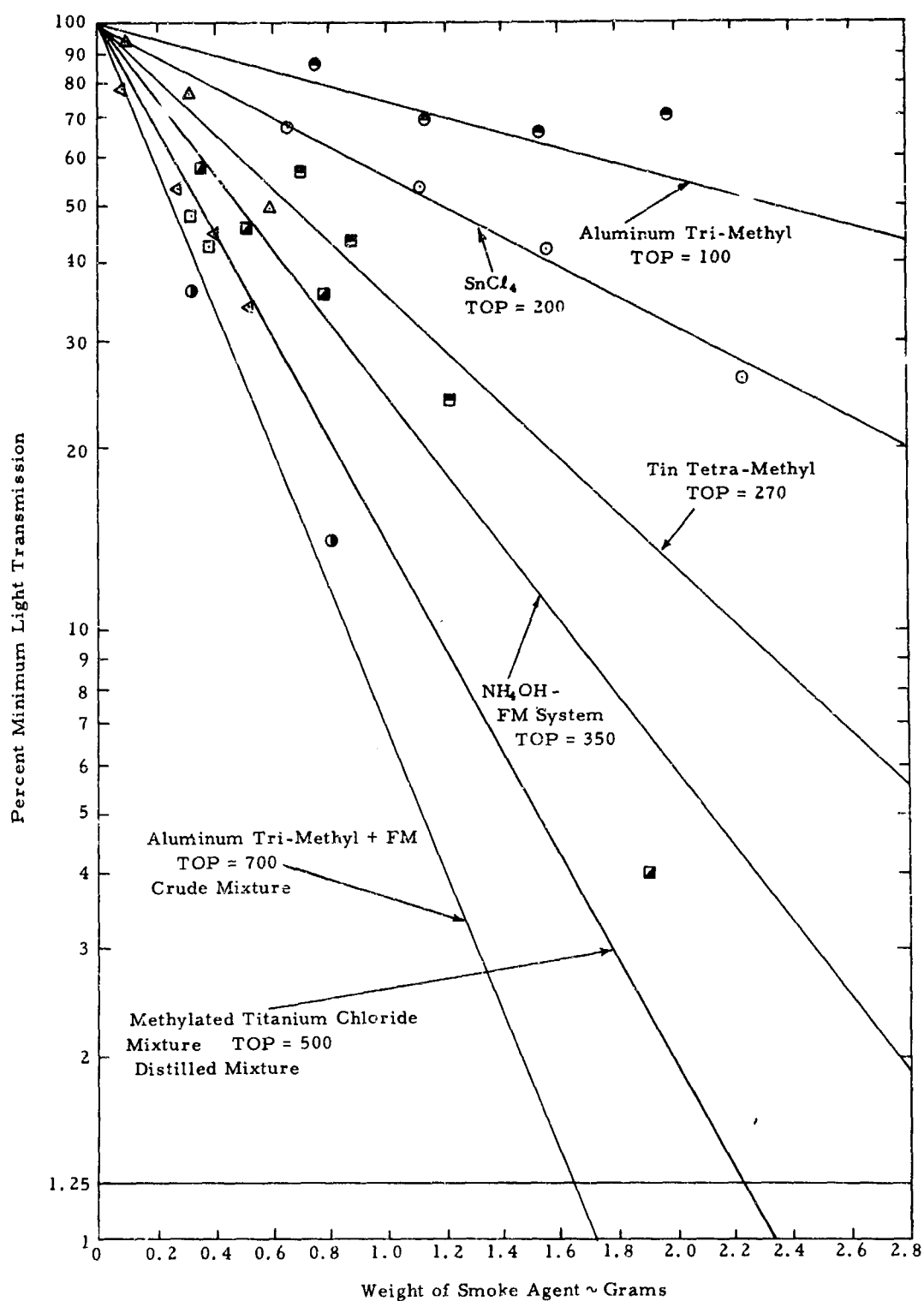


Figure 25. Transmission Data for Selected Aluminum and Tin Compounds,
I

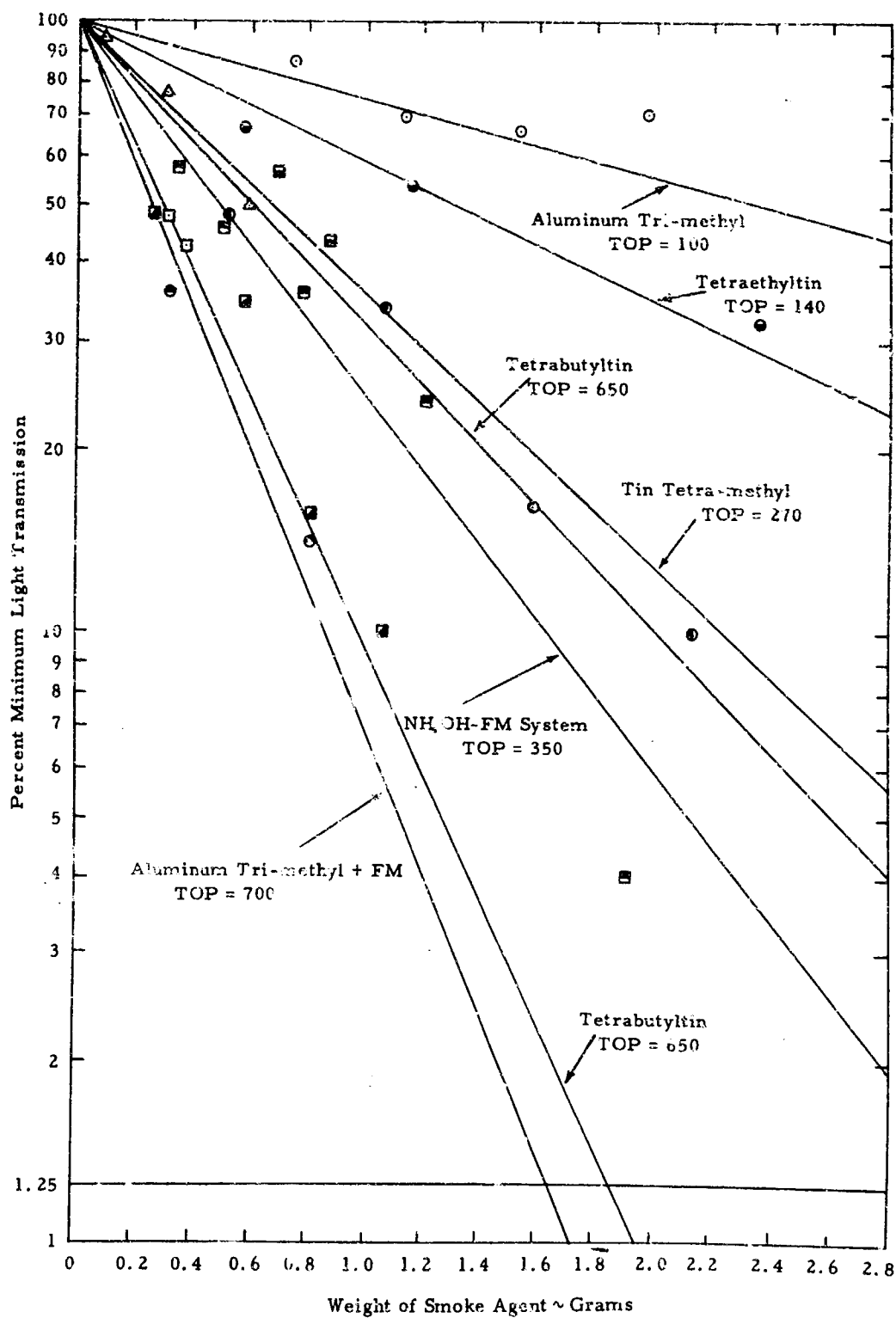


Figure 26. Transmission Data for Selected Aluminum and Tin Compounds,
II

and that the effective agent is possibly a high molecular weight hydrocarbon oil formed from the recombination of butyl radicals.

Diethyl zinc proved to be highly pyrophoric and required the special handling techniques developed for handling trimethylaluminum. Briefly, this procedure involves coupling the test material container to a system containing an argon atmosphere through which a small amount of test material is dropped into a container of more convenient working size. Data produced from the smoke chamber tests yielded a TOP of 175 for this compound. These results are documented in Figure 27. See Table V for results of preliminary tests performed on these compounds and Table VI for physical characteristics of these compounds.

The compounds investigated are listed below:

Tetraethyltin

Tetrabutyltin

Diphenyltin Dichloride

Bis (cyclopentadienyl) Titanium Dichloride

Hexaphenyl Ditin

Dimethyltin Dichloride

Benzene Phosphorus Dichloride

As a group, the metal-organic compounds investigated show little promise as operational smoke agents for use in existing airborne tankage systems.

b. Titanium Chloro Alkyls

A study of methylated titanium chlorides was undertaken to determine whether the substitution of a methyl group for a chlorine atom would be beneficial in producing a more desirable smoke producing agent. There are two reasons for believing that a substitution of a methyl group for a chlorine atom in titanium tetrachloride: (1) if the smoke is formed primarily of $\text{TiO} \cdot \text{H}_2\text{O}_x$ or $\text{Ti}(\text{OH})_4$, the use of a lighter group should increase the TOP and (2) the bond energy of $\text{H}_3\text{C}-\text{Ti}$ bond is somewhat lower than $\text{Ti}-\text{Cl}$ bond energy which should increase the rate and extent of hydrolysis with atmospheric water.

The general synthesis is discussed in the literature. The major deviation from reported procedures occurred when trimethylaluminum

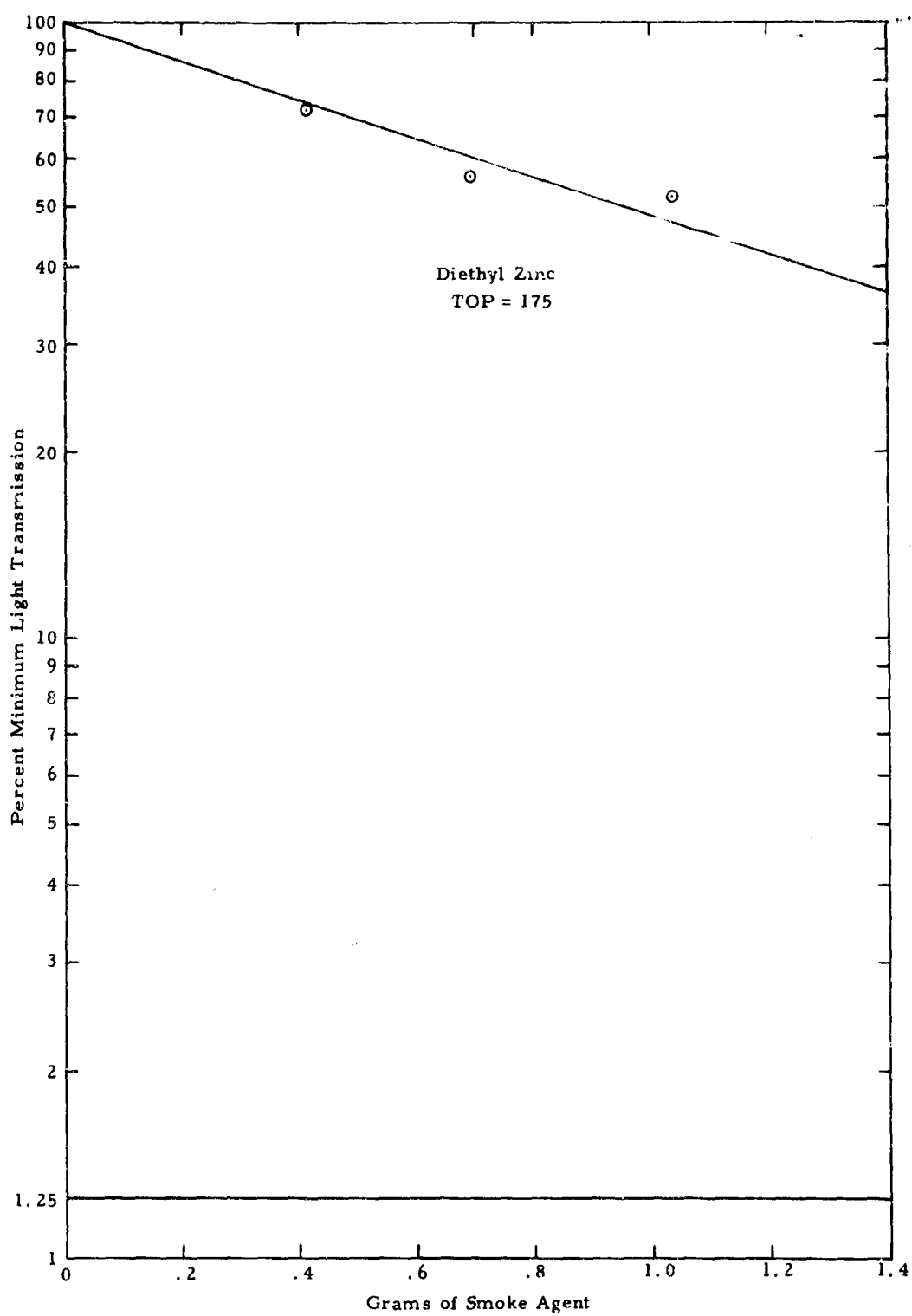


Figure 27. Transmission Data for Diethyl Zinc

TABLE V
RESULTS OF PRELIMINARY TESTS FOR
METAL-ORGANIC COMPOUNDS

<u>Metal-organic Compounds</u>		<u>Pyrophoric</u>	<u>Water Soluble</u>	<u>Com- bustible</u>	<u>Produces Smoke (Hot Plate)</u>
Zirconium tetrafluoride		-	-	-	-
Diphenyl tindichloride		-	-	-	-
Bis (cyclopentadienyl) titaniumdichloride		-	-	-	-
Germanium tetrachloride		-	-	-	-
*Tetraethyltin	140	-	-	+	+
*Tetrabutyltin	650	-	-	+	+
Hexaphenyl ditin		-	-	-	-
Dimethyltindichloride		-	+	-	-
Benzene Phosphorus dichloride		-	+	-	-

* Indicates smoke runs

TABLE VI
PHYSICAL DATA FOR SELECTED TIN AND
TITANIUM ALKYL DERIVATIVES

Tetraethyltin

$(C_2H_5)_4Sn$; Liquid; b. p. 179-182°C; sp. gr. (23°) 1.167

Tetrabutyltin

$(C_4H_9)_4Sn$; Liquid; m. q. 347.16; b. p. 145°C/10 mm; m. p. -70°C;
D(20°) 1.054²³; ref. index 1.4727²⁰; flash pt. 255°F

Diphenyltin Dichloride

$(C_6H_5)_2SnCl_2$; Solid; m. p. 42°C.; b. p. 333-337°C; with decomposition

Bis (cyclopentadienyl) Titanium Dichloride

$(C_5H_5)_2TiCl_2$; Solid; m. p. 278-289°C.

Hexaphenyl Ditin

$(C_6H_5)_3SnSn(C_6H_5)_3$; m. p. 228-232°C.

Dimethyltin Dichloride

$(CH_3)_2SnCl_2$; Solid; m. p. 107.5-108°C; b. p. 188-190°C.

Benzene Phosphorus Dichloride

$C_6H_5PCl_2$; sp. gr. (25°) 1.315; b. p. 224.6°C; m. p. -51°C;
n_D²⁵ 1.5958; soluble in common inert solvents, hydrolyzes rapidly
in water.

was introduced directly to the titanium tetrachloride with no intermediate dilution of either compound. This synthesis was selected because of the immediate availability of reactants due to their use on the program in other areas of investigation. The initial mixture was 80 percent TiCl_4 plus 20 percent trimethylaluminum. The trimethylaluminum was added to the titanium tetrachloride in droplet size quantities, and the exothermic reaction was controlled by the use of a water bath. The probable reaction is indicated by the following equation:



The mixture containing the products of reaction was believed to contain principally the mono and trimethyl titanium chlorides. These products are assumed because the literature indicates that dimethyl titanium chloride is somewhat unstable at room temperature. No effort was made to separate the mono and trimethyl grouped compounds, as it was felt that the time could be used more profitably in other areas of investigation and development. The mixture containing the mono and trimethyl titanium chlorides was tested in the smoke chamber. This data is documented in Figure 25. The results indicate that the alkyl substitution on the titanium chloride had an adverse effect on the test under the conditions. It was also observed that the mixture studied did not substantially improve the clogging problems encountered with the titanium tetrachloride agent.

The obscuration power of this mixture corresponded to a TOP of about 500 - 1200 depending on test conditions. Recent results from the phosphorus alkyl series indicates a possibility that a change in mechanisms may be effective in which the lower molecular weight alkyl derivatives react via a high temperature combustion mechanism to produce primarily P_2O_5 , whereas the higher derivatives react via a gas phase free radical polymerization to produce a combination of P_2O_5 and unburnt high molecular weight fog oils. If this change in mechanism is correct then it is probable that a similar change may also occur for select higher alkyl derivatives of titanium tetrachloride. Based on present results, the groups which could be predicted to be most promising in these organo metallic series are the isopropyl, tertiary butyl and higher molecular weight alkane derivatives.

c. Aluminum Trimethyl

Studies of the obscuration power of aluminum trimethyl indicated that this highly pyrophoric material had a TOP of about 100. This compares to a value for tetramethyltin of about 270. (Figure 25)

d. Alkyl Derivatives of Chlorosilane Smoke Agents

A study of the smoke producing capabilities of selected alkyl chlorosilanes was initiated and completed. Although it was recognized that the silicon derivatives would probably have relatively low obscuration power, the approach taken was to assume that alkyl silicon derivatives would behave in a manner similar to the titanium derivatives, which were suggested as potential smoke producing agents. The unavailability of the titanium derivatives prompted the use of the silicon derivatives.

In the investigations of this group, the compounds were tested to determine pyrophoricity, solubility in water, combustibility, and observed reaction when the compound is dropped on a hot plate. Pyrophoricity was tested by observing the extent of reaction which occurred after the test agent had been dropped from a syringe onto a watch glass. To determine solubility, the agent was added to water and agitated vigorously. The solution or mixture was allowed to stand three minutes before observations were made. To determine combustibility, the agent was first subjected to a match flame. If no reaction occurred, a gas torch flame was applied to the agent and the reaction was observed. The final test was the introduction of the material onto a hot plate maintained at 200°F. Ten drops of the test agent were ejected onto the hot plate and the smoke that evolved was observed. Results of these preliminary tests are tabulated in Table VII. All tests were performed under standard conditions. Less than half of the tested compounds in this group were capable of supporting combustion and/or producing smoke. The unmarked compounds produced very little or no smoke and were not considered further. The compounds marked by a single asterisk were abandoned from further consideration after visual observations indicated a probable TOP value of less than 100. The compounds marked with a double asterisk are those which were considered for further investigation as possible smoke producing agents. The agents selected were subjected to smoke evaluation tests in the laboratory and the results are documented in Figure 28. A list of the physical properties for these compounds is given in Table VIII. As a group, these compounds exhibited rather low TOP under the experimental conditions studied and therefore are not recommended for further study as possible smoke producing agents satisfactory to meet the objectives of this research effort.

TABLE VII
RESULTS OF PRELIMINARY TESTS FOR SELECTED CHLOROSILANE DERIVATIVE ALKYL

Chlorosilanes	TOP	Pyrophoric	Water Soluble	Combustible	Produces (Hot Plate)
Dimethyldiethoxysilane		-	-	+	very low
Diphenyldimethoxysilane		-	-	-	-
1, 2Dibromoethyltrichlorosilane		-	-	-	-
**Methyldiethoxysilane	185	-	+	+	+
**Dimethyldichlorosilane	250	-	-	+	+
Diphenyldichlorosilane		-	-	-	-
Trimethylchlorosilane	-	-	-	+	+
Methyldichlorosilane	130	-	+	+	+
**Ethyltrichlorosilane	160	-	-	+	+
Tetrachlorosilane		-	+	+	-
Methyltrichlorosilane		-	+	-	-
Triethylsilane		-	+	+	-
**Trichlorosilane	150	-	-	+	+
Tetraethylsilane		-	-	+	-
Ethyltriethoxysilane		-	-	+	-
Methyltriethoxysilane		-	-	+	-
Trihexylsilane		-	-	-	-

- Indicates negative results

+ Indicates positive results

** Indicates detailed TOP Measurements

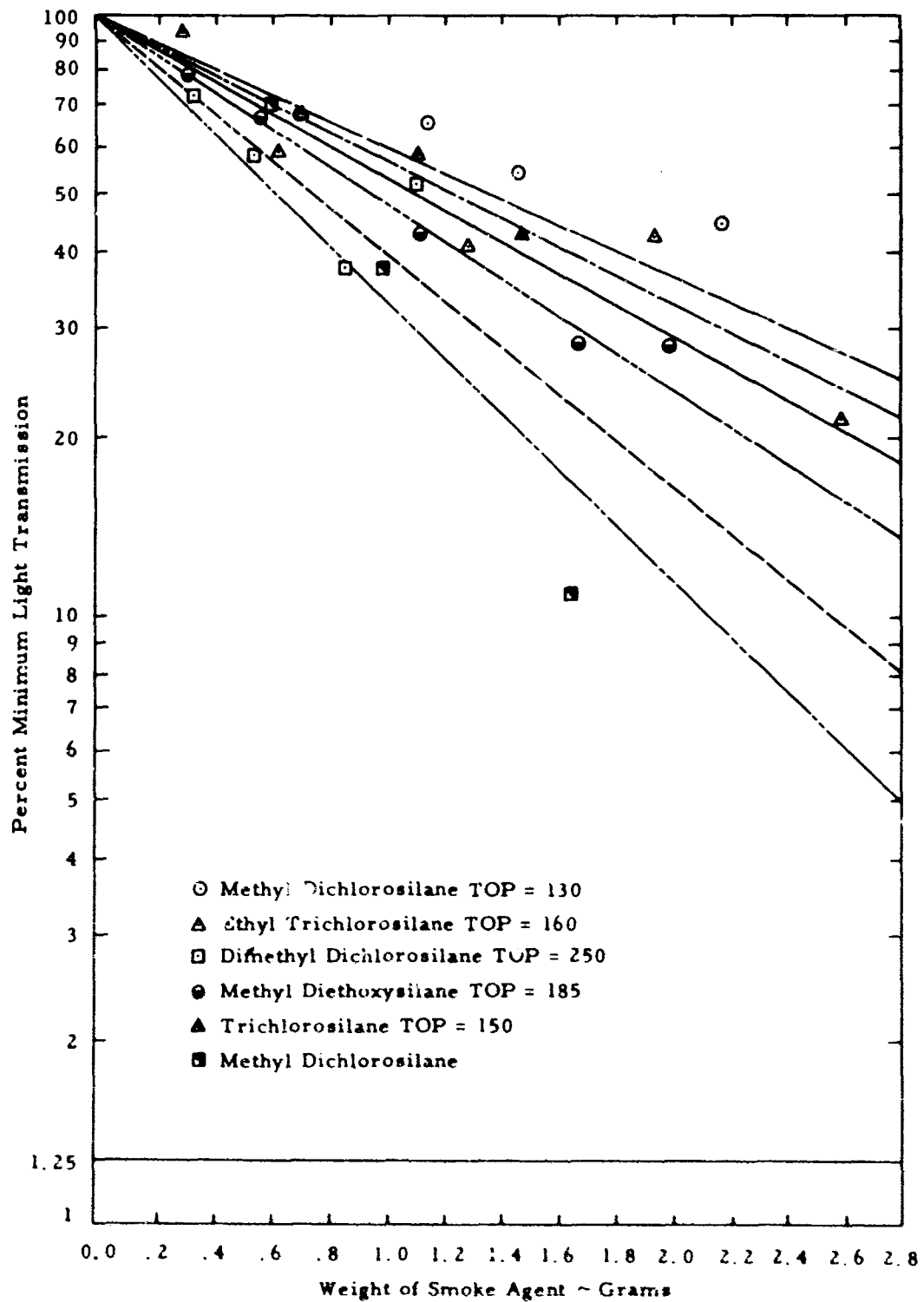


Figure 28. Transmission Data for Alkyl Chlorosilane Compounds

TABLE VIII
PHYSICAL PROPERTIES OF SELECTED ORGANIC DERIVATIVES
OF SILICON

Dimethyldiethoxysilane

$(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$; m. w. 148.28; wgt. per gal. 7 lbs.; b. p. 113.5°C ;
 $D(20^\circ)$ 0.8401²⁰; ref. index 1.3814²⁰; sp. gr. 0.848; flash pt. 86°F ;
Liquid

Diphenyldimethoxysilane

$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OCH}_3)_2$; m. w. 244.4; wgt. per gal. 8.5 lbs.; sp. gr. 1.080;
ref. index (25°) 1.5404; purity 95%; flash pt. 780°F .

1, 2-Dibromoethyltrichlorosilane

$\text{CH}_2\text{BrCHBrSiCl}_3$; b. p. $60-62^\circ/3$ mm; Liquid; n_D^{20} 1.5091

Methyldiethoxysilane

$\text{CH}_3(\text{C}_2\text{H}_5\text{O})_2\text{SiH}$; Liquid; b. p. 97°C ; ref. index (25°) 1.3724; d_4^{25} 0.829

Dimethyldichlorosilane

$(\text{CH}_3)_2\text{SiCl}_2$; Liquid; m. w. 129.1; b. p. 70.3°C ; m. p. -76°C ;
purity 99%; sp. gr. 1.073; wgt. per gal. 8.5 lbs; ref. index (25°)
1.4023; flash pt. -9°F

Diphenyldichlorosilane

$(\text{C}_6\text{H}_5)_2\text{SiCl}_2$; m. w. 253.2; b. p. 304°C ; m. p. -22°C ; purity 96%;
liquid; wgt. per gal. 10 lbs; sp. gr. 1.220; ref. index (25°) 1.5773;
flash pt. 142°F .

Trimethylchlorosilane

$(\text{CH}_3)_3\text{SiCl}$; Liquid m. w. 108.7; wgt. per gal. 7 lbs; b. p. 57.2°C ;
sp. gr. 0.856; ref. index (25°) 1.3893; purity 98%; flash pt. -18°F

Methyldichlorosilane

$\text{CH}_3\text{SiHCl}_2$; liquid; m. w. 115.0; b. p. 41°C ; sp. gr. 1.113; purity
97%; ref. index (25°) 1.3982; flash pt. -26°F .

Ethyltrichlorosilane

$\text{C}_2\text{H}_5\text{SiCl}_3$; liquid; m. w. 163.5; wgt. per gal. 10 lbs; b. p. 99.3°C ;
m. p. -105.6°C ; sp. gr. 1.4257; ref. index (25°) 1.4257; purity 98%;
flash pt. 14°F .

TABLE VIII (Cont.)

Methyltrichlorosilane

CH_3SiCl_3 ; liquid; m. w. 149.4; b. p. 66.4°C ; wgt. per gal. 10 lbs; m. p. -77.8°C ; sp. gr. 1.273; ref. index 1.415; purity 97.5% flash pt. 45°F

Triethylsilane

$(\text{C}_2\text{H}_5)_3\text{SiH}$; liquid; b. p. $107-108^\circ\text{C}$; sp. gr. (20°) 0.7318; ref. index (20°) 1.4119

Trichlorosilane

HSiCl_3 ; m. w. 135.5; b. p. 31.0°C ; $D(20^\circ)$ 1.336; ref. index (25°) 1.3990; purity 99%; flash pt. 7.0°F .

Tetraethylsilane

$(\text{C}_2\text{H}_5\text{O})_4\text{Si}$; liquid; b. p. $153-154^\circ\text{C}$; ref. index (20°) 1.4252; sp. gr. ($20^\circ/4^\circ$) 0.7661

Ethyltriethoxysilane

$\text{C}_2\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$; liquid; m. w. 192.3; wgt. per gal. 7 lbs; b. p. 160.9°C ; sp. gr. 0.889; ref. index 1.3853; purity 90%; flash pt. 105°F .

Methyltriethoxysilane

$(\text{CH}_3\text{O})_3\text{SiCH}_3$; liquid; m. w. 178.27; b. p. 141.0°C ; m. p. 75°C wgt. per gal. 7.5 lbs.; $D(20^\circ)$ 0.8947²⁰; ref. index 1.3831²⁰; sp. gr. 0.896; flash pt. 82°F .

Trihexylsilane

$(\text{C}_6\text{H}_{13})_3\text{SiH}$; liquid; b. p. $160^\circ\text{C}/1\text{ mm}$; ref. index (20°) 1.4476

Tetrachlorosilane

SiCl_4 ; liquid; m. w. 169.22; wgt. per gal. 12 lbs; b. p. 57.6°C ; m. p. 70°C ; $D(20^\circ)$ 1.463²⁰; ref. index 1.412²⁰; flash pt. 116°F

A list of compounds tested in this investigation follows:

* Dimethyldiethoxysilane	Methyltrichlorosilane
Dipenyldimethoxysilane	* Triethylsilane
1, 2 Dibromoethyltrichlorosilane	** Trichlorosilane
** Methyldiethoxysilane	* Tetraethylsilane
** Dimethyldichlorosilane	* Ethyltriethoxysilane
Dipenyldichlorosilane	* Methyltriethoxysilane
* Trimethylchlorosilane	Trihexylsilane
** Methyldichlorosilane	Tetrachlorosilane
** Ethyltrichlorosilane	

e. Triethyl Aluminum - Fog Oil Mixture (Ethyl TEA* Mix #90622T)

A mixture of TEA and fog oil was obtained from the Ethyl Corporation for smoke tests. The TOP value of this mixture as obtained in the laboratory smoke chamber is 400. This is at variance with Ethyl Corporation results which indicate the obscuration to be approximately equal to FM(1900). It appears that this mixture is an intimate oil smoke in which TEA acts as a fuel to vaporize the oil base. The observed particle size of the produced smoke is, therefore, probably non-optimum with respect to efficient scattering of normal incident light. It is probable that the TOP of this mixture is substantially less than fog oil (1100) partly for this reason and partly because of the TEA comprising 40 weight percent of the mixture. Handling properties of this mixture are good and it is assumed that the produced smoke is non-toxic. The TOP values varied between 250-600 depending upon relative humidity. At high humidity conditions, the TOP increased on an absolute basis but decreased relative to FS at similar conditions. On a volume basis at normal conditions (relative humidity 30%), the smoke effectiveness of Ethyl TEA Mix 60211 is considerably less than ten percent of FS.

A series of evaluation tests for Ethyl Mix #90622T were also performed in the large smoke tunnel using both optical attenuation and reflectance measurements. On a weight basis, the obscuration effectiveness relative to FS for this mixture varied from 9.5 percent to 17 percent, depending on relative humidity and measurement technique. On a volume basis, the relative effectiveness varied between 4.2 and 9.5 percent for similar humidity and temperature conditions. These tests

* Composition:	Triethyl Aluminum	10 lbs.
	Neutral Oil #75	11.9 lb.
	Methyl Napthalene	3.11 lbs.

verified measurements in the small laboratory smoke chamber and indicated a TOP of 400 or less under normal environmental conditions. The mixture tested was pyrophoric on air contact burning with a luminous blue flame near the liquid surface. Some handling difficulty was incurred when a 10 ml vial ignited pyrophorically with air in the laboratory. Our normal laboratory disposal procedure is to eject any such hazard out the window which, when performed in this case, resulted in a low order explosion as the liquid hit a snow bank. Subsequent controlled tests indicate a considerable hazard exists during a spill or fire extinguishment situation if any water is applied. Tests were performed to evaluate the relative effect of humidity on the smoke value of this mixture. The effectiveness of the smoke agent increases with increasing humidity on an absolute TOP basis, the TOP varying from about 250 to 600. However, it should be noted that the effectiveness of the smoke relative to FS decreases from seventeen percent to 9.5 percent with increasing humidity.

Approximately two gallons of this mixture were evaluated on field tests. These tests included dissemination from a simulated smoke tank attached to a moving wing section. The relatively low values to TOP obtained during previous laboratory measurements were verified. In addition, a major complication arose due to ignition of the TEA mixture on the ground and between the moving tank and the ground. No possible ignition source was present in the wing or cable assembly and it is apparent that the agent, as provided, may be pyrophoric when large quantities are dropped. The wing velocity at time of fire initiation was approximately twenty miles per hour.

4. Phosphorus Alkyl Derivatives

The alkyl derivatives of phosphorus provide a possible basis for improved smoke agents. A number of phosphorus compounds were synthesized and examined for their smoke producing capability. The experimental work performed in this area is reported in the following sections.

a. Phosphorus Alkyls

The literature survey had determined that the phosphorus alkyls represented a class of compounds which were characterized by a wide liquidus range and a high phosphorus content. The capability of these compounds to produce smoke and, thus, to act as smoke agents was unknown. As a first approximation, it was assumed that the smoke

producing capability of the phosphorus alkyls would be directly related to their ability to produce a phosphorus-type smoke via the processes of combustion and hydrolysis. If this were true, then the expected TOP value could be directly correlated with the weight of phosphorus in the molecule, and with the observed TOP value of white phosphorus. A possible exception to this correlation would exist if the produced particles were of sufficiently different size so as to markedly affect the light scattering properties of the smoke.

In order to perform preliminary testing of this hypothesis, a typical phosphorus alkyl compound was evaluated. This compound was chosen for its availability from commercial sources, not because it represented the most favorable combination of liquidus range and phosphorus content. The primary purpose of obtaining TOP values for this compound was to prove or disprove the working hypothesis. Results of relative TOP measurements for phosphorus tributyl and phosphorus are compared in Figure 29. This figure is a plot of observed minimum percent transmission versus the weight of phosphorus contained in the smoke agent. It should be noted that the actual TOP value for this alkyl compound is lower by an amount proportional to the weight of the hydrocarbon content of the molecule. Examination of the data supports the validity of this hypothesis. From these results, it was concluded that the smoke producing capability of most of the phosphorus alkyls is directly proportional to their weight percentage of contained phosphorus. The implication of this result is that this class of compounds can be used for smoke agents which will have a potential TOP capability between 1900 and 2300 depending on the compound or mixture of compounds used. These values compare with the TOP values of 2500 for FS and 1900 for FM. Based on this synthesis, a systematic investigation was begun. Synthesis of several diphosphine derivatives was accomplished. Many of these compounds are pyrophoric. Visual observations indicate some compound smoke profusely without an apparent combustion reaction. Because of the difficulty in synthesis, large quantities of these materials are not available but considerable promise as smoke agents is indicated by both visual and TOP observations. An outline of some of the synthetic procedures is given in Appendix A. The TOP values of the tested phosphorus alkyl derivatives vary between 1200 and 500 (Figure 30). The higher values are associated with non-pyrophoric derivatives.

For the compounds studied, the smoke output was not directly proportional to the weight percent contained phosphorus as was expected. A possible explanation is that a change in basic kinetic reaction

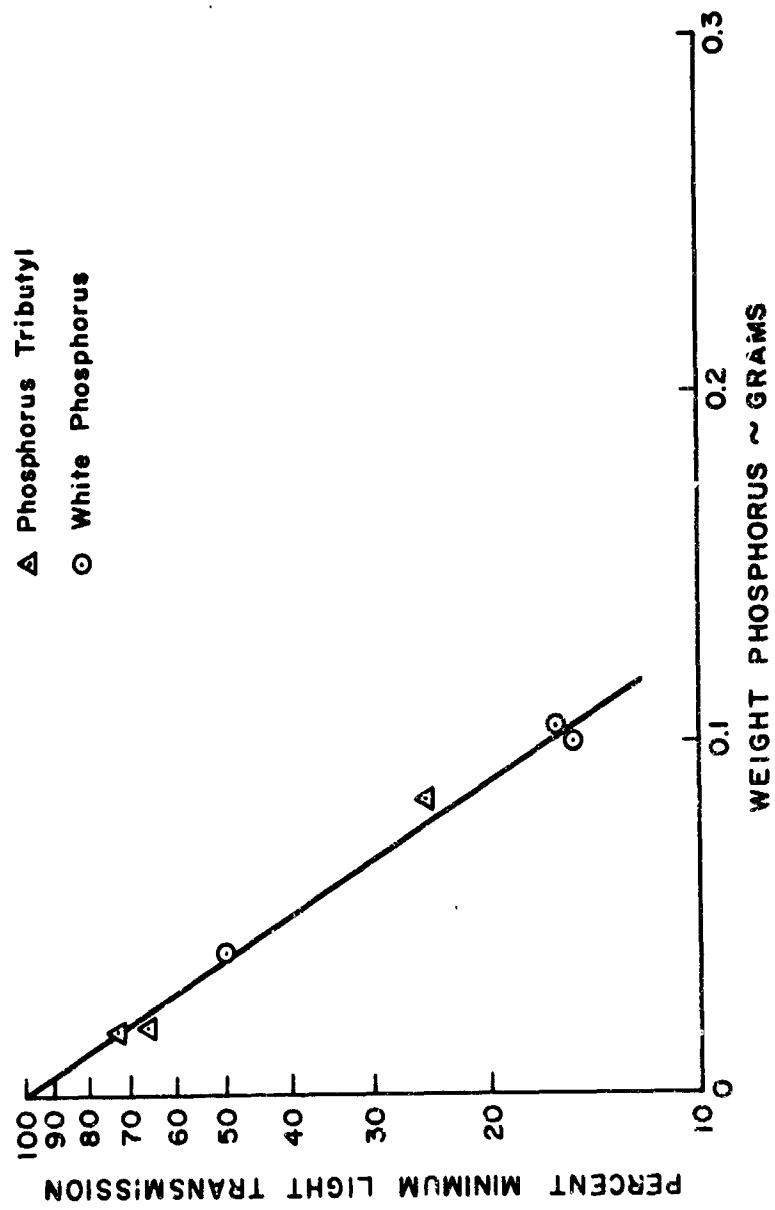


Figure 29. Transmission Data for Phosphorus Tributyl and White Phosphorus

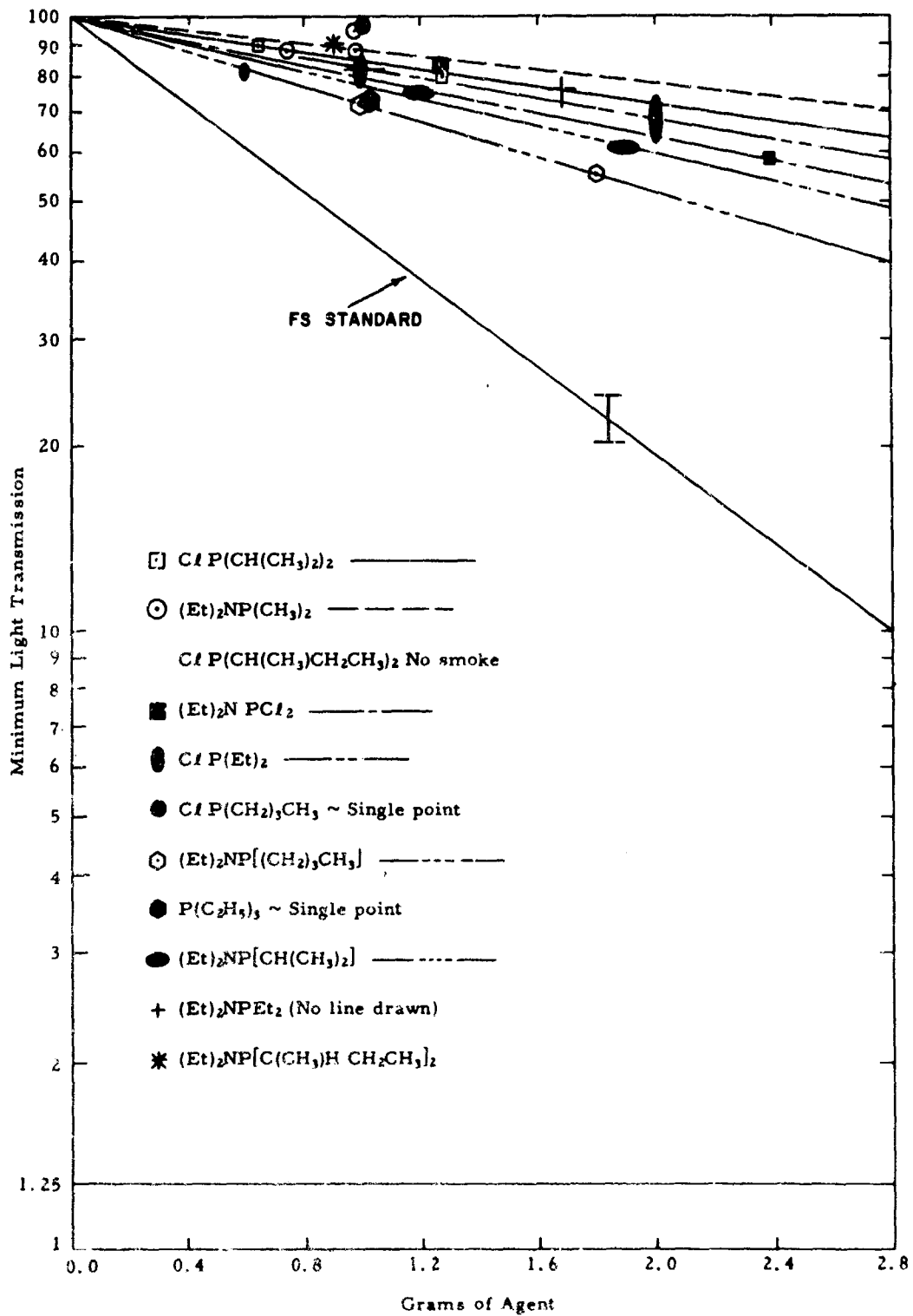


Figure 30. Transmission Data For Selected Phosphorus Alkyl Smoke Agents

mechanism involving smoke production occurs in which a hot flame combustion reaction is replaced by a cool oxidation-polymerization reaction. The work on these compounds is at a very early stage. Considerable promise exists in this area if the compounds are not too toxic to be handled in the liquid form.

b. Alkyl Derivatives of Phosphorus Amide

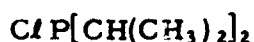
A series of alkyl amino phosphorus alkyls were synthesized and evaluated to determine their obscuration power. In all cases smoke runs were performed using the large smoke tunnel test facilities. Results of these runs are tabulated in Table IX. A plot of minimum percent light transmissions vs. weight of agent used is presented in Figure 30. The smoke values for these compounds varied between 550 and 1300. The higher values of 1300 are somewhat lower than values obtained for FM under similar conditions of test. The basic molecular structure of these compounds consists of a phosphorus nitrogen bond with alkyl groups attached to both the nitrogen and phosphorus. To aid in the interpretation of results, the same alkyl substituents were retained on the nitrogen, and systematic changes were made in the substituents attached to the phosphorus atom. These substituents included methyl, chlorine, n-butyl, isopropyl derivatives.

The light alkyl derivatives methyl, ethyl, and propyl of the dialkyl phosphoroamide diethyl series of compounds burn with a hot luminous carbon flame and are pyrophoric with air at elevated temperatures (150°C). Diisopropyl phosphorus diethyl amide (I) and di-n-butyl phosphorus diethyl amide (II), under similar conditions, oxidize in a completely different manner. These latter two compounds produced substantial smoke having a TOP value corresponding to FM. Compound I burns with a barely visible cold phosphorescent flame in air at a temperature of approximately 150°C.

Compound II does not appear to burn under these conditions but does produce copious quantities of smoke. The measured TOP of the light members of this series was evaluated at above 900. The measured TOP of Compound I was 750 and Compound II was 1100.

The chemical reaction mechanism which determines the obscuration power of these smokes is not clear. A possible mechanism is one in which a combustion or hydrolysis of the phosphorus amide occurs to produce a phosphorus based smoke. Evidence for this mechanism includes the high persistency of the smoke together with considerations

TABLE IX
SUMMARY OF EXPERIMENTAL RESULTS FOR
SELECTED PHOSPHORUS ALKYL DERIVATIVES



1cc

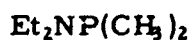
1.28 grams/cc

MLT 81%

Had to be ignited twice by match. Ignited by itself when heated. Very strong pungent odor. Good persistent smoke. Very little residue after burning.

.5cc

MLT 90%



1cc

.925 g/cc

MLT 87%

Good persistence - non-pyrophoric - smoked when it hit the hot plate - strong pungent odor.

.8cc

MLT 87%

Similar results. Ignited (Burst into flame when it hit hot plate). The hot plate was much hotter than it was during previous run. Some residue left after burning.



Non-pyrophoric - no vapors seen - did not ignite with hot plate lit with a match. Did not appear to burn or smoke. No smoke seen. No liquid was left after test. Concluded that the liquid must have vaporized without smoking before match was applied. No materials left for further testing.



1cc

1.296 g/cc

MLT 83%

Good persistence - fairly slow reacting. Smoked when it hit hot plate - no flame noticed. No appreciable odor.

2cc

MLT 59%

Ignited with match - will not support combustion in an open flame smoked when it originally hit the hot plate - burst into flames when match was applied but extinguished by itself.

TABLE IX (Cont.)

 ClPEt_2

1cc

1.004 g/cc

MLT 83%

Did not smoke on air contact - Burst into flame upon hitting hot plate.
Erratic flame - pungent odor.

2cc

MLT 74 to 62%

The MLT kept decreasing at a slow rate. Kept the recorder running for 90 minutes and the MLT decreased from 74 to 62%. Otherwise results were the same as above. Recorder came back to 100% after evacuation.

.6cc

MLT 84% to 80%
at T + 45 minutes

Had to be ignited with a match as hot plate hadn't been on long enough. Vaporized a little on contact with hot plate but couldn't tell if it was smoke or vapor. This may explain the slow release of smoke on previous run. Ran test smoke for 1 hour - the MLT reading decreased at a slow rate. However, the recorder came up to only 86% after smoke was evacuated which leads us to believe that at least some of the above results were due to recorder drift. No more material remained for testing so the above tests were inconclusive.

 $\text{ClP}(\text{CH}_2)_3\text{CH}_3$

1cc

1.01 g/cc

MLT 96%

Did not smoke on contact with air - Smoked when it hit hot plate - was not ignited - came slowly down to 96% and back to 100% after evacuation.

 $\text{Et}_2\text{NPC}[(\text{CH}_3)(\text{C}_2\text{H}_5)]_2$

1cc

.93 g/cc

MLT 90%

Did not smoke on contact with air - smoked a little bit on contact with hot plate. Would not ignite by lighting it with matches. MLT reading went down to 90% after a few minutes.

1.8cc

Did not smoke - put material on hot plate without lighting it.

TABLE IX (Cont.)



1cc

1.19 g/cc

MLT 75%

Does not burn spontaneously at room temperature in air. Does not hydrolyze when placed on concrete. Burns spontaneously when placed on hot plate. Crumble but does not readily sustain combustion. Very low bluish flame with marked phosphorescence on hot plate. Good persistence.



1.6cc

MLT 61%



1.1cc

.95 g/cc

MLT 85%

Does not burn on contact with cold air or cement. Ignites spontaneously on hot porcelain vessel. Not difficult to handle. Bright carbon flame.

1.8cc

.95 g/cc

Same results - the MLT reading decreased at a slow rate after the initial burning in both runs. Started at 79% MLT at burning and decreased to 74% at T + 12 minutes.



1cc

.90 g/cc

MLT 73%

Does not smoke when placed on cold concrete. Smokes but does not ignite when placed on hot plate. Did not burn. Porcelain dish not too hot.



2cc

.90 g/cc

MLT 55%



1cc

1.08 g/cc

MLT 83%

Had to be lit with a match. No smoke noticed when it hit hot plate.

of the weight-contained-phosphorus. As can be determined from Table IX, the smoke value for diethylamide phosphorus dimethyl (A) is greater than diethylamide phosphorus diethyl. The weight of contained phosphorus decreases for these compounds from 23% for the dimethyl to 19.3% for diethyl derivatives, respectively. A direct correlation with the percent contained phosphorus would require an increase of about 15% which, within the experimental error, is what is observed. It is, however, not clear whether the important constituent forming the base smoke is to be associated with the oxidation of phosphorus or, alternatively, the phosphorus nitride linkage. If the phosphorus alone were completely combusted to form an oxide P_2O_5 , then the smoke value would be in the vicinity of a TOP of 1000 which is, in fact, not observed. Under the conditions of test, it is not possible to distinguish between a possible inefficient combustion process and an effective phosphorus nitride reaction.

As the alkyl weight fraction increases, it is expected that a decrease in TOP would result if the above mechanism is valid. This decrease was not, in fact, observed. Rather, the TOP of the diethylamine phosphorus diisopropyl derivative is considerably higher than the lighter methyl and ethyl alkyls. Similar results were observed for diethylamine phosphorus di-n-butyl which had the highest TOP of the compounds studied. For these compounds, an inverse correlation of TOP with percent contained phosphorus was observed. A possible explanation for this result is that the important mechanism consists of the formation of an oil smoke via a gas phase polymerization reaction. The principle problem to be answered here is whether a better smoke can be produced by forming a longer chain polymer using long chain alkyl groups or whether emphasis should be placed on improving the rate of a decomposition reaction by using relatively weak carbon phosphorus bond linkages, as, for example, tertiary butyl grouping or similar derivatives. In either case, additional work will be necessary to determine which direction is best in terms of advanced smoke agents.

An observation of some interest is the persistence of diethylamino phosphorus diethyl. For this compound it was observed that, instead of increased light transmission as a function of time, the obscuration increased at a very slow rate. This fact was further confirmed during a ninety minute observation of the time vs. percent-light-transmission curve in which a decrease of four percent in MLT was documented. It is possible that the very slow hydrolysis of a phosphorus nitride is responsible for this behavior. See Table X for physical properties of phosphorus alkyls.

TABLE X
PHYSICAL PROPERTIES OF SELECTED PHOSPHORUS ALKYLs

Phosphorus Alkyls

Ethyl phenylphosphine $(C_2H_5)(C_6H_5)PH$

Mol. Wt.	138.15	22.4% P
B. P.	225	
Solubility	s. org., d. H_2O	
Characteristics	- liquid, colorless	

p - Ethylphenyl phosphine $C_2H_5C_6H_4PH_2$

Mol. Wt.	138.15	22.1%
B. P.	200	
Solubility	s. org., d H_2O	
Characteristics	- liquid, colorless	

Propyl phosphine $C_3H_7PH_2$

Mol. Wt.	76.08	40.7% P
B. P.	50-3	
Solubility	s. org.	
Characteristics	- liquid, colorless	

i - Propyl phosphine $C_3H_7PH_2$

Mol. Wt.	76.08	41% P
B. P.	41	
Solubility	s. org., d. air	
Characteristics	- liquid, colorless	

Cyclohexyl phosphine $C_6H_{11}PH_2$

Mol. Wt.	116.15	26.7% P
Vapor Pressure	97 ¹⁶⁰	
Solubility	s. org., d. H_2O	
Characteristics	- liquid, colorless	

Triethyl phosphine $(C_2H_5)_3P$

Mol. Wt.	118.16	26.2% P
B. P.	127	
Specific Grav.	(15) 0.812; (18.6) 0.8000	
Solubility	s. org.	
Characteristics	- liquid, colorless	

TABLE X (Cont.)

Di-i-propyl phosphine $(C_3H_7)_2PH$

Mol. Wt.	118.16	26.2%
B. P.	118	
Solubility	s. org.	
Characteristics	- liquid, colorless	

Trimethyl phosphine $(CH_3)_3P$

Mol. Wt.	76.08	41%
Sp. Gr.	0.748	
M. P.	-85.9	
B. P.	35.5 - 42	
ΔH vap	6.92 K cal/mol	
Solubility	s. org.	
Characteristics	- liquid, colorless	

Methyl ethyl phosphine $CH_3(C_2H_5)PH$

Mol. Wt.	76.08	41% P
B. P.	59	
Sol.	s. org., d. air	
Characteristics	- liquid, colorless	

Methyphosphine CH_3PH_2

Mol. Wt.	48.03	65%
B. P.	-14	
V. P.	0(1.75) atm.	
Solubility	sl. d. (H_2O) (alc)	
	s. eth.	
Characteristics	- gas, colorless	
	toxic, spont. infl.	

Dimethyl phosphine $(CH_3)_2PH$

Mol. Wt.	62.05	50%
B. P.	25	
V. P.	-47 ³⁰	
Solubility	s. org., d. air	
Characteristics	- liquid, colorless	
	Spont. infl.	

TABLE X (Cont.)

Di-i-propyl phosphine $(C_3H_7)_2PH$

Mol. Wt.	118.16	26.2%
B. P.	118	
Solubility	s. org.	
Characteristics	- liquid, colorless	

Trimethyl phosphine $(CH_3)_3P$

Mol. Wt.	76.08	41%
Sp. Gr.	0.748	
M. P.	-85.9	
B. P.	35.5 - 42	
ΔH vap	6.92 K cal/mol	
Solubility	s. org.	
Characteristics	- liquid, colorless	

Methyl ethyl phosphine $CH_3(C_2H_5)PH$

Mol. Wt.	76.08	41% P
B. P.	59	
Sol.	s. org., d. air	
Characteristics	- liquid, colorless	

Methylphosphine CH_3PH_2

Mol. Wt.	48.03	65%
B. F.	-14	
V. P.	0(1.75) atm.	
Solubility	sl. d. (H_2O) (alc)	
	s. eth.	
Characteristics	- gas, colorless toxic, spont. infl.	

Dimethyl phosphine $(CH_3)_2PH$

Mol. Wt.	62.05	50%
B. P.	25	
V. P.	-47 ⁵⁰	
Solubility	s. org., d. air	
Characteristics	- liquid, colorless Spont. infl.	

TABLE X (Cont.)

Ethyl phosphine $C_2H_5PH_2$

Mol. Wt.	62.05	50%
B. P.	25	
Solubility	s. org., d. air	
Characteristics	- gas, colorless	

Diphosphine DerivativesDimethyl diphosphine $(CH_3)_2PPH_2$

B. P. (760)	115-125°
liquid at room temperature	

Diethyl diphosphine $(C_2H_5)_2PPH_2$

B. P. (760)	-20-2°
liquid at room temperature	

Dipropyl diphosphine $(C_3H_7)_2PPH_2$

B. P. (15)	144-5°
liquid at room temperature	

Dibutyl diphosphine $(C_4H_9)_2PPH_2$

B. P. (15)	180-182
liquid at room temperature	

c. Alkyl Derivatives of Phosphorus Chloride

A series of alkyl derivatives of phosphorus chloride were synthesized and examined for their smoke producing capability. These compounds were: diisopropyl phosphorus chloride $((\text{CH}_3)_2\text{CH})_2\text{PCl}$ (I); di-n-butyl phosphorus chloride $(\text{C}_4\text{H}_9)_2\text{PCl}$ (II); diethyl phosphorus chloride $(\text{C}_2\text{H}_5)_2\text{PCl}$ (III); and n-butyl phosphorus dichloride $\text{C}_4\text{H}_9\text{PCl}_2$ (IV).

The smoke producing capability of these compounds was evaluated in the large smoke tunnel. Results from these tests are tabulated in Table IX. A plot of MLT vs. weight of agent used is given in Figure 10. For this series, the maximum TOP observed was 625 for compound I. The fraction phosphorus in the compounds is 0.28, 0.17, 0.25, 0.19, respectively. If the percent contained phosphorus was effectively controlling the obscuration power of the produced smoke, the TOP of III should be about ten percent greater than I. Instead, the reverse relation holds in which the produced smoke is inversely related to the percent phosphorus. A possible conclusion drawn from this data is that the isopropyl radical dissociates to form a polymeric particle which increases the obscuration value of the smoke via a formation of an organic "oil" droplet.

If the smoke value is related to the percent contained hydrocarbon, then, for an optimum particle size of produced smoke, it would imply a smoke value of about 800 for (I). Since it can be reasonably anticipated that non-optimum particle sizes are formed because of an inefficient in-situ combustion process, a TOP value of 600 would tend to support the possibility of a fog oil smoke. A second type of evidence indicating the effective smoke agent is the persistence values obtained from time-MLT curves. For an optimum oil smoke, a trace indicating high persistence would be expected. Similarly, in all the phases of this program, it has been observed that generally a flat trace was produced tending to support a phosphorus based smoke. Without further studies it is not possible to choose between these alternatives and it is, therefore, concluded that probably both mechanisms play a role in the formation of the produced smokes with the possibility of the production of a relatively poor phosphorus smoke due to incomplete hydrolysis of the phosphorus chloride which is augmented by the production of oil or polymeric organic scattering particles. The reaction mechanism for this smoke is definitely not clear but a correlation is to be expected between the obscuring power of the produced smoke and the ease with which the oxidation-hydrolysis reaction can take place. As a

general rule, it is expected that the isopropyl, tertiary butyl, and isobutyl groups are more easily removed from a phosphorus atom than straight chain hydrocarbon derivatives. The best oil polymers would then be formed by a free radical gas phase polymerization reaction yielding oils with a molecular weight several times that of the base monomer. The fact that diisopropyl phosphorus chloride has a better TOP than diethyl phosphorus chloride is, therefore, consistent with the oil mechanism. At the same time, the fact that diethyl phosphorus chloride produces a smoke with a TOP of 500 would support the thesis that a certain underlying smoke value is associated with the phosphorus content. In this case, dissociation into ethyl radicals would tend to produce sizable quantities of ethylene ethane and butane derivatives all of which have vapor pressures considerably in excess of that required for formation of condensed phases.

5. Slurries, Mixtures, and Solutions of WP

WP provides the best military chemical smoke. Because of limitation in physical properties (freezing point $+44^{\circ}\text{C}$), this agent cannot readily be used for aircraft dissemination. There are three major techniques which can be used to provide liquid having high WP concentrations. These methods involve the development of mixtures, solutions, and slurries. All three techniques were investigated and smoke agents having favorable liquid characteristics were developed for each. An outline of the major results of these tests is presented in the following sections.

a. White Phosphorus

White phosphorus is used in numerous military applications. There is a great quantity of data available concerning its properties as a smoke agent. In addition to the highest TOP available, it is a relatively good reference material for purposes of comparing various smoke agents. For much of the work accomplished on this contract, WP was used as a primary standard. The reason for this was that of the agents tested, it had inherently greater reproducibility. The only major difficulty arose when values of minimum light transmission close to 100% were desired for the laboratory test chamber. These values required weighing very small quantities of WP and, because of a water coating, some systematic deviations were apparent. However, for most of the intensities required, the weight was not a problem. Some of the typical results of these runs are shown in Figure 31. As has been previously outlined, TOP values agreeing substantially with literature values were

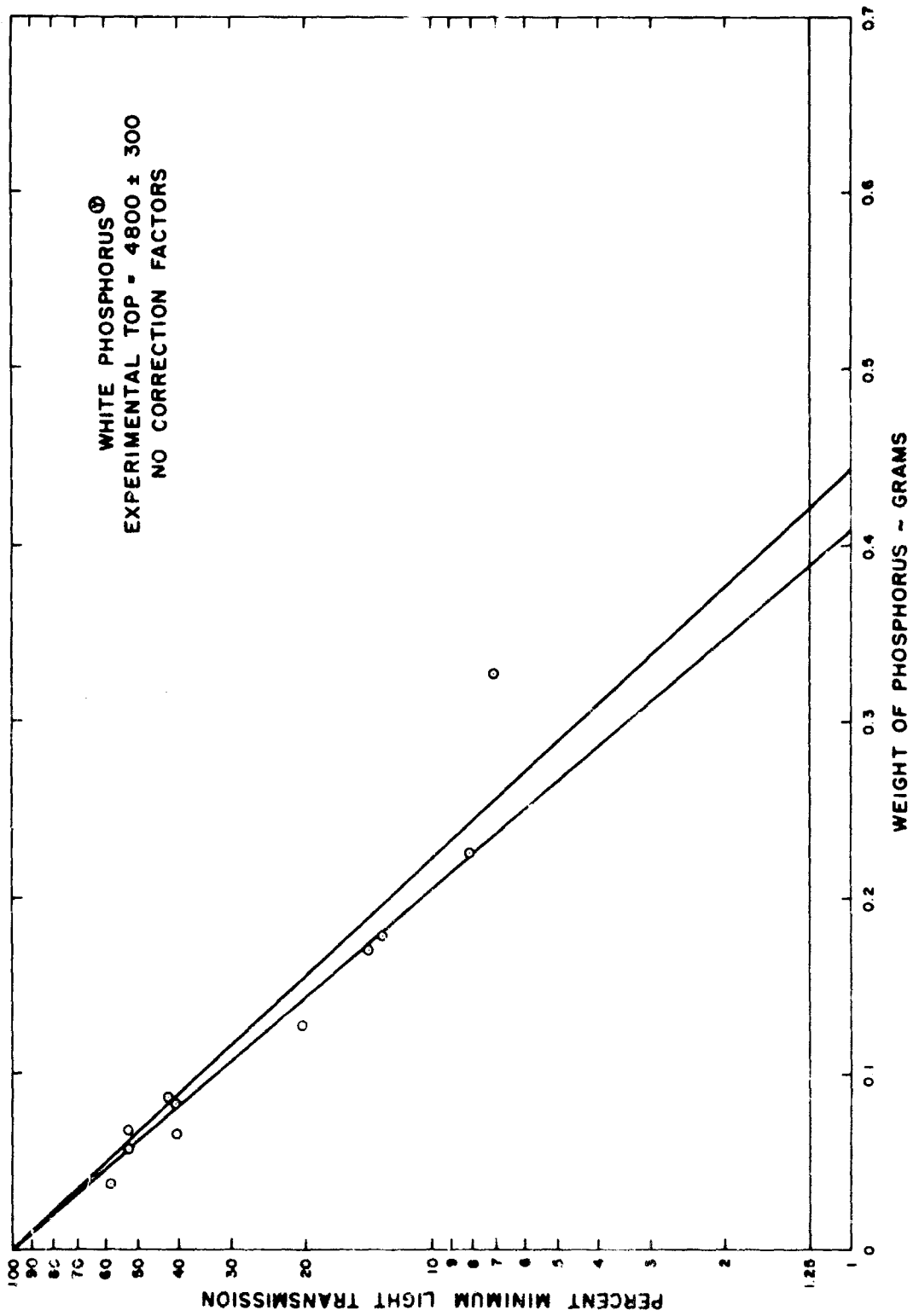


Figure 31. Typical Data Obtained From WP in Small Test Chamber

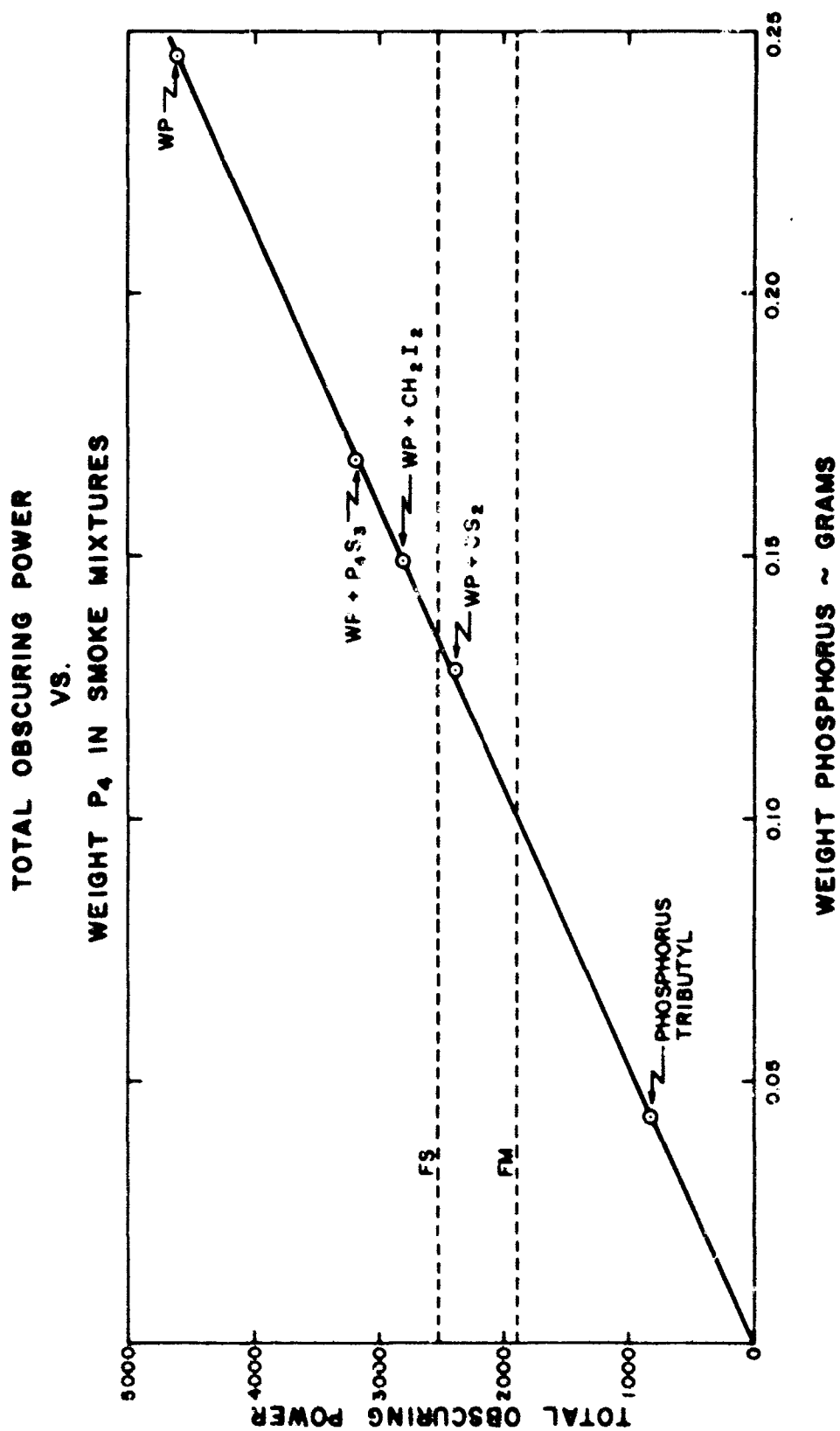


Figure 32. Correlation of Obscuring Power with Weight Percent Contained Phosphorus

obtained using the small test chamber. The basis for calculating TOP values for WP is given in the discussion concerned with TOP laboratory smoke chamber modification B. The two solid lines indicate the range of accuracy of this data. Test results from the large smoke tunnel are reported in previous discussions. There, results were consistently high and TOP values between 5500 and 6000 were obtained. The reason for this variance was not determined but may be due, in part, to the color temperature of the light source and/or humidity conditions. Corrosion tests of this smoke are reported in a following section.

b. Eutectic White Phosphorus (EWP)

A promising technique for the development of a phosphorus based smoke agent is the use of a eutectic mixture of white phosphorus in phosphorus sesquisulfide. This mixture results in a freezing point lowering to about -40°C with good thermal stability and corrosion characteristics. Investigations were made of the smoke producing capabilities of a eutectic mixture of phosphorus-phosphorus sesquisulfide. Theoretical predictions indicate a potential TOP of approximately 3500. Experimental results (Figure 33) indicate a TOP of at least 2700. Four mixtures were studied (Figure 34) which varied in percent contained phosphorus between 76 and 82 percent. The data obtained have been averaged and been plotted (Figure 35) as one mixture due to experimental scatter in the observed points. These mixtures are relatively easily handled under an inert atmosphere or under water (but could be a problem for untrained personnel). The conditions of dispersement and combustion of EWP during the obscuration tests performed are such that incomplete burning probably occurred. It is expected that the reported values are, therefore, somewhat low and the true TOP value should lie between 300 and 500 points higher. Corrosion studies indicate that corrosion of common materials such as iron and aluminum, and polyethylene is not a problem. A more complete study of the corrosive and materials degradation properties of an EWP mixture is reported in the section describing corrosive tests for selected smoke agents. Experience in handling this mixture has indicated that no unusual precautions need be observed other than those obviously necessary in handling a pyrophoric material. It should be noted that, although the research results are substantially in agreement with literature values concerned with the observed freezing point of this mixture, white phosphorus is noted for its strong tendency to form a metastable super-cooled liquidus state and that long term storage at low temperatures are necessary to ensure against such a possibility with eutectic mixtures. Additional

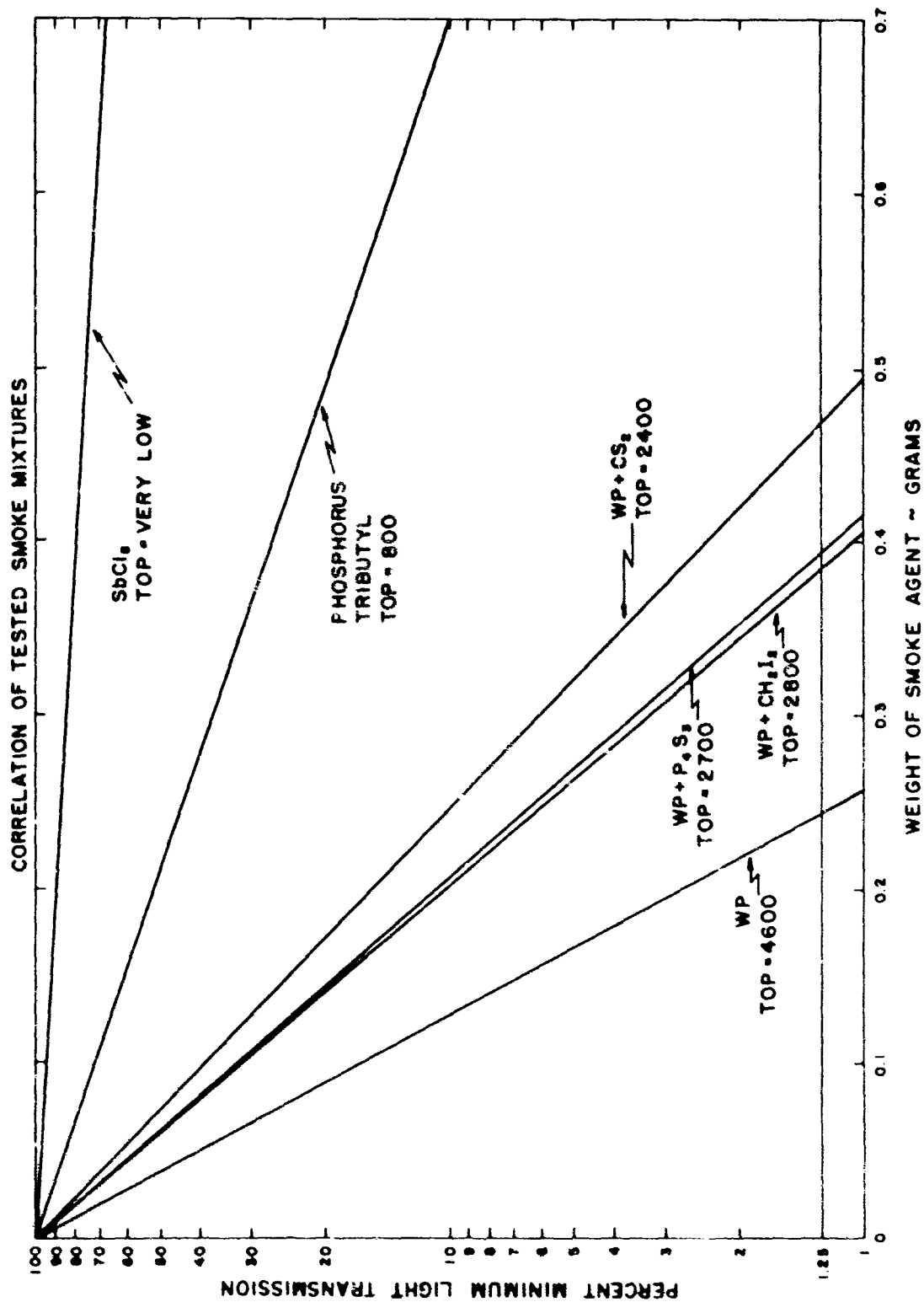


Figure 33. Transmission Data for WP Slurries, EWP; and MIP Smoke Agents

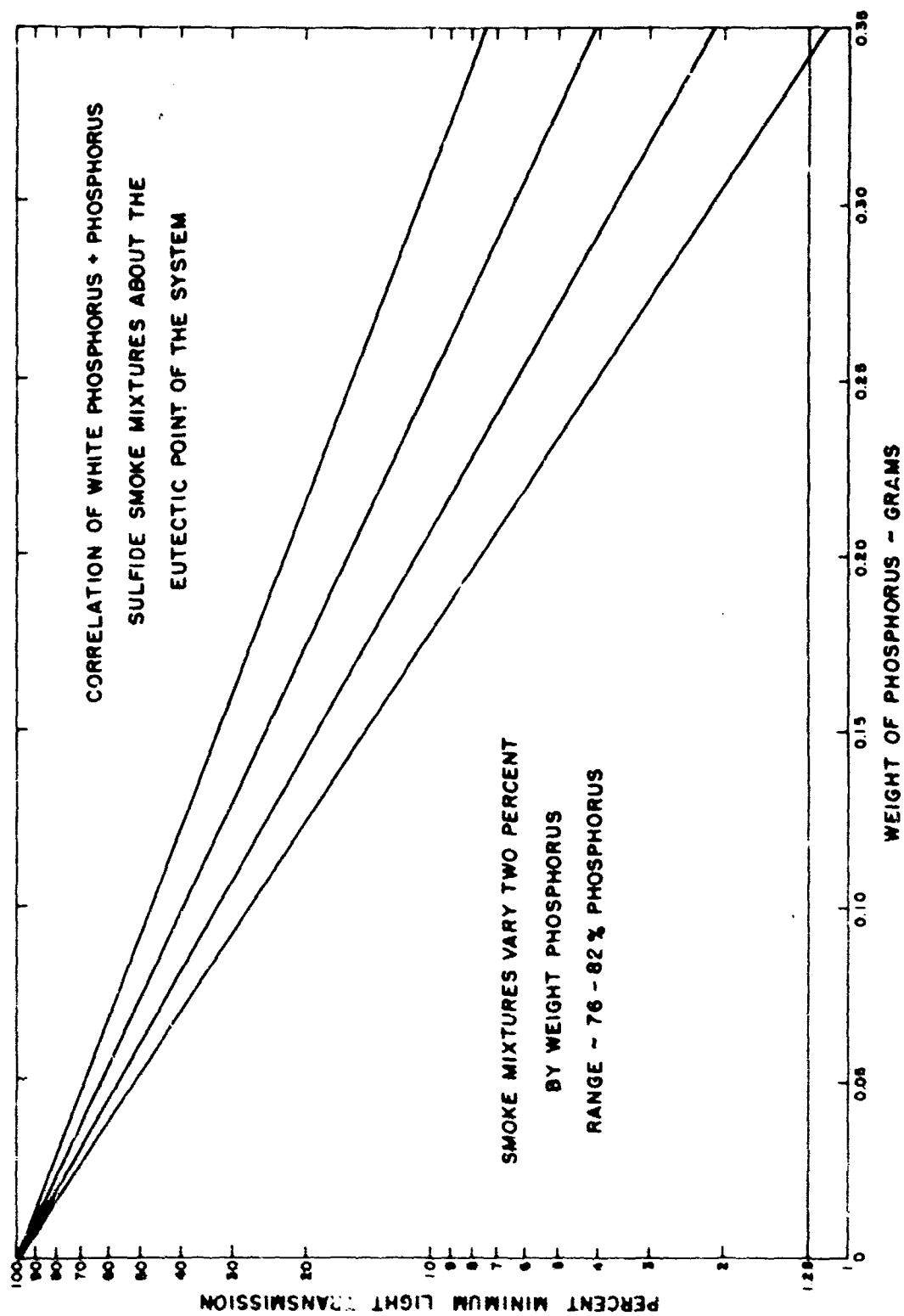


Figure 34. Transmission Data for Smoke Mixtures of White Phosphorus + Phosphorus Sulfide about the Eutectic Point

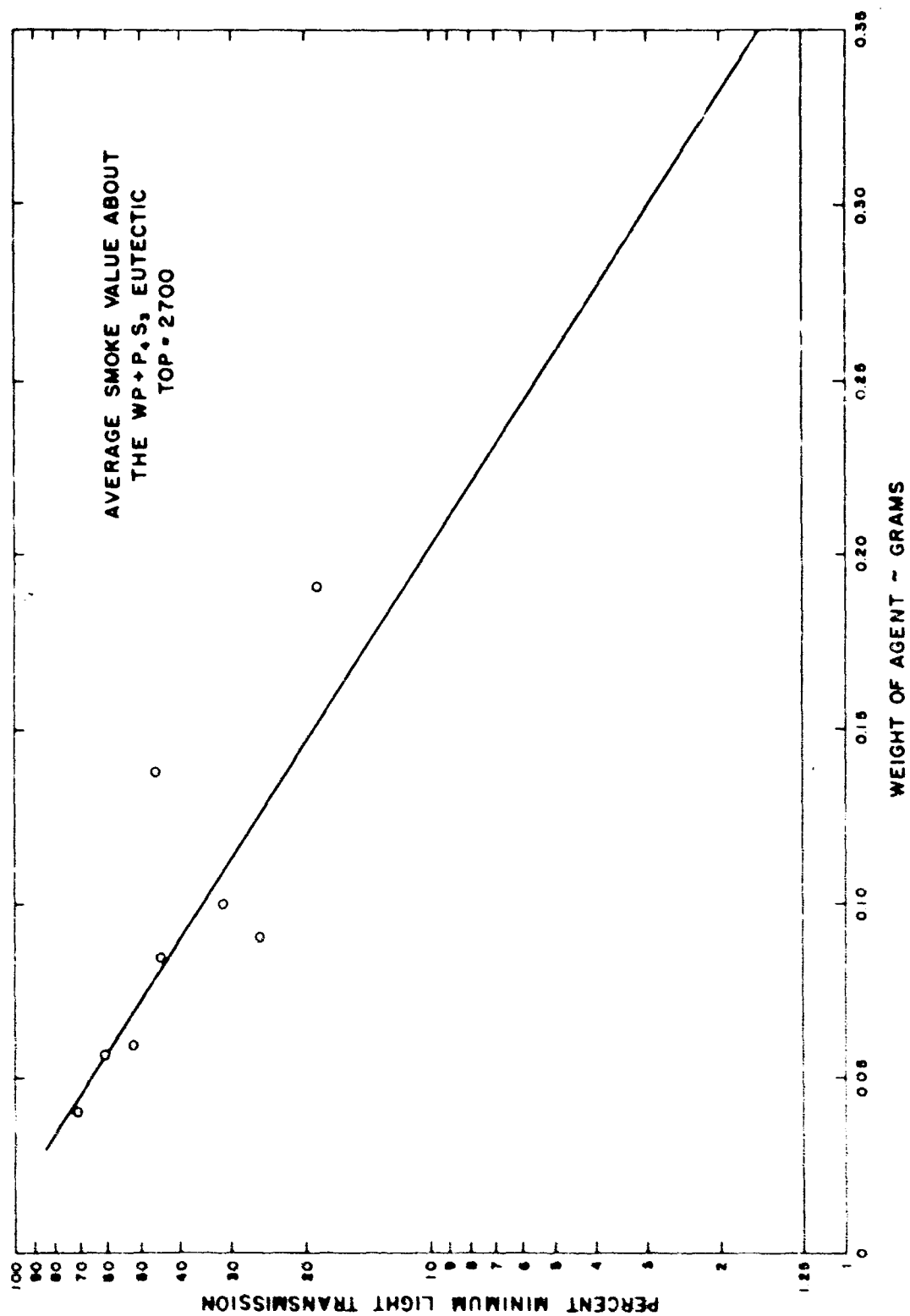


Figure 35. Average Transmission Data for EWP Mixtures

work in this area is certainly warranted with emphasis on two problems. The first is a more careful study of exact phase diagram of phosphorus and sulfur. The second major problem is to evaluate the obscuration power under other than precisely controlled laboratory conditions. A series of field tests were performed for this agent where the unmodified material was disseminated from an airborne tank. Extensive fire was observed, in the clouds relatively close to the wing area. The rate of flame travel, however, was less than the vehicle velocity and little or no damage occurred by fire to the wing structure from the dissemination operation. Also, no substantial ground fire damage was observed. In one case, the agent was not fully outflowed from the tank during flight and a fire with only minor damage to the wing structure occurred by afterburning. A combination of MIP and EWP further reduced this problem.

c. Phosphorus Slurries

A possible approach for obtaining liquids with high phosphorus loadings is the introduction of a surfactant agent to stabilize phosphorus particles into a slurry. Since it is also possible to form metastable supersaturated WP solutions, initial efforts in this field have been to evaluate the shelf-life of slurries utilizing various solvents and surfactants. The survey was limited to the use of three solvents; carbon disulfide, methylene iodide, and methylene chloride. Six surfactant agents were selected at random from the group of available surfactants for the series of tests. A list of these agents is as follows:

1. Tamol SN, Lot 5057, Rohm and Haas Co.
2. Separan NP20, Lot 2084, Dow Chemical Co.
3. Natrosol 250, Lot 1717, Type HR, Hercules Powder Co.
4. Pluronic P104, Lot C, 20262C, Wyandotte Chemical Co.
5. Alkanol OL, Lot 3, 033950, duPont de Nemours Co.
6. Avitex

The procedure followed was to prepare slurries consisting of one percent surfactant, thirty-nine percent solvent, and sixty percent white phosphorus. These slurries were then homogenized by utilization of a Virtis "45" homogenizer run at high speed for a period of one to two minutes. It was observed that several of the surfactant agents were incompatible with the solvent used and homogenization did not occur.

The objective of this work was to demonstrate that a stable slurry could be made which possesses a TOP greater than the FS smoke mixture since the basic idea was to achieve a dynamic liquid system in which the phosphorus would dissolve at elevated temperatures, incorporating a surface active agent to suppress the formation of large particles as the temperature is lowered. A slurry of WP Avitex was made. The TOP value of the slurry was measured to be about 2400, which is relatively good. For this mixture, the temperature of freezing was about zero degrees Fahrenheit. This mixture also was not pyrophoric and required ignition. This latter disadvantage would imply that a requirement for a liquid chemical ignitor may be necessary. A likely prospect for such an ignitor would be a mixture using select phosphorus alkyls compounds. A brief systematic study of a number of surface active agents for the formation of stable emulsions and slurries was performed.

A series of long-term storage tests were initiated in March 1965, to evaluate whether a significant supercooling problem existed for slurries of white phosphorus with methylene iodide, methylene chloride, and carbon tetrachloride using several selected surfactant stabilizers. Mixtures were made using Tamol SN, Separan NP20, Natrosol 250, Pluronic P104 and Alkanol OJ surfactant agents. In order to standardize as much as possible, mixtures using 0.1 gms. of surfactant, 6.0 gms. WP, and 3.9 gms. solvent were used in all studies. A total of approximately 25 sample mixtures and slurries were prepared. The samples were then sealed under an argon atmosphere in a polyethylene capped glass vial. After approximately six months, the methylene iodide - WP Pluronic P104 mixtures were all liquids. The solubility of WP in methylene chloride is relatively low and tests using this solvent were discontinued after two months. The carbon bisulfide-WP mixtures became solid after about three to four months. In this case, it is possible that the solidification of CS_2 - WP was caused by the permeability of CS_2 through the polyethylene cap with consequent evaporational loss of the carbon bisulfide. The results of this long term storage program indicate that the methylene iodide - WP mixtures are stable liquids.

The upper limit which should be set on TOP value available from a slurry was not determined. This is primarily a matter of freezing-point optimization. However, a reasonable educated estimate would be about 3200. Exploration of additional slurry stabilizers should be performed on a systematic basis. One advantage of using a stabilized slurry is that the specific gravity of the slurry mix can be adjusted to operational systems requirements for specific missions. These

slurries can be improved in TOP by a number of means, one of which would be the incorporation of phosphorus in a phosphorus alkyl base liquid. Work in this area, which is reported in the smoke agent literature, is limited to plasticized white phosphorus PWP, but, from DRI experiments, it is believed that advanced smoke agents may be developed using stabilized phosphorus slurries.

d. Phosphorus Sulfides

A relatively complete series of TOP measurements were taken with the phosphorus sulfides. The compounds examined were phosphorus trisulfide, phosphorus pentasulfide, and phosphorus sesquisulfide. It was reported that these compounds would burn to produce a mixture of P_2O_5 and SO_2 . These products would then be expected to result in a higher TOP value than would be expected considering the phosphorus weight. Under the conditions of the experiment, this was not observed (Figure 36). Instead, the appearance of a stable liquid layer was observed to form during the combustion process. It was assumed that this was liquid sulphur because of its color and freezing point. Curves showing the percent transmission vs. weight for this system are contained in Figure 37. The data obtained indicated that the burning rates of these compounds can be controlled with the possibility of reducing pillaring effects characteristic of white phosphorus smokes. These compounds are solids and, therefore, further work was discontinued since the development of liquid agents was the objective of this research. With the exception of examination of EWP mixtures, no attempt was made to dissolve these compounds into selected liquids.

e. Methylene Iodide - WP Solutions (MIP)

One approach to increase phosphorus content of a smoke agent has been to try to dissolve high weight concentrations of phosphorus in a solvent. The problem with this approach is that with the exception of carbon disulphide, the solubility of phosphorus in most common solvents is too low for an effective smoke agent. Since it would be desirable to find other liquids which might also act as suitable solvents for phosphorus, an analytical approach was developed to predict possible new solvents for phosphorus. The analysis was based on theoretical work involving the theory of regular solutions as developed by Hildebrand et al. for non-associated liquids. The central parameter in this theory involves the internal cohesive energy at constant volume, which is also commonly denoted by the term "solubility parameter". Using this theory, calculations indicated that three compounds 1, 2 Dichloroethane,

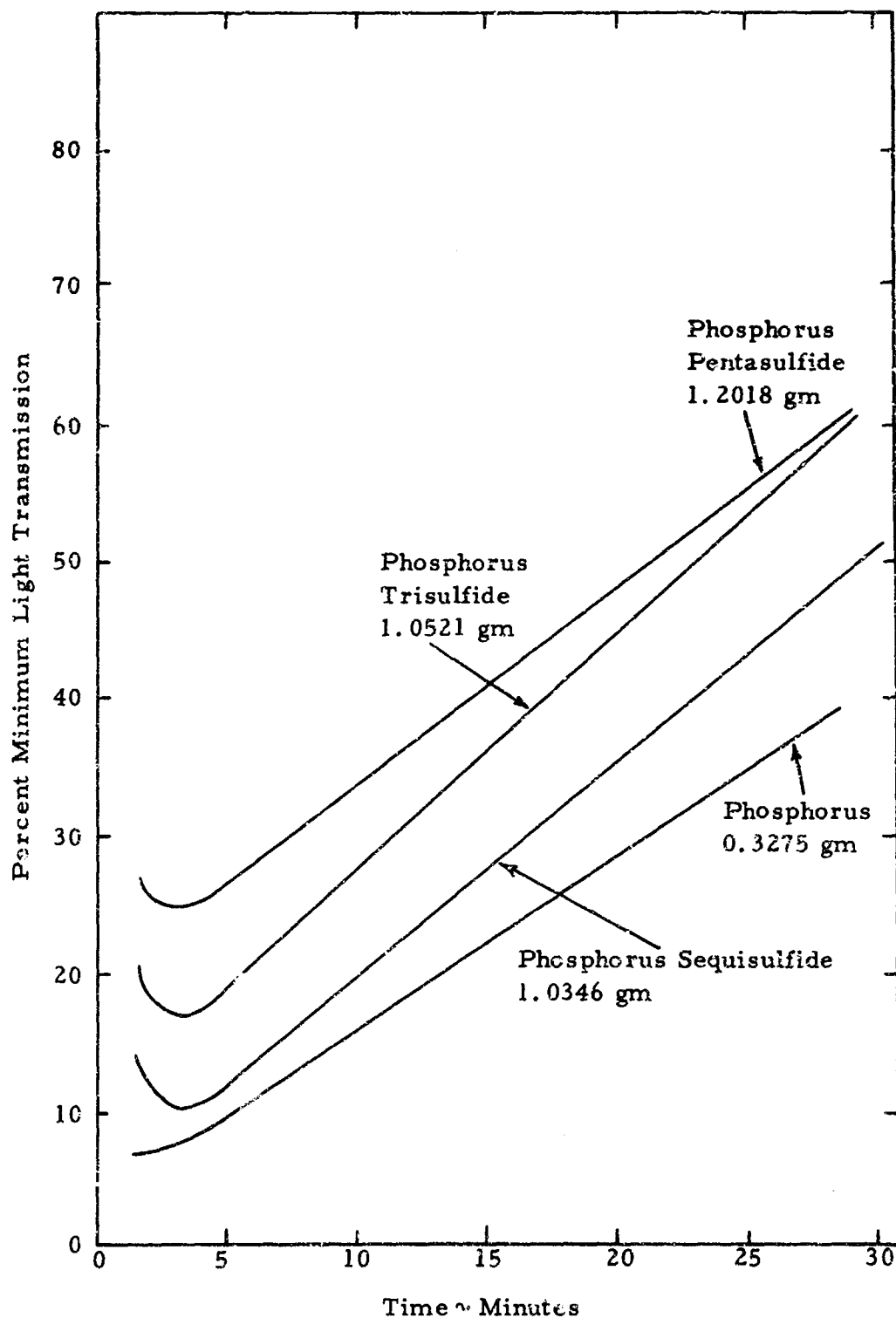


Figure 36. Transmission Persistency Data for Phosphorus Sulfide Smokes

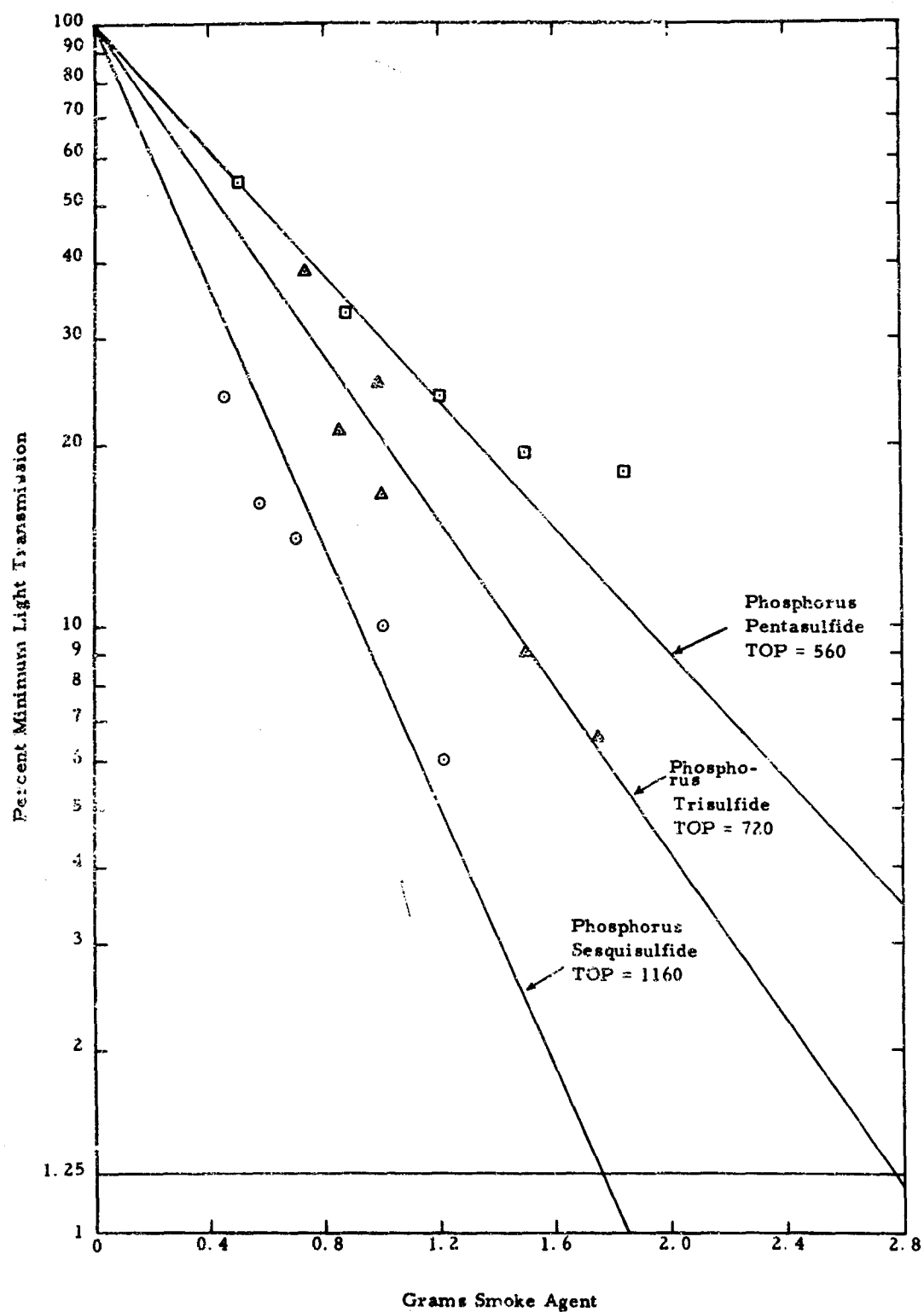


Figure 37. Transmission Data for Selected Phosphorus Sulfide Compounds

methylene iodide, and bromoform might dissolve appreciable amounts of phosphorus. The best solvent of these three was predicted to be methylene iodide. This prediction has been verified by experiment and a mixture of phosphorus in methylene iodide was tested in the smoke chamber. Upon ignition, the TOP value of this mixture was about 2800. Two difficulties are that the freezing temperature of methylene iodide is about 0°C , which is too high for use as an operational smoke agent and an ignitor is necessary. However, a mixture of MIP and EWP has much better physical properties for military application. These mixtures are discussed in other portions of this report. It has been demonstrated, however, that this analytical approach can predict the solvolysis capability of potential solvents for phosphorus, and therefore, possibly a new smoke agent may more easily be developed. Chemical solvents which are predicted to have some merit, although less solubility, are methylene bromide and its derivatives.

Additional experimental work was performed using methylene bromide, methylene chlorobromide, and methyl dichlorosilane as possible solvents for white phosphorus, and mixtures were made of each potential solvent with 30 percent white phosphorus. Methylene bromide and methylene chlorobromide proved to be relatively poor solvents for the phosphorus, but two smoke chamber runs were made on each solution. The results indicate that the smoke contribution was made almost entirely by the phosphorus contained in the solution. Since the previously tested CH_2I_2 - white phosphorus solutions were quite successful as smoke agents, it was felt that SiH_2I_2 would be analogous to CH_2I_2 , and, therefore, might be a promising solvent for phosphorus. Since SiH_2I_2 was not readily available, methyl dichlorosilane was used as a substitute. A mixture was prepared and tests were run in the smoke chamber. The data produced by these runs indicate a TOP value of 260. This TOP is approximately an order of magnitude less than the reported value for methylene iodide - phosphorus and is, therefore, not satisfactory for meeting the program's objectives. Additional work in this area should be continued to evaluate SiH_2I_2 , specifically, and to further understand the mechanism of dissolution of phosphorus in general.

f. Mixed Smoke Agents Based on MIP and EWP (MIPEW)

A series of experiments were performed to determine the feasibility of using mixed smoke agents consisting of mixtures of phosphorus-methylene iodide (MIP) and/or EWP - with FM and fog oil. Earlier work had indicated considerable reaction was present when phosphorus

was placed directly into FM. Similar reactions were expected, but not found for mixtures of FM with MIP and EWP. Both EWP and MIP were compatible with FM under the conditions of study. Probably because of a marked density difference between MIP and FM, mixtures of these two agents consisted of a two-phase liquid system. Similar results were observed for mixtures of FM-EWP even though the density difference is much less. Mixtures of EWP with alpha methyl naphthalene, and neutral solvent #75, and MIP with these same fog oils were made. Again, due to large differences in density, a two-phase liquidus system was formed in both the above cases as well as for 50/50 mixtures of mixed fog oil--EWP-MIP. Characteristically, the organic solvents tended to activate ignition of the phosphorus based compounds. It is probable that the smoke observed was principally a phosphorus smoke with little, if any, fog oil produced.

Mixtures were made of EWP and MIP, ranging from 50 percent of each by volume, to approximately 12 percent MIP and 88 percent EWP. These mixtures were completely miscible under all conditions. The MIP substantially depressed the pyrophoric ignition of EWP. Typical results for these mixtures was the nonspontaneity of pyrophoric combustion of 50/50 mixtures placed outdoors in a small ceramic dish for periods of several hours. Tests which were performed in both the direct sunlight and shade, while not consistent, were also negative in terms of pyrophoric combustion. A second type of experiment in which the same mixtures were ejected from a spray nozzle onto a rough wood surface resulted in spontaneous combustion after a period corresponding to two to three minutes.

Evidently, for mixtures of EWP and MIP, the reactivity is considerably suppressed by the addition of methylene iodide. Mixtures were made of FM and several MIP-EWP solutions. Apart from a phase separation, these mixtures were relatively good smoke agents. In all cases, the burning of the MIP or EWP was delayed until substantially all of the FM had evaporated--a period of several minutes. Although the smoke TOP values were not evaluated directly, it can be assumed that TOP values range from somewhat higher than FM and somewhat lower than EWP or MIP. A mixture of EWP-MIP with FM would appear to be a possible compromise if suitable stabilization of the FM-EWP-MIP liquid phases could be achieved via emulsification or slurring. The possibility of dissolving WP into a fluorocarbon oil was briefly investigated. Two oils, Freon 113 and Freon 112, were used. Although slight solubility was observed, the results were negative for a smoke agent purpose. A mixture of MIP-EWP has considerable potential as a

good smoke agent. The effect of MIP addition is to strongly suppress the pyrophoric ignition of EWP. Optimization should be made between ignition delay and ease of operational handling. An additional study should be implemented to determine the effectiveness of water or FM suppression under airborne dispersement conditions.

6. Corrosion Testing for FS, MIP and EWP Smokes and Liquid Agents

A study of the corrosive effects produced by candidate smoke agents was performed. This study was designed to compare the corrosive effects of promising smoke agents on various materials with the effects caused by the standard smoke agent, FS, under similar test conditions. The principle emphasis was to evaluate corrosive effects on several common metals and to determine the reduction in tensile strength caused by exposure of nylon and other materials. Corrosivity testing concentrated on establishing relative data concerning the corrosive effects of the produced smoke. The conditions of test were chosen to be twelve hours at seventy percent minimum light transmission in the small chamber (6 cubic feet). Additional tests have been performed for liquid agent effects on selected steels. No adverse effects were found for phosphorus-based liquid agents under the conditions studied.

a. Liquid Corrosion Studies

A series of experiments were designed to determine the extent of storage and handling problems for the methylene iodide--white phosphorus, and EWP smoke agents. For this purpose, the principal objective was to establish whether these agents were compatible in the liquid state with common storage container steels. The procedures used were to seal up the agents in 1/4-inch tubes and periodically break open the container and examine for corrosion defects. Both EWP and CH_2I_2 -WP mixtures were compatible with the mild and hard steels used. The maximum storage period was eight weeks after which no detectable difference between control and agent vessels could be determined by either visual macroscopic or microscopic observations. Similar work with plastics was not undertaken.

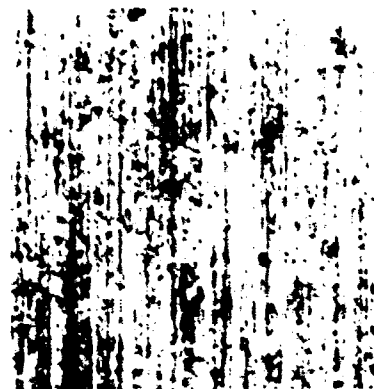
Accelerated storage data at 150°C was attempted but discontinued due to difficulties in keeping constant temperature profiles using available equipment. It was concluded from these studies that no significant container compatibility problems are anticipated if common mild steel containers are used.

b. Corrosive Effects Produced by Smokes from Candidate Agents

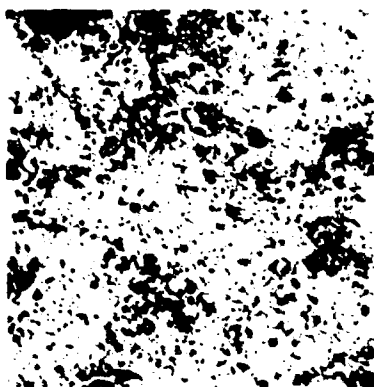
A group of hard test specimens has been fabricated from 1020 cold rolled steel, 6061 aluminum, magnesium alloy, and plexiglas. These specimens were designed to give an indication of the optimum size and shape for this particular corrosion study. The above materials were selected to correspond to the most commonly used materials for military purposes. The data is of both a qualitative and quantitative nature. Quantitative data which was analyzed includes surface profile, surface pitting, weight loss, and corrosive effect on the tensile strength of the test specimens. Three sets of specimens were exposed to FS, WP + Methylene Iodide, and EWP smoke agents (one set of specimens per smoke). These exposure tests were conducted in a closed environmental test chamber with a heavy concentration of smoke for a duration of twelve hours. Figures 38, 39 & 40 illustrate a comparison between control specimens and the surface corrosion exhibited by 6061 aluminum, magnesium alloy and plexiglas as a result of the twelve hour exposure. The 1020 steel specimens are not illustrated but had a severe rusting and staining condition.

Figure 38 illustrates the corrosive effect of FS on the specimens as indicated. It can be seen that mild surface corrosion has occurred on all of the materials. Of the three specimens, aluminum is apparently the most corroded and plexiglas the least. The specimens illustrated in Figure 39 indicate the corrosive effect of WP + Methylene Iodide. Again, aluminum appears to be the most highly corroded specimen. Large pitting has occurred over the entire surface of the specimen. The least affected material of this group appears to be the magnesium alloy, although some definite small pits have developed over the entire surface. The corrosivity of FS is much greater than either of the two smoke agents studied for all metals. There is no indication in the present studies that a weakening of metal via an interstitial lattice defect mechanism involving phosphorus or phosphorus iodide migration occurs.

Figure 40 illustrates the effect of EWP smoke agent on these various materials. The plexiglas has evidently sustained the highest degree of corrosion of any in this set, as large pits can be seen in the picture of the exposed specimen. Pitting has also developed in the magnesium alloy specimen, but to a lesser degree. The aluminum specimen appears to indicate very little corrosion as a result of its exposure to EWP.



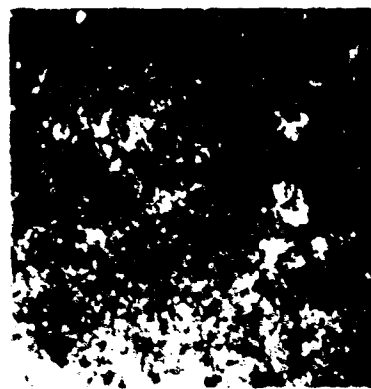
6061 Aluminum
Control Specimen X100



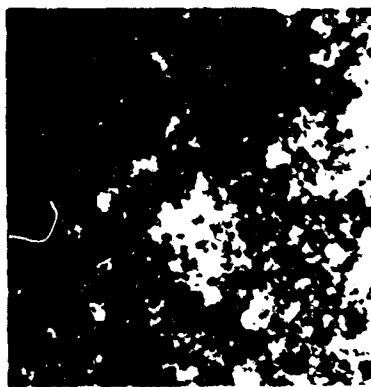
Magnesium Alloy
Control Specimen X100



Plexiglas
Control Specimen X100



6061 Aluminum
Test Specimen X100



Magnesium Alloy
Test Specimen X100

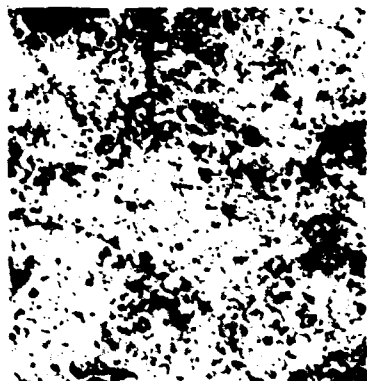


Plexiglas
Test Specimen X100

Figure 38. Twelve Hour Test Illustrating Corrosive Effects of FS on 6061 Aluminum, Magnesium, Alloy, and Plexiglas Specimens



6061 Aluminum
Control Specimen X100



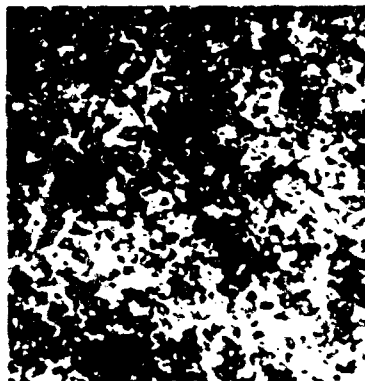
Magnesium Alloy
Control Specimen X100



Plexiglas
Control Specimen X100



6061 Aluminum
Test Specimen X100



Magnesium Alloy
Test Specimen X100

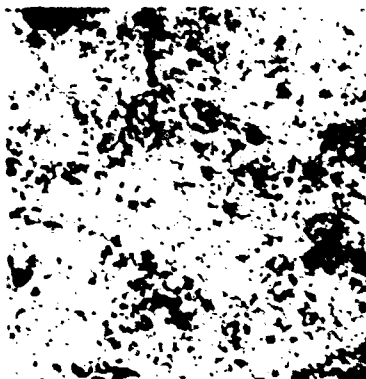


Plexiglas
Test Specimen X100

Figure 39. Twelve Hour Test Illustrating Corrosive Effects of MIP on 6061 Aluminum, a Magnesium Alloy, and Plexiglas Specimens



6061 Aluminum
Control Specimen X100



Magnesium Alloy
Control Specimen X100



Plexiglas
Control Specimen X100



6061 Aluminum
Test Specimen X100



Magnesium Alloy
Test Specimen X100



Plexiglas
Test Specimen X100

Figure 40. Twelve Hour Test Illustrating Corrosive Effect of EWP on 6061 Aluminum, a Magnesium Alloy, and Plexiglas Specimens

In addition to the hard specimens, parachute weight nylon fabric, fatigue uniform cotton fabric, and butyl rubber were exposed to the smoke, simultaneously with the hard specimens. The nylon fabric tensile strength tests indicate that approximately 90% degradation in tensile strength occurred in the specimens which were exposed to FS smoke, 65% degradation of those specimens which were exposed to WP + Methylene Iodide smoke, and 55% degradation of those specimens which were exposed to EWP smoke. The tensile strength tests which were conducted with the cotton fabric indicated 95% degradation of those specimens exposed to FS smoke, and no degradation whatsoever to those specimens which were exposed to both WP + Methylene Iodide and EWP smoke. The specimens fabricated from butyl rubber exhibited no degradation at all as a result of exposure to any of the smokes used in the experiment. It is obvious that the most severe degradation of the nylon and cotton fabrics results from exposure to FS smoke. The degradation of nylon caused by exposure to WP + Methylene Iodide and EWP smokes is considerably less, and non-existent in respect to cotton fabrics.

V. FIELD TESTING

To further evaluate selected smoke agents, a series of airborne dispersement tests were conducted. The selection of specific smoke agents for these tests was based on their relative promise in terms of obscuration power or handling properties. A rating system to determine which agents should be selected for this purpose is outlined in the section on engineering systems studies. The agents selected were FS as a standard, Mixture 90622T, EWP, and MIP. Other agents which would be desirable to test but were not available in sufficient quantity include the phosphorus alkyl derivatives and mixtures of MIP-EWP. The tests were performed between 1/10 to 1/20 scale of full size tankage - the exact scale size being determined by smoke agent availability.

A. Test Wing

A facility to simulate airborne dispersement was fabricated. This facility consists of an F-86 wing section which is "flown" by a cable drop technique with appropriate tankage fastened below. The maximum speed of operation is estimated to be about fifty MPH which could be increased substantially by rocket thrust augmentation.

This facility uses a small smoke tank simulating a 1/8 scale model of the E39R1 tank. This facility was developed for field testing the obscuration characteristics of the selected smoke agents and to provide a means for studying possible improvement of dissemination techniques.

In preliminary tests, the experimental tank was fabricated from polyvinyl chloride. This material was selected because of its inertness to acids, such as those found in several of the smoke agents, and easy workability. This tank was cylindrical in shape, approximately 6-1/2 inches in diameter and 18 inches long. The ends are sealed with plate glass which is explosively destroyed to allow dissemination of smoke agent during smoke run. The tank was secured to a 6-foot wing section from a surplus F-84 aircraft which was fastened to a four-inch channel iron frame support structure. During the latter phases of field testing, a different design was used in which the smoke agent was placed in a mild steel tank constructed of 1/16-inch plate, and a mechanical release mechanism was employed to eliminate a possible ignition source, such as a blasting cap. Outflow was through a series of 1/2-inch parts in the bottom of the tank which had been covered with tape or similar material. The complete wing-tank unit is suspended by a trolley-type

carriage assembly from a 3/8-inch wire cable having a length of approximately 500 feet and a slope of 10 degrees. For a test run, this unit was allowed to drop from the higher elevation to the bottom where it encountered a braking device. The whole assembly could move freely on the cable on low friction support wheels. The cable was suspended from two anchor posts one at the top and one near the bottom of a steep hill. The top post was anchored using a 2-1/2-ton truck as a dead man.

The bottom post consisted of a heavy gage steel pipe sunk deeply into the ground. Tension on the cable was maintained by using the truck as a power wench. The use of the hillside allowed a rise angle of approximately 10-15 degrees. Wing flight velocities were estimated from camera records to be approximately forty to fifty miles per hour. The simulated flight apparatus was stopped using a series of four to six one-half-inch nylon ropes which were attached to two heavy automobile front wheel springs, in turn bolted to two fourteen-foot railroad ties. The stopping distance was about 10 to 15 feet and the damage to the hardware was modest for most runs. A picture of the simulated airborne dispersal facility is given in Figure 41. Several tests were run testing this facility with moderate to good success for each test performed. During the preliminary runs, it was intended that the tank be filled with plastic spheres, evacuated, filled with smoke agent materials, and placed in position for the run. A materials incompatibility problem developed during the loading operation in the first attempt to make a test run and the test was aborted. The incompatibility is thought to have existed between the FS and the plastic spheres, although preflight tests of these materials indicated that they were compatible enough to be used in the prescribed manner. Subsequent runs were performed successfully without the plastic spheres. Because the flight altitude was low (50 feet) a satisfactory dispersment of smoke agent to ground level was obtained for all tests.

B. Field Tests

A series of tests were performed using this test wing. The purpose of these tests was to evaluate field handling techniques for selected phosphorus mixtures and solutions and to obtain documentary evidence relating to the obscuration characteristics of these agents under simulated field conditions. Documentation of the relative obscuring power and smoke effectiveness, in this case, relied on 16 mm film coverage. Four agents were tested (1) a methylene iodide - white phosphorus solution, (2) a eutectic mixture of phosphorus and phosphorus



a. Wing Assembly



b. EWP Run 1



c. EWP Run 2

d. EWP Smoke Screen

Figure 41. Airborne Dispersement of Smoke Agents I, EWP

sesquisulfide, (3) Ethyl Smoke Agent 90622T, and (4) FS. In general, these tests showed that the light attenuation and cloud reflectance effects are important to the effectiveness of a smoke screen. The reflectance of phosphorus based smokes was quite pronounced.

1. FS

FS was used as a standard for comparison. Results of a typical smoke run for FS are given in Figure 42. This smoke is characterized by good persistence, by the obscuration of factiveness, is not as high as for white phosphorous smokes. In part, this may be due to the high reflectivity of phosphorus smokes.

2. Eutectic White Phosphorous

EWP provided by far the most opaque smoke cover. A literal wall of smoke was obtained for each of three tests. This agent is pyrophoric and, therefore, may be somewhat difficult to handle under field conditions. However, it can be handled with reasonable ease under water. This agent tended to burn about twenty and forty feet from the tank. This could be corrected, in part, by use of aluminum spheres or similar techniques, or by the development of combustion inhibitors to control burning of the EWP. Photographs of this agent, showing a dispersal run and the cover produced are given in Figure 41.

3. TEA Mix 90622T

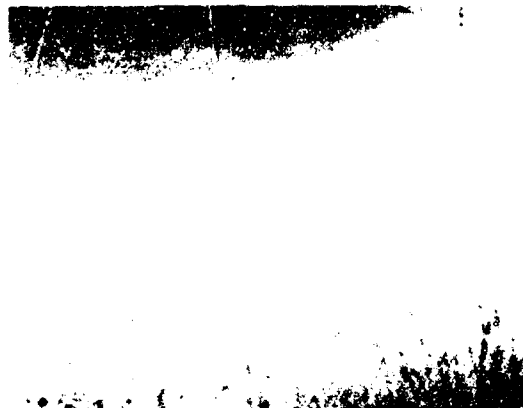
Ethyl Mixture 90622T did not provide a good smoke. The low TOP values observed during laboratory tests were confirmed and, in addition, this agent was pyrophoric when dispersed under these experimental conditions. There is no possible ignition source in this cable drop test which could cause secondary ignition of the agent. The pyrophoricity of MX 90622T is apparent from the fire appearing near the ground in Figure 43. The persistence of this agent was poor as is shown in Figure 42.

4. MIP

The best smoke cover was provided by a solution of methylene iodide in white phosphorous. Under these experimental conditions of test, an intense cloud was produced along the line of dispersement rising to a height of about 20 feet. Ignition of the agent was delayed until about



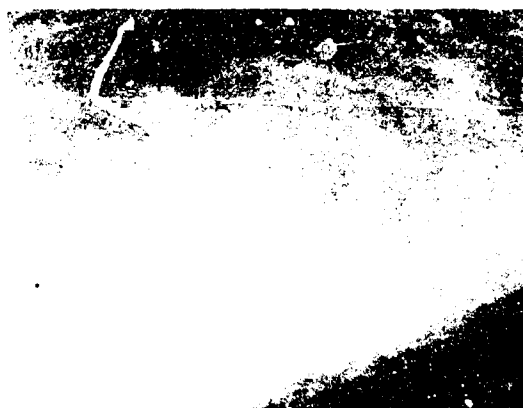
FS Smoke Run



FS Smoke Screen



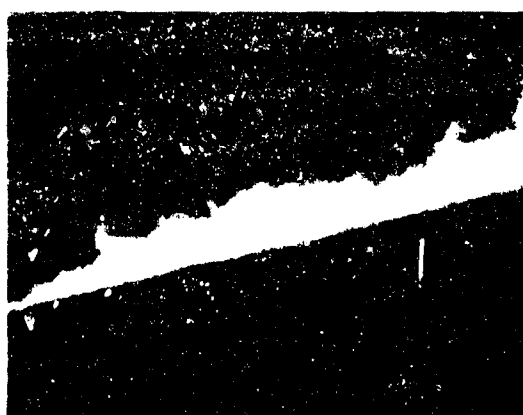
TEA Smoke Run



TEA Smoke Screen



MIP Smoke Run



MIP Smoke Screen

Figure 42. Airborne Dispersement on Smoke Agents II, FS, MIP, and TEA MIX



**Figure 43. Illustration of the Pyrophoricity
Exhibited by TEA MIX During an
Airborne Dispersement Run**

two-three minutes after ground contact, even though it was finely atomized by the outflow from the airborne tank. A picture of a typical dispersement run is given in Figure 42. It is apparent from this photograph that combustion of the agent does not occur in the air. The smoke produced was not irritating and was highly persistent. Field handling procedures used for this work used a water displacement technique to aid in loading of the tankage. Use of an inert gas blanket to control the pyrophoricity was not necessary with this agent during field operations.

5. Summary

Both EWP and MIP produced as good or better smoke screen cover as FS. Handling problems are relatively minimal in both cases; however, MIP is probably the easier to handle under field conditions. TEA mix did not produce as good smoke as FS. While somewhat easier to handle than EWP or MIP, the TEA mixture was pyrophoric under experimental conditions and initiated a ground fire. Results of tests to date indicate that a mixture of EWP and MIP should be evaluated.

VI. LITERATURE SURVEY

Introduction

A review of the literature has been performed as part of this research program. The purpose of this review is to establish families of chemical compounds that offer the greatest promise for further development of future smoke agents for delivery by air craft. The principal criteria used to evaluate possible smoke agents are:

1. that they be liquids or slurries capable of dispersement from an airborne smoke tank under normal operating conditions,
2. the produced smoke have an obscuring power approximately equal to FS,
3. the smoke produced be less corrosive and less irritating than FS,
4. the toxicity of the produced smoke be negligible and the toxicity of the agent itself be low,
5. the flash point of the agent be high.

In this section, a series of tabular sheets are presented listing the properties of the smoke agent and the properties of the produced smoke. Included in the properties of the smoke agent are chemical composition, molecular weight, boiling point, freezing point, density, viscosity, flash point, heat of vaporization, toxicity, compatibility with metals and plastics, stability, and the mechanism by which the aerosol smoke particles are produced. Included in the properties of smoke is the obscuring power, persistence, toxicity, corrosivity, and other data where applicable. The data listed was obtained from a variety of sources and, in some cases, includes the results of experimental findings made during this research program. A reference bibliography is provided at the end of this report covering reference material used in this and in succeeding sections.

The number of chemicals which have been tested and found to be capable of producing white smoke is both large and varied. It is thus necessary to divide these chemicals into separate categories in order to more clearly discuss their relative merits. Any such classification must be somewhat arbitrary, and numerous exceptions must be expected because sharp distinctions cannot always be drawn between chemical

types, and because, in some important cases, two or more chemical agents may be incorporated into a single smoke agent to provide a more suitable military agent. The discussion in this section covers all of the chemical agents known to the authors which have been used to any appreciable extent for military operations requiring liquid smoke agents. The literature surveyed consists principally of that associated with technological developments of the United States, Britain, and Soviet Russia.

General

White smokes can be produced using a variety of chemical compounds and reaction mechanisms. Generally, smokes can be prepared in two ways, (1) condensations from the gas phase, and (2) by break up and dispersion of a bulk phase. Most smoke producing mechanisms are based on the first method. For the purpose of this report, the mechanisms for producing smoke are classified in the following ways: (1) hydrolysis of a metal chloride or a sulfur oxide derivative, (2) the oxidative burning of a fuel with air to produce either an aerosol particle or a particle which is highly hydroscopic, (3) the formation of particles via other chemical reaction in the gas phase, (4) the vaporization and recondensation of a fog oil, (5) the dispersion of solid particles. Because of considerations involving logistic efficiency, it is important that maximum effect be obtained on a per-unit-weight or per-unit-volume basis. On a weight basis, the relative effectiveness of different smoke agents is rated in terms of TOP or total obscuring power. For volume limited situations, it is also useful to define a similar quantity relating the TOP and fluid density. Thus, a volume obscuring power (DOP) is defined as the total obscuring power of the agent multiplied by its specific gravity.

A difficulty arose in describing the compatibility and corrosive character of the smoke agents and the produced smoke. The difficulty, in this case, is caused by the need to quantify the relative corrosivity of the smoke agents for the purpose of establishing whether common materials of construction would be severely affected by contact with these agents. The principal materials of construction considered were aluminum, mild steel, copper, rubber, and type plastics. For many of the agents and smokes described in the literature, little or no detailed data was found describing tests relating the problem of corrosion for simulated environmental conditions encountered during appropriate extended

military operations. Since it was difficult to assign a meaningful quantitative value that would have the same basis for all the agents considered, the corrosivity and capatibility of the agents and smokes are, therefore, described in qualitative terms, such as, moderate, or good. The guiding principle used for this assignment is whether it might reasonably be expected that common materials of construction could be used for the necessary hardware required to ship, store, and disseminate the agent under operational conditions. A similar criterion was applied to the produced smoke where it was necessary to evaluate whether or not severe corrosion would occur to Army field equipment. For a few selected agents, a series of experimental tests were performed to systematically evaluate these effects on a common basis. Results of the tests performed under this contract are described in the latter sections of experimental testing procedures.

A. Hygroscopic Chemical Smoke Agents

Many of the important smoke producing chemical agents depend on a reaction mechanism in which the agent vapors react with atmospheric moisture to produce aerosol particles. These particles contain many times the original weight of the agent in the form of the chemically bound water. A direct correlation exists between the heat of hydration for these agents and their ability to produce an effective smoke. A similar correlation should exist relating the surface energy to smoke obscuration characteristics through a surface-free energy function. However, probably because of the difficulty in measurement, this latter parameter is not discussed in the smoke literature and it is assumed that dilute acid particles possess similar surface energies which are not strongly dependent on the chemical composition of the solute. Among the chemical agents which depend upon hydrolytic action for their smoke effectiveness are the many inorganic chlorides and derivatives of sulfuric acid. Inorganic chlorides which have been used for liquid smoke agents include titanium tetrachloride, silicon tetrachloride, and stannic chloride. Compounds or mixtures containing the oxides of sulfur which have been used for this purpose include sulfur trioxide, chlorosulfonic acid, and oleum. A solution of 55 percent SO_3 with 45 percent by weight chloro-sulfonic acid is widely used as a standard smoke mixture known as FS. Both the sulfur derivatives and the inorganic chlorides have been used as part of a dual smoke agent system in which ammonia or amine derivatives are used to either neutralize the acid produced during the hydrolysis and thus reduce corrosivity and irritation factors, or to form an ammonium chloride solid particle aerosol. A brief discussion of these hygroscopic smoke agents is given in the following sections.

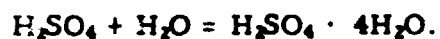
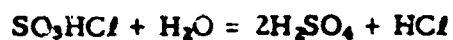
1. Chemical Smoke Agents Based on the Hydrolysis of Sulfur Compounds.

a. FS

In this class of compounds, the principle smoke agent of military use is FS. FS consists of a mixture of chloro-sulfonic acid and sulfur trioxide. Each of these components can individually produce an effective screening smoke, but the mixture offers the advantage of improved physical properties. The TOP value for SO_3 is approximately three times greater than that of HClSO_3 and is, therefore, the principle effective agent. In the presence of water, this agent rapidly forms sulfuric acid which is extremely corrosive to most metals. Strong materials degradation effects are also observed, both for the agent and the produced smoke, when in contact with most plastics including several types of polyethylene. FS can be dispersed by mechanical atomization, thermal vaporization, or simple evaporation. It can be disseminated from aircraft spray tanks to produce either an aerial or a ground based smoke screen. To produce a ground level smoke screen, hollow aluminum spheres are used to transport the agent from flight altitude to ground level. Upon impact, these spheres break open to release the agent which then disseminates by evaporation from the ground spill. The smoke consists of droplets of dilute sulfuric acid admixed with dilute hydrochloric acid, and is corrosive to anything affected by these compounds. The smoke is not toxic but is quite irritating to the mucuous membranes and lungs. In any appreciable concentrations, considerable gagging occurs, probably caused by unreacted sulfur trioxide. If no moisture is present FS is not corrosive to most metals of construction. Because of its strong dehydration and oxidation capability, severe skin burns are obtained upon contact with the liquid agent. Although the 45% chloro-sulfonic acid - 55% sulfur trioxide solution is used by the U. S. Army, mixtures up to 65% sulfur trioxide still freeze at relatively low temperature. These mixtures do not form a simple solution, but rather tend to be two separate compounds with empirical formulas $\text{SO}_3 \cdot \text{HSO}_3\text{Cl}$, and $2\text{SO}_3 \cdot \text{HSO}_3\text{Cl}$.

The standard 45%-55% mixture used by the U. S. Army has a -80 degree freezing temperature if chemically pure, but because the technical grade materials in its production contain a small amount of sulfuric acid and other degradative reaction products (three and seven percent), the freezing temperature is raised substantially.

The mechanism by which this agent produces smoke is the formation of dilute sulfuric acid upon hydrolysis with atmospheric moisture. The overall chemical equation is given by:



Two data sheets are listed for FS, one corresponding to the mixture used by the U. S. Army, and the second corresponding to the properties of the agent reportedly used by the Russian Army in World War II.

Smoke Producing Chemical Data Sheet FS

(U.S. Army)

I. Properties of the Smoke Agent

A. Composition:	45% HClSO_3 ; 55% SO_3
B. Molecular Weight:	N/A
C. Boiling Point °C:	62°C
D. Freezing Point °C:	-79°C
E. Density gm/cc:	1.8976
F. Viscosity, cp:	.060 poise (25°C)
G. Flash Point °C:	N/A
H. Heat of Vaporization:	--
I. Toxicity:	Severe Burns
J. Compatibility:	
Metals:	Moderate Corrosion - High Corrosion in presence of water
Plastics:	High
K. Stability:	Good
L. Mechanism for Producing Smoke:	
	$\text{HClSO}_3 + \text{SO}_3 = \text{H}_2\text{SO}_4 + \text{HCl}$
	$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{Hydrated Sulfuric Acid Droplets}$

II. Properties of the Smoke

A. Obscuring Power:	High (TOP 2500) (DOP 4744)
B. Persistence:	Good
C. Toxicity:	Limited
D. Corrosivity:	High
E. Remarks:	Standard Military Smoke
F. Irritation:	High

Smoke Producing Chemical Data Sheet FS

(Russian Army)

I. Properties of the Smoke Agent

A. Composition:	40% SO ₃ ; 60% HClSO ₃
B. Molecular Weight:	--
C. Boiling Point:	88°C
D. Freezing Point:	-83.6° C
E. Density:	1.844 gm/cc
F. Viscosity:	--
G. Flash Point:	N/A
H. Heat of Vaporization:	--

Other properties of the agent and the smoke are similar to those previously listed.

b. Oleum

Oleum is a mixture of SO_3 in H_2SO_4 . Liquid sulfur trioxide is miscible in all proportions with sulfuric acid and, thus, the composition and physical properties of oleum may vary through wide limits. The chemical characteristics of oleum are similar to those of sulfur trioxide. Although SO_3 is miscible in all proportions with sulfuric acid, there are two eutectic melting points on the melting point diagram. These points are located at -14.3 and 0.1 degrees C. In addition, there exists a dystectic point corresponding to a 50-50 mole proportion indicating that the compound pyrosulfuric acid is formed. The technical mixture oleum probably consists of either a mixture of sulfuric and pyrosulfuric acids, or of pyrosulfuric acid with sulfur trioxide depending on the composition of the mixture used. Because of the relatively high melting point, substantial problems have resulted in applying this mixture to military uses. However, use of an oleum mixture having a high SO_3 content is not uncommon. The agent is dispersed in a similar manner as FS. The chemical reactions during smoke production are also similar and the smoke consists of "dilute" sulfuric acid droplets. Oleum is corrosive to most metals and is, therefore, usually stored in glass lined or stainless steel containers. The smoke is irritating but non-toxic. The major usage of the material for military smoke production occurs when supplies of other agents are limited. Oleum is a relatively common intermediate in the chemical industry production; therefore, large quantities can usually be obtained.

c. Sulfur Trioxide

Sulfur trioxide has been widely used for military screening smokes either directly or in conjunction with other chemical agents. Because of its relatively high melting point, SO_3 is usually incorporated into other agents to provide a suitable liquidus range. A solution of sulfur trioxide in sulfur dioxide and carbonic acid was used during World War I, and solutions of sulfur trioxide in chlorosulfonic acid and sulfuric acid have been described in the preceding sections. As a smoke agent, the pure material has a TOP of about 3000 as compared to FS at 2500. The agent is commonly dispersed by thermal vaporization or mechanical atomization. The chemical action of this agent is the production of sulfuric acid upon contact with atmospheric moisture. The dispersed acid particles then absorb more water to produce a cloud consisting of "dilute" sulfuric acid particles. The liquid agent itself, if dry, does not attack most metals, but will cause severe corrosion and

burns to personnel. The smoke is highly irritating but non-toxic. When liquid or solid sulfur trioxide is put into water, a violent thermal reaction occurs. Due to its affinity for water, sulfur trioxide acts as a strong dehydrating agent on plant and animal tissues and, therefore, special precautions must be taken in working with this substance.

Smoke Producing Chemical Data SheetSulfur TrioxideI. Properties of the Smoke Agent

A. Composition:	SO ₃
B. Molecular Weight:	80.06
C. Boiling Point °C:	44.6
D. Freezing Point °C:	16.83
E. Density gm/cc:	1.923 (α modification)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	118.5 (15°)/g(53°C)
I. Toxicity:	8 hr. exposure - /mg/m ³
J. Compatibility:	
Metals:	Moderate Corrosion - High Corrosion in presence of water
Plastics:	High Corrosion
K. Stability:	Gas at Moderate Temperatures
L. Mechanism for Producing Smoke:	
SO ₃ + H ₂ O	= H ₂ SO ₄
H ₂ SO ₄ + H ₂ O	= Hydrated Sulfuric Acid

II. Properties of the Smoke

A. Obscuring Power:	(TOP 3000) (DOP 5769)
B. Persistence:	Good
C. Toxicity:	Low
D. Corrosivity:	High
E. Remarks:	Base for FS Smoke
F. Irritation:	High

Smoke Producing Chemical Data Sheet

Sulfur Dioxide

I. Properties of the Smoke Agent

A. Composition:	SO ₂
B. Molecular Weight:	64.06
C. Boiling Point °C:	-10.0
D. Freezing Point °C:	-75.5
E. Density gm/cc:	liq. 1.434(0°) 2.264 (A)
F. Viscosity, cp:	0.4 (3°C)
G. Flash Point °C:	--
H. Heat of Vaporization:	91.3(15°)/g (0°C)
I. Toxicity:	50 - 100 p.p.m. Max. perm. amt. for 30 - 60 min. exposure 400 - 500 p.p.m. is immediately dangerous to life
J. Compatibility:	
Metals:	Moderate Corrosion
Plastics:	Degradation
K. Stability:	Good (Gas at room temperature)
L. Mechanism for Producing Smoke:	Used as modifier to Basic FS Smoke Agent

II. Properties of the Smoke (See FS)

A. Obscuring Power:	Only used in conjunction with other agents
B. Persistence:	N/A
C. Toxicity:	N/A
D. Corrosivity:	High
E. Remarks:	N/A
F. Irritation:	High

d. Chlorosulfonic Acid

Chlorosulfonic acid can be used either by itself, or in combination with other agents. Smoke is produced by hydrolytic action with atmospheric moisture to form sulfuric and hydrochloric acid particles. These particles then undergo further hydrolysis to produce stable dilute solutions. The smoke, therefore, is corrosive to anything affected by these acids. When used by itself, the TOP value of this agent is reported as 1400. The smoke is not toxic, but is highly irritating to mucous membranes and skin. Handling and storage problems for this agent are similar to those associated with the handling of FS. The density of chlorosulfonic acid is about 1.8, and the vapor pressure is given on the following data sheet. Upon heating this agent undergoes partial decomposition to form sulfuryl chloride and sulfuric acid, the back reaction does not readily occur with the resultant degradation of the material if stored at elevated temperatures. Many non-ferrous metals are directly attacked by this acid. These metals include lead, copper, and tin. For tin, the reaction is given by the equation:



Chlorosulfonic acid does not react with mild steel in the absence of water at normal storage temperatures, but does directly corrode ferrous materials at elevated temperatures. Chlorosulfonic acid acts as a powerful dehydrating agent on fabrics, woodfibers, leather, rubber, nylon, and plastics causing substantial carbonization. For this reason, special protective equipment must be provided for personnel protection against spills and mishandling. Industrial chlorosulfonic acid is usually black or brownish in color because of carbonization of organic impurities. The chemical composition of this technical grade material consists of 90 percent HSO_3Cl , 4 to 7 percent sulfuric acid, about 3 percent pyrosulfuric acid and sulfuryl chloride, and 1 percent sulfur trioxide. Chlorosulfonic acid is often used in combination with sulfur trioxide to form FS. The most efficient production of smoke using this combination depends on relatively complete thermal volatilization. This vaporization has been accomplished by injection into ships' smoke stacks and by chemical reaction with slaked lime, or in a mixture of $\text{SO}_3(\text{FS})$.

Smoke Producing Chemical Data Sheet

Chlorosulfonic Acid

I. Properties of the Smoke Agent

- | | |
|-----------------------------------|--|
| A. Composition: | HC/ISO ₃ |
| B. Molecular Weight: | 116.52 |
| C. Boiling Point °C: | 151.5 (765 mm) |
| D. Freezing Point °C: | -80 |
| E. Density gm/cc: | 1.787 (25°C)
$\delta_t = 1.7847 - 0.001615 + 1.21 \times 10^{-6}t^2 - 4.1 \times 10^{-9}t^3$ |
| F. Viscosity, cp: | 1.9 (50°C)
$\eta_t = 0.000698/v_t - 0.554$ |
| G. Flash Point °C: | -- |
| H. Heat of Vaporization: | 110.2(15°)/g (151°C) |
| I. Toxicity: | -- |
| J. Compatibility: | |
| Metals: | Does not act on ferrous metals in
absence of moisture, Pb, Cu,
Sn attacked |
| Plastics: | Degradation of plastics occur |
| K. Stability: | Good |
| L. Mechanism for Producing Smoke: | Used in a 40 to 60 percent mixture with sulfur trioxide
principally to lower the freezing point of the mixture. |
| M. Vapor Pressure: | $\log P = 7.6401 - \frac{2101.8}{T}$ |

II. Properties of the Smoke

- | | |
|---------------------|--------------------------|
| A. Obscuring Power: | (TOP 1400)
(DOP 2502) |
| B. Persistence: | Good |
| C. Toxicity: | Low |
| D. Corrosivity: | High |
| E. Remarks: | -- |
| F. Irritation: | High |

e. Sulfuryl Chloride and Pyrosulfuryl Chloride

Sulfuryl chloride is similar to chlorosulfonic acid and sulfur trioxide and is handled and dispersed using the same techniques and equipment as these other materials. It reacts with atmospheric moisture to produce a smoke composed of a combination of sulfuric, sulfurous, and hydrochloric acid droplets. Sulfuryl chloride can be considered to be chemically similar to sulfur trioxide in which one of the oxygen atoms has been replaced by two chlorine atoms. Similarly, pyrosulfuryl chloride can be considered as a chlorinated dimer of sulfur trioxide. The reported TOP of this agent is about 1200 which represents a smoke value about equal to the better oil fogs. Sulfuryl chloride has been characterized as possessing a gagging effect when inhaled. When heated, sulfur dioxide decomposes to sulfur dioxide and chlorine. At ordinary temperature it does not affect ferrous materials, but causes extensive corrosion if moisture is present, or at elevated temperatures. Similar behavior is found for pyrosulfuryl chloride, except that the gas phase decomposition products at elevated temperatures also include substantial amounts of sulfur trioxide. The density of sulfur dioxide is 1.68 at 20°C and the density of pyro compound is somewhat greater, 1.84. The colligative properties are favorable to the range of temperature required for military operations.

f. Mixtures of Sulfur Trioxide and the Sulfuryl Chlorides

Liquid sulfur trioxide is miscible in all proportions with sulfur dioxide chloride. From the melting point diagram it can be determined that several compounds are formed, one of which is dichlorosulfuryl chlorosulfonate $\text{Cl}_2(\text{OSO}_2\text{Cl})_2$. This is a fuming liquid having a melting point of -19°C and a density of 1.633. No reported data indicating the TOP of this compound was found in the available literature. It is assumed that the toxicity, materials compatibility, and general smoke producing mechanisms for this compound is the same or similar to FS.

Smoke Producing Chemical Data Sheet

Sulfuryl Chloride (Sulfuric Oxychloride)

I. Properties of the Smoke Agent

- A. Composition: SO_2Cl_2
- B. Molecular Weight: 134.97
- C. Boiling Point °C: 69.1(760 mm);
 Vapor Pressure mmHg: $\log P = 7.918 - \frac{1725}{T}$
- D. Freezing Point °C: -54.1
- E. Density gm/cc: $1.9 (20^\circ)$; $\delta_t = 1.7081 - 0.0021t + 1.07 \times 10^{-6}t^2 - 1.81 \times 10^{-8}t^3$
- F. Viscosity, cp: $0.85 (25^\circ\text{C})$; $\eta_t = \frac{0.0759}{v_t - 0.5114}$
- G. Flash Point °C: --
- H. Heat of Vaporization: 49.45 cal/gm
- I. Toxicity: Not established
- J. Compatibility:
 Metals: Fe not affected at ordinary temp. corrodes in presence of moisture
 Plastics: Degradation occurs
- K. Stability: Good
- L. Mechanism for Producing Smoke:
 $\text{SO}_2\text{Cl}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_3 + \text{HCl}$
 $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{Hydrated Sulfuric Acid Droplets}$
- M. Surface Tension
 dynes/cm: 35.26(13°); 32 °C(23.5°)
 28.40(47 °C)

II. Properties of the Smoke

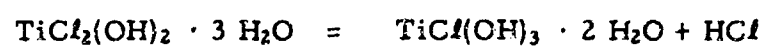
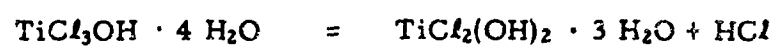
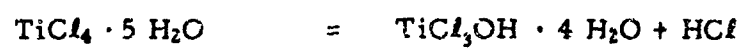
- | | |
|---------------------|--------------------------|
| A. Obscuring Power: | (TOP 1200)
(DOP 2280) |
| B. Persistence: | Good |
| C. Toxicity: | Similar to FS |
| D. Corrosivity: | Somewhat less than FS |

2. Smoke Agents Based on Inorganic Chlorides

A large number of hygroscopic metal chlorides have been used to produce white smoke. The chlorides of the elements in Group IV of the periodic table are the most important of these materials and titanium tetrachloride, silicon tetrachloride, and stannic chloride have all been used as liquid smoke agents. All three substances are fuming liquids which vaporize easily. The vapors of these substances then react with atmospheric moisture to produce a complex combination of hydrochloric acid, hydrated metal hydroxides, and metal chlorides. In addition to these three widely used compounds, many other of the metal chlorides are also capable of producing efficient smoke agents. These metal chlorides are all hygroscopic in nature and, as a general rule, their smoke effectiveness is directly proportional to the weight increase incurred during hydrolysis. Since many of these latter compounds are normally solids, an external heat source must be provided in many cases. Usually this heat is in the form of a pyrotechnic mixture and, therefore, their usage in an airborne tankage application is limited.

a. Titanium Tetrachloride (FM)

FM or titanium tetrachloride is a faintly colored fuming liquid having an acrid odor. This substance's ability to form smoke in moist air is due to the formation of a complex series of hydration and hydrolysis products. FM smoke agents are extremely hygroscopic, undergoing extensive polymerization upon contact to moist air. This polymerization results in extensive clogging and, therefore, the cleaning procedures to maintain dissemination equipment in operable condition are a major consideration. When used for screening, this agent can be disseminated from aircraft spray tank, the major problem being associated with post operation cleaning of the polymerization products from tankage inlet and outlet surfaces. A considerable effort has been devoted to the development of anticlogging agents, with little success. The reaction of FM with water is relatively complex. There is evidence which indicates that the titanium tetrachloride is first hydrated and then subsequently, hydrolyzed to produce particles of titanium hydroxide, dilute hydrochloric acid, and intermediate products consisting of a complex distribution of the oxychlorides of titanium. A possible sequence of reactions is given below:



Smoke Producing Chemical Data Sheet

Titanium Tetrachloride

I. Properties of the Smoke Agent

- A. Composition: TiCl_4
- B. Molecular Weight: 189.73
- C. Boiling Point °C: 136.4
 Vapor Pressure mmHg: 10.05(20°); 26.50(40°)
 $\log P = 7.644 - \frac{1948}{T}$
- D. Freezing Point °C: -30
- E. Density gm/cc: liq. 1.726; $\delta_t = 1.761 - 0.0017t - 7.3 \times 10^{-7}t^2 - 2.1 \times 10^{-9}t^3$
- F. Viscosity, cp: 0.88(14°); $\eta_t = \frac{1}{93.64 + 1.10t}$
- G. Flash Point °C: --
- H. Heat of Vaporization: 47.22 cal/gm(25°); 45.43 cal/gm(135.8)
- I. Toxicity: No limit set
- J. Compatibility:
 Metals: Moderate
 Plastics: Degradation and swelling high
- K. Stability: Good
- L. Mechanism for Producing Smoke:

$$\begin{aligned} \text{TiCl}_4 + \text{H}_2\text{O} + \text{Air} &= \text{Ti(OH)}_4 \cdot \text{H}_2\text{O} + \text{Ti(OH)}_x(\text{Cl})_y + \text{HCl} \\ &= \text{TiO} \cdot \text{H}_2\text{O} + \text{HCl} \end{aligned}$$
- M. Surface Tension: 35.1 dynes/cm (30°)
- N. Heat of Formation: -184.5 Kcal/mol.

II. Properties of the Smoke

- | | |
|---------------------|-----------------------------------|
| A. Obscuring Power: | (TOP 1900)
(DOP 3279) |
| B. Persistence: | Good |
| C. Toxicity: | Moderate to low |
| D. Corrosivity: | Corrodes metals |
| E. Remarks: | Standard military screening smoke |
| F. Irritation: | High |

The liquid is not corrosive to metals at ordinary temperatures, provided no moisture is present. It can be stored in steel aluminum and similar containers. It has been reported that a 0.2% phosphorus solution in CS_2 and CCl_4 reduces the clogging of spray nozzles. However, tests performed at Denver Research Institute on this contract indicated that only marginal improvement was obtained. The smoke produced by this agent is considerably less irritating and less corrosive than FS. While the smoke is generally assumed to be non-toxic in normal concentrations, there is evidence to indicate that all metal chloride smokes are somewhat toxic. For storage containers and gaskets, a number of plastic materials have been considered. Phenolic laminated paper base plastics, teflon, and some forms of polyethylene or polypropylene have shown reasonable stability against attack by the agent. Cellulose and styrene based materials have been reported to undergo considerable degradation. Titanium tetrachloride can also be disseminated when dissolved in dichloroethane and similar solvents. Mixtures of FM and solutions or mixtures of phosphorus prepared under this contract, were chemically stable but underwent phase separation.

b. Silicon Tetrachloride

Silicon tetrachloride is another liquid metal-chloride which has been used to produce smoke. However, silicon tetrachloride is less hygroscopic than titanium tetrachloride, and, unless considerable moisture is present, little smoke is produced. The smoke particles produced from the reaction of silicon tetrachloride with water vapor are probably dilute hydrochloride acid droplets, and hydrated silicon oxides. The reaction between silicon tetrachloride and water vapor is assumed to be similar to that between titanium tetrachloride and water vapor and a mixture of oxy and hydroxy silicon chlorides are probably formed in addition to orthosilicic acid.

Although the reactions take place rapidly in the liquid phase, the kinetics of the gas phase hydrolysis are slow. The silicon tetrachloride vapor and/or aerosol is used up slowly giving rise to a persistent smoke. The HCl produced probably remains in a gaseous state and the orthosilicic acid condenses to form smoke particles.

Silicon tetrachloride is less corrosive to metals than titanium tetrachloride. If dry, it can be stored in aluminum or steel containers. With moisture, silicon tetrachloride forms a gummy deposit which clogs equipment. Flesh burns from silicon tetrachloride are similar to hydrochloric acid burns. There are some toxic effects associated with the

smoke of this agent. However, the principal difficulty in use, apart from a relatively low obscuration power, is associated with its slow formation of smoke particles, particularly in dry climates.

Smoke Producing Chemical Data SheetSilicon TetrachlorideI. Properties of the Smoke Agent

- A. Composition: SiCl_4
- B. Molecular Weight: 169.89
- C. Boiling Point °C: 57.6
- Vapor Pressure mmHg: Liquid: $\log P = 7.644 - \frac{1572.1}{T}$;
195.9 mmHg(20°)
Solid: 1 mmHg(-70°)
- D. Freezing Point °C: -70
- E. Density gm/cc: 1.4^{+3} gm/cm^3 (20°); $\delta_t = 1.524 - 0.00201t - 5.61 \times 10^{-7}t^2 - 3.2 \times 10^{-8}t^3$
- F. Viscosity, cp: 0.501CP(15°); $\eta_t = \frac{0.000662}{v_t - 0.5369}$
where v_t is specific volume
- G. Flash Point °C: --
- H. Heat of Vaporization: 36.1 (15°)/g (57°C)
- I. Toxicity: Moderate
- J. Compatibility:
Metals: Moderate: no reaction with most metals in absence of water.
Plastics: Degradation and swelling high
- K. Stability: Good
- L. Mechanism for Producing Smoke:
$$\text{SiCl}_4 + \text{H}_2\text{O} + \text{Air} = \text{Si(OH)}_4 \cdot x\text{H}_2\text{O} + \text{SiO}_2 \cdot x\text{H}_2\text{O} + \text{HCl}$$
- M. Surface Tension: 16.9 dynes/cm (19°);
14.2 dynes/cm (45°)

II. Properties of the Smoke

- | | |
|---------------------|--------------------------|
| A. Obscuring Power: | (TOP 1500)
(DOP 2225) |
| B. Persistence: | Good |
| C. Toxicity: | Moderate |
| D. Corrosivity: | Moderate |
| E. Irritation: | High |

c. Stannic Chloride

The reactions of stannic chloride with water vapor are similar to those previously discussed in conjunction with FM. In this family of chlorides, both stannous and stannic chlorides produce smoke, but the effectiveness of the lower valence compound is considerably less. Stannic chloride is utilized in a similar manner as titanium tetrachloride and silicon tetrachloride. The dispersed phase of the smoke is a mixture of HCl droplets and solid particles of the hydrates of orthostannic acid, and chloral anhydrides of stannic acid. The obscuring power of this agent is somewhat less than FM and its corrosive effects are principally associated with the formation of hydrochloric acid. Upon contact with the skin stannic chloride produces strong acid burns and the smoke is reported as being irritating but nontoxic. Operational problems include a severe gumming of spray equipment and the need to prevent air or moisture contact. Material compatibility characteristics are assumed to be similar to the other liquid metal chlorides previously described. The smoke is moderately toxic and somewhat irritating.

Smoke Producing Chemical Data SheetStannic ChlorideI. Properties of the Smoke Agent

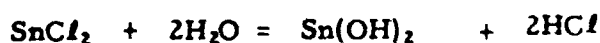
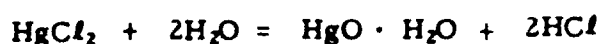
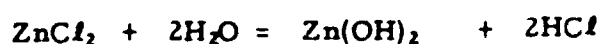
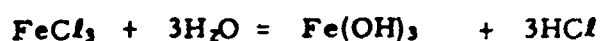
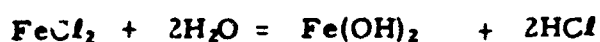
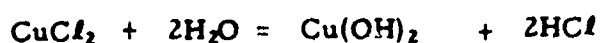
- A. Composition: SnCl_4
- B. Molecular Weight: 260.53
- C. Boiling Point °C: 114.1
Vapor Pressure mm Hg: 2.73 (-10°); 5.53 (0°); 10.33 (10°);
18.58 (20°); 31.3 (30°)
- D. Freezing Point °C: -30.2
- E. Density gm/cc: $2.226 \text{ (RT)}; \delta_t = 2.2744 - 0.00261t$
 $+ 1.05 \times 10^{-6}t^2 - 1.15 \times 10^{-8}t^3$
- F. Viscosity, cp: 0.9 (25°C); 1.011 (15°);
 $\eta = \frac{0.0439}{v - 0.4027}$
- G. Flash Point °C: --
- H. Heat of Vaporization: 30.3 cal/gm (15°)
Heat of Fusion: 8.40 cal/gm
- I. Toxicity: --
- J. Compatibility:
Metals: Moderate; does not corrode most
metals in absence of water.
Plastics: Moderate
- K. Stability: Good
- L. Mechanism for Producing Smoke:
 $\text{SnCl}_4 + \text{H}_2\text{O} + \text{Air} = \text{Sn(OH)}_4 + x\text{H}_2\text{O} + \text{SnO}_2 + x\text{H}_2\text{O}$
 $+ \text{HCl}$

II. Properties of the Smoke

- | | |
|---------------------|---|
| A. Obscuring Power: | (TOP 1850)
(DOP 4118) |
| B. Persistence: | Fair |
| C. Toxicity: | Moderate |
| D. Corrosivity: | Does not corrode Fe in absence
of moisture; otherwise, similar
to FM |
| E. Irritation: | Moderate |
| F. Remarks: | The TOP values reported were
not verified in the experimental
work performed under this
contract |

d. Solid Metal-Chlorides

Many metallic chlorides whose boiling points are not too high can be volatilized and will produce good smokes. Solid, hygroscopic metal-chlorides are normally disseminated by thermal vaporization followed by condensation. In most cases, the energy required to vaporize these agents is provided by a pyrotechnic heat source. The hydrolysis reactions for the metal chlorides which have been used as smoke agents are:



The detailed mechanism of the hydrolysis reactions is not completely understood. Chemical reactions giving rise to intermediate oxychlorides similar to those discussed in the hydrolysis of TiCl_4 are probably important in most of the above reactions. There is some evidence to indicate that the high temperature volatilization of the chlorides is followed by a condensation of supersaturated metal chloride vapors as very fine particles. In the case of ZnCl_2 and AlCl_3 this volatilization to the unreacted chloride is particularly pronounced. Subsequent hydrolysis reactions occur at a relatively slow rate on these airborne dusts of metal chlorides. There is limited evidence regarding the smoke value of alkyl derivatives of these agents. These compounds exist largely as dimeric liquids and might be of interest as potential smoke agents.

Smoke Producing Chemical Data SheetCupric ChlorideI. Properties of the Smoke Agent

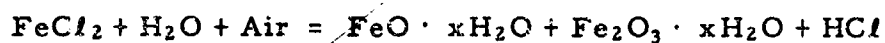
A. Composition:	CuCl_2
B. Molecular Weight:	134.48
C. Boiling Point °C:	Forms Cu_2Cl_2 993°
D. Freezing Point °C:	498
E. Density gm/cc:	3.054 (RT)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	--
J. Compatibility:	
Metals:	Moderate
Plastics:	Moderate
K. Stability:	Good
L. Mechanism for Producing Smoke:	

II. Properties of the Smoke

A. Obscuring Power:	Low
B. Persistence:	Low
C. Toxicity:	Moderate to High
D. Corrosivity:	Moderate
E. Irritation:	Moderate

Smoke Producing Chemical Data SheetFerrous ChlorideI. Properties of the Smoke Agent

A. Composition:	Fe Cl ₂
B. Molecular Weight:	126.76
C. Boiling Point °C:	1023 (decomposes)
D. Freezing Point °C:	674
E. Density gm/cc:	2.7 (RT)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	--
J. Compatibility:	
Metals:	Moderate
Plastics:	Good
K. Stability:	Fair
L. Mechanism for Producing Smoke:	

II. Properties of the Smoke

A. Obscuring Power:	Poor
B. Persistence:	Fair - Poor
C. Toxicity:	Moderate
D. Corrosivity:	Moderate
E. Irritation:	--

Smoke Producing Chemical Data Sheet

Ferric Chloride

I. Properties of the Smoke Agent

A. Composition:	FeCl_3
B. Molecular Weight:	162.22
C. Boiling Point °C:	315
Vapor Pressure (mm Hg):	40 (250°C)
D. Freezing Point °C:	298
E. Density gm/cc:	2.804 (11°)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	--
J. Compatibility:	
Metals:	Good
Plastics:	Good
K. Stability:	Good
L. Mechanism for Producing Smoke:	
$\text{FeCl}_3 + \text{H}_2\text{O} + \text{Air} = \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{Fe}_3\text{O}_4 \cdot x\text{H}_2\text{O} + \text{HCl}$	

II. Properties of the Smoke

A. Obscuring Power:	Poor
B. Persistence:	Poor
C. Toxicity:	Low
D. Corrosivity:	Moderate
E. Irritation:	--

Smoke Producing Chemical Data Sheet

Aluminum Chloride

I. Properties of the Smoke Agent

A. Composition:	$AlCl_3$
B. Molecular Weight:	133.34
C. Boiling Point °C:	182.7
Vapor Pressure (mm Hg):	108 (150°)
D. Freezing Point °C:	194 5.2 atm
E. Density gm/cc:	2.44 (25°/4)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	No threshold limit for Al
J. Compatibility:	
Metals:	Good
Plastics:	Good
K. Stability:	Good
L. Mechanism for Producing Smoke:	
$AlCl_3 + H_2O = Al_2O_3 \cdot xH_2O$	

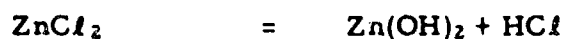
II. Properties of the Smoke

A. Obscuring Power:	Poor
B. Persistence:	Moderate
C. Toxicity:	Moderate
D. Corrosivity:	Moderate
E. Irritation:	--

Smoke Producing Chemical Data SheetZinc ChlorideI. Properties of the Smoke Agent

A. Composition:	ZnCl_2
B. Molecular Weight:	136.29
C. Boiling Point °C:	732
D. Freezing Point °C:	365
E. Density gm/cc:	2.91(25°)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	45 mg/m ³ was tolerated for 20 min. by man
J. Compatibility:	
Metals:	Good
Plastics:	Good
K. Stability:	Good

L. Mechanism for Producing Smoke:



Used in conjunction with solid oxidizers and heat sources in smoke pots, e.g. BM Mixture

II. Properties of the Smoke

A. Obscuring Power:	Fair
B. Persistence	Good
C. Toxicity:	Moderate
D. Corrosivity:	Moderate
E. Irritation:	Moderate

Smoke Producing Chemical Data SheetCadmium ChlorideI. Properties of the Smoke Agent

A. Composition:	CdCl_2
B. Molecular Weight:	183.32
C. Boiling Point °C:	960
D. Freezing Point °C:	568
E. Density gm/cc:	4.047 (25°/4)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	325 mg. taken orally was not fatal; 0.1 mg. of Cd/m^3 to provide safe daily exposure
J. Compatibility:	
Metals:	Good
Plastics:	Good
K. Stability:	Good
L. Mechanism for Producing Smoke:	
$\text{CdCl}_2 + \text{H}_2\text{O} = \text{Cd}(\text{OH})_2 + \text{HCl}$	

II. Properties of the Smoke

A. Obscuring Power:	Fair - Poor
B. Persistence:	Good
C. Toxicity:	Moderate
D. Corrosivity:	Moderate

Smoke Producing Chemical Data SheetMercuric ChlorideI. Properties of the Smoke Agent

A. Composition:	HgCl ₂
B. Molecular Weight:	271.52
C. Boiling Point °C:	304
D. Freezing Point °C:	277
E. Density gm/cc:	5.44 (RT)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	--
J. Compatibility:	
Metals:	Moderate - Poor
Plastics:	Good
K. Stability:	Fair
L. Mechanism for Producing Smoke:	
$\text{Hg Cl}_2 + \text{H}_2\text{O} + \text{Air} = \text{Hg(OH)}_2 -$	

II. Properties of the Smoke

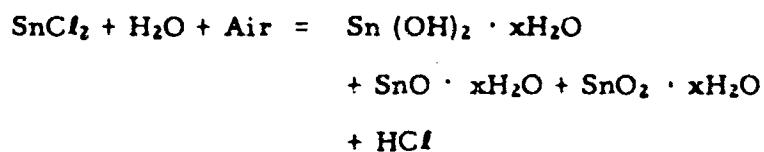
A. Obscuring Power:	Poor
B. Persistence:	Low
C. Toxicity:	High
D. Corrosivity:	Moderate

Smoke Producing Chemical Data Sheet

Stannous Chloride

I. Properties of the Smoke Agent

A. Composition:	SnCl_2
B. Molecular Weight:	189.61
C. Boiling Point °C:	623
D. Freezing Point °C:	246.8
E. Density gm/cc:	3.393 (245°) liquid
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	No limit of safe exposure has been set
J. Compatibility:	
Metals:	Moderate
Plastics:	Moderate
K. Stability:	Moderate
L. Mechanism for Producing Smoke:	

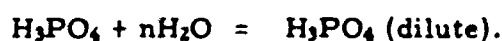


II. Properties of the Smoke

A. Obscuring Power:	Poor
B. Persistence:	Fair - Poor
C. Toxicity:	Moderate
D. Corrosivity:	Moderate

B. White Smokes Containing Phosphorus

In the white smokes containing phosphorus, which have been used for military purposes, the particles are small droplets of phosphoric acid. These droplets are formed by the reaction of phosphorus pentoxide, formed by the burning of phosphorus or phosphorus-containing compounds in the air, and the water vapor in the air, or



The concentration of phosphoric acid in the droplets is determined by the relative humidity. Methods which have been used to form phosphorus pentoxide for military smokes containing phosphorus include:

1. burning white phosphorus, which is spontaneously inflammable in air,
2. burning red phosphorus vapor, which has been evaporated from a fuel oxidant mixture, in air,
3. burning of phosphine, produced by the action of a metal-phosphide with water, in air.

Other methods for producing phosphorus containing smokes include the solution WP into selected solvents and the use of eutectic mixtures and phosphorus containing compounds.

Phosphorus vapor is toxic but, being very reactive, it is not present after the smoke is formed. Phosphorus pentoxide and phosphoric acid are not toxic in small concentrations, although they may be somewhat irritating to the eye, respiratory track, and skin. Phosphorus smokes have relatively little effect on metals and can be considered to be relatively noncorrosive to plastic materials.

1. White Phosphorus

Phosphorus is the most efficient smoke produced on a weight basis. However, for bursting-type dispersed, most of the charge burns within seconds of the burst, resulting in a smoke concentration many times that required for effective screening. The temperature-rise in the cloud immediately surrounding the burst is sufficient to produce a

strong, thermal updraft which tends to lift the cloud from the ground so that the smoke cloud pillars. This is helpful for signaling purposes but generally reduces the effectiveness of white phosphorus as a screening smoke.

Two general ways to improve smoke-producing efficiency are possible. The first involves reduction of the heat of combustion, which can be accomplished by using different phosphorus compounds, e.g. the eutectic mixture discussed previously. The second method, involves controlling the rate of combustion as in PWP, plasticized white phosphorus. This consists of an intimate mixture of granulated white phosphorus in a viscous rubber solution. The material burns more slowly and the particles do not disintegrate by melting. As a result, pillaring is reduced and the effective screening time is greatly prolonged. Test results have indicated that plasticized white phosphorus produces distinctly better smoke screens than unmodified white phosphorus agents. Similar effects have been demonstrated under this contract for solutions of methylene iodide and white phosphorus, and for a eutectic mixture consisting of about forty-five weight percent phosphorus in the experimental phase of study. The latter smoke agents provide a substantial gain in weight obscuring power and density obscuring power over FS.

Smoke Producing Chemical Data Sheet

Phosphorus

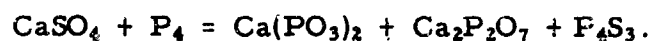
I. Properties of the Smoke Agent

- A. Composition: P_4
- B. Molecular Weight: 123.92
- C. Boiling Point °C: 280
- Vapor Pressure mmHg: Liquids; $\log P = 11.57 - \frac{2893}{T} - 1.257 \log T$
- Solid; $\log P = 9.651 - \frac{3297}{T}$
- D. Freezing Point °C: 44.1
- E. Density gm/cc: 1.82 (20°C) $\delta_T = 1.783 - 0.009 T$
liq. 1.745 (44.5°)
- F. Viscosity, cp: (liquid) P_4 2.34 (21.5°C) 1.04
(45°C) 0.88 (60°C)
- G. Flash Point °C: --
- H. Heat of Vaporization: 130 cal/gm (B. P.)
Heat of Fusion: 5.03 cal/gm
- I. Toxicity: Fatal dosage is 50 mg.
MAC 0.1 mg/m³
- J. Compatibility:
- Metals: Good; reacts with many metals
but does not corrode iron or
iron alloys.
- Plastics: Good; does not react with poly-
ethylene to any appreciable
extent after 2-month storage,
contact.
- K. Stability: Good
- L. Mechanism for Producing Smoke:
- $$P_4 + \text{Air} = P_2O_5$$
- $$P_2O_5 + H_2O = H_3PO_4 \cdot xH_2O$$

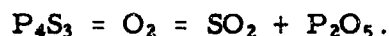
II. Properties of the Smoke

- | | |
|---------------------|--|
| A. Obscuring Power: | Very high (TOP 4600)
(DOP 8372) |
| B. Persistence: | Good |
| C. Toxicity: | Low |
| D. Corrosivity: | Low; corrosion is caused by
phosphoric acid which is rela-
tively non-corrosive for most
metals and plastics. |
| E. Irritation: | Low |

Red phosphorus, the comparatively inert allotropic form of phosphorus, is used in burning-type munitions mainly for signalling purposes. Compositions consisting of red phosphorus, and certain oxidants or fuels, can be made which are slow-burning; these compositions are sometimes used in sea markers. The chemical reactions can be quite involved. For example, the main reaction for a burning mixture of calcium sulfate and red phosphorus used in certain sea markers appears to be:

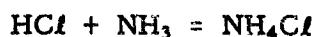
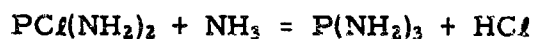
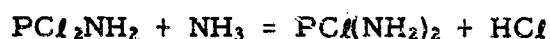
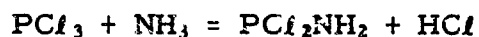


The heat produced by this reaction vaporizes the remaining red phosphorus contained in the smoke mixture. The phosphorus vapor burns on contact with air. Some sulphur dioxide is probably formed when the P_4S_3 , produced in the above reaction, burns along with the phosphorus vapor:



Methods for producing phosphorus-containing smokes include:

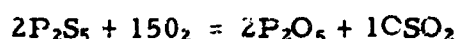
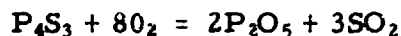
1. the dispersion of phosphorus in a solvent, such as methylene iodide or carbon bisulphide, *
2. the reaction of phosphorus trichloride with bases such as ammonia and amines (the reactions are complex as illustrated in the following example:



the smoke is composed of a mixture of the amino-phosphorus chlorides and NH_4Cl ; the smoke produced is considered irritating but not toxic; phosphorus bichloride is not excessively corrosive to any metal affected by hydrochloric acid; it is quite corrosive to flesh, wet or dry), and

* See discussion page (213) and Recommendations (12).

3. the dispersion of phosphorus sulfides in carbon bisulfide (the solvent evaporates and the finely-divided particles of phosphorus sulfide burn readily in air; total combustion of these sulfides will yield phosphorus pentoxide and sulphur dioxide:



both the products react with water to produce sulfurous acid and phosphoric acid; the sulfides of phosphorus are harmless to both metals and flesh; the smoke produced is also relatively harmless to metals and personnel).

2. Phosphorus-Phosphorus Sesquisulfide Eutectic Mixture

The phosphorus-phosphorus sesquisulfide eutectic consists of 55% by weight of white phosphorus and 45% by weight of phosphorus sesquisulfide. The total elemental composition by elements is 80% P and 20% S. The composition of the fuel is not critical, and a reasonable amount of deviation is allowable from the true eutectic proportions. The fuel, when settled free from water, is a clear, yellow, heavy liquid of low surface tension, moderate viscosity, and oily appearance.

The specific gravity of the eutectic at 20°C is 1.840 and eutectic fuel freezes at approximately -42°C. The EWP mixture is light sensitive, probably caused by the conversion of white phosphorus into the red phosphorus modification. When the liquid is stored in the dark, or in opaque containers, no deterioration takes place.

Storage under a layer of distilled water in a closed container for several weeks at ambient temperature was reported to result in no appreciable reaction beyond the formation of a slight yellow scum at the interface and the gradual acidification of the aqueous phase; however, when the fuel is stored under water in a vessel open to the atmosphere, gradual deterioration takes place, with the slow formation of corrosive acid products. The material is stable at temperatures between -40° and +55°C with no adverse effects reported for temperature cycling. EWP is not affected by CO₂ absorption. On this contract, strips of different materials were immersed in vessels containing eutectic fuel under a layer of water. No severe corrosion was observed after several days.

The mixture is pyrophoric with air, causing some handling problems during tank loading operations. A considerable reduction of this pyrophoricity can be accomplished by agitations with water and/or the addition of methylene iodide. The CH_2I_2 is miscible in all proportions with both WP and EWP and serves to substantially reduce the handling hazard. During the experimental portion of this program, field handling was accomplished by simple decantation or pouring of the liquid agent into a smoke tank with a nitrogen blanket. Based on experience gained during this contract, the recommended handling procedure for this loading agent is by simple water displacement.

Smoke Producing Chemical Data Sheet

EWP

I. Properties of the Smoke Agent

A. Composition:	55% WP 45% P_4S_5
B. Molecular Weight:	--
C. Boiling Point °C:	--
Vapor Pressure mm Hg:	--
D. Freezing Point °C:	-42°
E. Density gm/cc:	1.8 + 1.840
F. Viscosity, cp:	--
G. Flash Point °C:	Low
H. Heat of Vaporization:	--
Heat of Fusion:	--
I. Toxicity:	Assumed same as phosphorus
J. Compatibility:	
Metals:	Good
Plastics:	Good
K. Stability:	Good
L. Mechanism for Producing Smoke:	
	$EWP \rightarrow P_2O_5 + \text{Sulfur Products}$
	$P_2O_5 + H_2O \rightarrow H_3PO_4$

II. Properties of the Smoke

A. Obscuring Power:	High (2800 to 3000 TOP) (5051 DOP)
B. Persistence:	Good
C. Toxicity:	Low
D. Corrosivity:	Low
E. Irritation:	Low
F. Remarks	--

Smoke Producing Chemical Data Sheet

Phosphorus Pentasulfide

I. Properties of the Smoke Agent

A. Composition:	P_2S_5
B. Molecular Weight:	222.26
C. Boiling Point °C:	514
D. Freezing Point °C:	276
E. Density gm/cc:	2.03 (RT)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	--
J. Compatibility:	
Metals:	Good
Plastics:	Good
K. Stability:	Good
L. Mechanism for Producing Smoke:	
$P_2S_5 + \text{Air}$	$= P_2O_5 + SO_2$
$P_2O_5 + H_2O$	$= H_3PO_4 \cdot xH_2O$
$SO_2 + H_2O$	$= H_2SO_3$ (Not effective)

II. Properties of the Smoke

A. Obscuring Power:	Moderate
B. Persistence:	Good
C. Toxicity:	Low
D. Corrosivity:	Moderate
E. Irritation:	Low

Smoke Producing Chemical Data SheetPhosphorus SesquisulfideI. Properties of the Smoke Agent

A. Composition:	P_4S_3
B. Molecular Weight:	220.10
C. Boiling Point °C:	468 (760 mm)
D. Freezing Point °C:	172.5
E. Density gm/cc:	2.03 (17°)
F. Viscosity, cp:	--
G. Flash Point °C:	--
H. Heat of Vaporization:	--
I. Toxicity:	Not established
J. Compatibility:	
Metals:	Good
Plastics:	Good
K. Stability:	Good
L. Mechanism for Producing Smoke:	
$P_4S_3 + \text{Air}$	$= P_2O_3 + SO_2$
$P_2O_3 + H_2O$	$= H_3PO_4 \cdot xH_2O$
$SO_2 + H_2O$	$= H_2SO_3$ (Not effective)
M. Ignition Point:	100°

II. Properties of the Smoke

A. Obscuring Power:	High
B. Persistence:	Good
C. Toxicity:	Low
D. Corrosivity:	Moderate
E. Irritation:	Low

Smoke Producing Chemical Data Sheet

MIP*

I. Properties of the Smoke Agent

A. Composition:	33% MI 66% WP
B. Molecular Weight:	--
C. Boiling Point °C:	--
Vapor Pressure mm Hg:	--
D. Freezing Point °C:	<0°C
E. Density gm/cc:	2.37 2/cc
F. Viscosity, cp:	--
G. Flash Point °C:	<20°C
H. Heat of Vaporization:	--
Heat of Fusion:	--
I. Toxicity:	Assumed same as P ₄
J. Compatibility:	
Metals:	Fair
Plastics:	Good
K. Stability:	Good
L. Mechanism for Producing Smoke:	MIP → P ₂ O ₅ + Other Products P ₂ O ₅ + H ₂ O → H ₃ PO ₄ (dilute)

II. Properties of the Smoke

A. Obscuring Power:	(TOP 2800) (DOP 6350)
B. Persistence:	Good
C. Toxicity:	Moderate
D. Corrosivity:	Moderate
E. Irritation:	Mild
F. Remarks:	--

* Methylene iodide - white phosphorus solution

Smoke Producing Chemical Data SheetPhosphorus TrichlorideI. Properties of the Smoke Agent

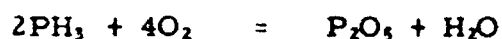
A. Composition:	PCl_3
B. Molecular Weight:	137.35
C. Boiling Point °C:	75.95 (760 mm)
D. Freezing Point °C:	-111.8
E. Density gm/cc:	$1.574 \left(\frac{20.8^\circ}{4} \right)$
F. Viscosity, cp:	0.7 (18°C)
G. Flash Point °C:	--
H. Heat of Vaporization:	51.4 (15°)/g (78°C)
I. Toxicity:	0.5 p.p.m. threshold limit
J. Compatibility:	
Metals:	Moderate
Plastics:	Poor
K. Stability:	Good
L. Mechanism for Producing Smoke:	
$\text{PCl}_3 + \text{Air}$	$= \text{P}_2\text{O}_5 + \text{HCl}$
$\text{P}_2\text{O}_5 + \text{H}_2\text{O}$	$= \text{H}_3\text{PO}_4$

II. Properties of the Smoke

A. Obscuring Power:	Fair
B. Persistence:	Good
C. Toxicity:	Moderate
D. Corrosivity:	Moderate (HCl)
E. Irritation:	Moderate (HCl)
F. Remarks:	Corrosivity and irritation effects would probably be attributable to the formed hydrochloric acid.

3. Metal Phosphides

Metal phosphides, especially calcium phosphite, have been used in sea markers. In these markers, the metal phosphide reacts with water to form diphosphine, which is then burned in air to produce phosphorus pentoxide and water. For calcium phosphide:



The rate-of-reaction is determined by controlling the access of the water and by the back-pressure of the gas produced. Calcium phosphide has been the most satisfactory of the metal phosphides for this purpose inasmuch as aluminum phosphide is difficult to react and slow-burning, whereas, magnesium phosphide reacts too rapidly. Sodium phosphide has been used in a development program with modest success. No data is available on the use of lithium, strontium, or barium phosphides. These latter compounds would be expected to provide good smoke agents. For example, the TOP of Li_3P might be expected to be in the neighborhood of 2800 if all the weight of contained phosphorus was effective.

Experimental TOP values obtained on this contract were inconsistent and, therefore, not reported. Generally, these compounds can be expected to provide TOP values in accordance with their weight percent contained phosphorus. For use over swampy areas, these materials would be good since direct water contact is advantageous. Some possibilities for the use of these agents include incorporation in a slurried form with other compatible liquid smoke agents as for example, white phosphorus eutectic mixture or phosphorus alkyls. Because the use of these agents in an airborne tank does not appear readily feasible within the scope of this project, work along these lines was discontinued.

4. Phosphorus Trichloride

Tests were performed using phosphorus trichloride. This agent had a low obscuring power as determined by visual observation. The tests included vaporization from a hot plate held at about 100°C , but only marginal improvement was observed. Further work was discontinued because of the obviously low smoke value of this agent. The vapors of this agent are both irritating and toxic. Similar results were observed with phosphorus oxychloride.

Smoke Producing Chemical Data Sheet

Phosphorus Trichloride

I. Properties of the Smoke Agent

A. Composition:	PCl_3
B. Molecular Weight:	137.35
C. Boiling Point °C:	75.95 (760 mm)
D. Freezing Point °C:	-111.8
E. Density gm/cc:	$1.574 \frac{(20.8^\circ)}{4}$
F. Viscosity, cp:	0.7 (18°C)
G. Flash Point °C:	--
H. Heat of Vaporization:	51.4 (15°)/g(78°C)
I. Toxicity:	0.5 p.p.m. threshold limit
J. Compatibility:	
Metals:	Moderate
Plastics:	Poor
K. Stability:	Good
L. Mechanism for Producing Smoke:	
$\text{PCl}_3 + \text{Air}$	$= \text{P}_2\text{O}_5 + \text{HCl}$
$\text{P}_2\text{O}_5 + \text{H}_2\text{O}$	$= \text{H}_3\text{PO}_4$

II. Properties of the Smoke

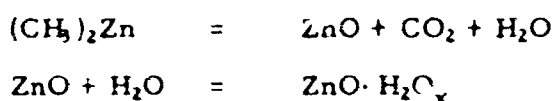
A. Obscuring Power:	Fair - Poor
B. Persistence:	Good
C. Toxicity:	Moderate
D. Corrosivity:	Moderate
E. Irritation:	--
F. Remarks:	--

C. Organo-Metallic Compounds

A number of organic-metallic compounds can be used for the production of smoke. These compounds are pyrophoric with air and burn to produce metal oxides and hydroxides. The sequence of reaction between an organic-metallic compound, air, and atmospheric moisture is exceedingly complex. The smoke produced from these processes of combustion is nonirritating and, depending on the metal used, may be nontoxic. For very high combustion rates, if the metal possesses a high boiling oxide, it is possible to have a smoke particle consisting only of the metal oxide. In this case, the particles may either be solid or hollow shells of the refractory oxide. For particles consisting of a solid metal oxide spheroid, the obscuration value can be expected to be no greater than about the range available from good oil smokes. For hollow spheroids, far higher values can be expected, but no substantiating data evaluating the obscuration power of the agents is available in the literature. Most of the compounds studied thus far are light alkyl derivatives such as dimethyl zinc, triethyl aluminum, and isobutyl titanium. However, zinc, aluminum, phosphorus, silicon, and titanium metal organic compounds all exist as liquids which could be used as potential smoke agents. A brief description of these compounds is given in the following sections.

1. Dimethyl Zinc

Dimethyl zinc compounds have been used to produce smoke. No data is available which describes the TCP of this agent in other than qualitative terms. The assumed reaction for the production of smoke is:



In this case, the particles would be expected to consist of solid zinc hydroxide particles. The toxicity of the smoke is low and little corrosion would be expected to occur. As far as can be determined, the obscuring power of this agent is low. Major problems exist in the handling of the agent because of its pyrophoricity.

2. Aluminum Alkyls

Aluminum alkyl derivatives have been investigated during the experimental portions of this program. When used alone, these agents

do not provide an effective military smoke. Under conditions involving air diffusion flames, some smoke was produced. Examination of the particles under high power microscopes indicated particles, approximately one to ten microns in cross section, consisting of solid aluminum oxide spheroids were formed. The major problem in using these derivatives is that their extremely high pyrophoricity causes extensive handling problems for the liquid agent. The smoke would be nonirritating, nontoxic and noncorrosive. A mixture of these compounds with fog oils has been used in the form of an intimate oil smoke. This technique requires the addition of fire retardants to quench a rapid reaction of the agent with air. The TOP of this agent was approximately 400 and had relatively poor persistence. A more extended discussion of the aluminum alkyl base smoke agents is given in the discussion on intimate oil smokes.

3. Phosphorus Alkyls

Phosphorus forms a series of alkyl derivatives involving both the formation of phosphine and diphosphine derivatives. These latter compounds, in general, possess exceedingly wide liquidus ranges. The methyl derivatives boil relatively low, but the higher propyl and isobutyl derivatives are stable liquids between the range of temperatures usually encountered during military operations. The smoke produced from these compounds is probably a mixture of dilute phosphoric acid and an oil smoke for higher derivatives. The agents are pyrophoric for the methyl and ethyl derivatives, which action decreases markedly as longer alkyl chains are employed. These compounds are extremely rare and evaluation of their properties requires a considerable synthetic program. While the smoke produced is nontoxic, nonirritating and noncorrosive, the agents themselves are possibly toxic. Except for the methylated phosphines, little or no data was obtained concerning the degree of toxic hazard associated with the handling of these liquids.

4. Silicon Alkyls

Use of silicon alkyls was not reported in the available literature. Tests were performed to assess the smoke producing capability of these derivatives and are described in greater length in following sections. The smoke produced is probably a mixture of silicon oxide and oxychlorides formed by combustion reaction of the agent in an air diffusion flame. In general, the TOP of these compounds was found to be low. Advantages in their use would be associated with the inert character of the produced smokes and the nontoxicity of the agents.

5. Titanium Alkyls

The use of titanium alkyls as a smoke agent has been limited to research evaluating the obscuring power of these agents. During this program, a mixture of methylated chloro titanium derivatives were synthesized. The TOP of these derivatives was marked up lower than that of FM and although improvements to higher TOP values may be achieved by further work. These compounds form a smoke through an air hydrolysis reaction similar to FM. The liquids themselves are subject to gum formation in a manner similar to FM. The smoke is somewhat irritating but less so than FM. The advantages and disadvantages of these compounds are similar to those of FM.

D. Smoke Agents Based on Vaporization-Condensation Phenomena

1. Fog Oils

A very satisfactory white screening smoke can be produced by the vaporization and condensation of an oil that has a high boiling point and a low volatility. To provide the heat necessary for evaporation, and, the airflow necessary in order to produce condensate particles of closely controlled physical dimensions, relatively complex devices must be used. For these reasons, no consideration of oil smokes could be made under this contract. The only alternative to this complexity is to use an intimate oil mixture which is discussed in more detail in the following section. The toxicity, handling, and materials compatibility of these oil smokes are all excellent.

2. Intimate Oil Smokes

An intimate oil smoke is a smoke agent in which a fuel is incorporated into a fog oil or hydrocarbon system. The fuel burns with the air releasing heat which is used to vaporize the fog oil. The ideal mixture is one in which the fuel is oxidized upon air contact. Upon recondensation of the fog oil, an oil smoke is produced.

Two partially satisfactory, intimate oil smoke generators have been developed. The first consisted of a mixture of sawdust and charcoal, impregnated with a solution of potassium chlorate and a high boiling oil, Diol, which had been jelled by the addition of 2-1/2 to 3 percent soap. The other mixture consisted of jellied oil and black gunpowder. Both systems produced an air-oil smoke. The TOP of these

systems was below that for pure fog-oil, partly because a non-optimum particle size distribution was produced. The handling characteristics of the agent, and the physical and chemical characteristics of the produced smoke, are similar to that produced by the fog-oil base.

A more recent development in intimate fog-oil smoke has been accomplished by using a pyrophoric fuel consisting of one of the light metal alkyls. These have been under development by the Ethyl Corporation. The fuels which have been evaluated include triethyl-aluminum, diethyl zinc, tri-n-butyl aluminum, trimethyl silicon monochloride, and tetrabutoxytitanium. The fog-oil base consisted of a mixture of naphthalene and alpha-methylnaphthalene. The SE smoke agents are relatively easily handled and the produced smoke is probably similar to fog-oil. Preliminary development programs described in the former experimental sections using 90622T indicate a marked tendency of the produced smoke agent or cloud to ignite when dispersed from a standard airborne tankage. Additional problems exist because of a low intensity diffusion flame which occurs when the agent is placed in contact with air. The work under this contract indicated that these mixtures have low TOP, are normally pyrophoric, and tend to produce ground fires when dumped in large quantities.* These agents have fire retardants to prevent ignition of the oil base.

The major source of uncertainty at the present time is the obscuration capability of these agents. The Ethyl Corporation values as reported indicate an obscuration capability of about the same as FM, whereas, values obtained on this contract indicate that the TOP of these agents as provided is no greater than 400-500. There are important differences in the methods used to measure these smoke values. The work under this contract used four separate measurement techniques, three of which are quantitative in nature and one qualitative. These included observations in a small laboratory chamber, a large smoke tunnel using both reflectance and obscuration methods, and field tests performed using about one gallon quantities. These tests provided consistently low values for TOP. The work performed at Ethyl Corporation used a smoke tunnel to provide a time-integrated relative intensity curve. The major critical aspect to this latter method is the requirement for using an optical path length of about two inches because of the high concentrations used. It is possible that the characteristics of

* See Figure 42.

either the agents developed or the standard agents used to calibrate the system were substantially modified by the high concentration used. These materials are generally water sensitive and tend to undergo violent reaction when placed in contact with liquid water. This characteristic could be of detrimental value for operational uses since the agents normally burn with a low flame when, for example, they are placed in an open beaker exposed to air. The work performed under this contract with the 90622T agent provided that this combustion occur and be visible in the dark. Because of the produced oil smoke, this phenomenon was not normally observed under daylight conditions. Since this work represents a development which is recent, an outline of the Ethyl work is abstracted in the following discussion. Further discussion of the results obtained under this contract is given in the experimental sections.

a. Triethyl Aluminum Smokes

Based on a series of survey reactions a triethyl aluminum (TEA) agent was prepared (90622T) with composition TEA (40% wt), α -methyl-naphthalene (12.4%), neutral oil #75 (47.6%). This mixture had the best handling and obscuring characteristics of a number of similar agents. Important physical properties of this mixture are thermal stability from -40°F to 120°F, density 0.85.

b. Diethylisobutylaluminum Smokes

A series of candidate diethylisobutylaluminum agents were prepared, which were similar to TEA formulations except for the aluminum alkyl $\text{Et}_2\text{Al}(\text{i-Bu})$, which was prepared in-situ, from TEA and triisobutylaluminum (TIBA) by disproportionation:



In smoke tunnel studies, this agent, 37.4 wt % $\text{Et}_2\text{Al}(\text{i-Bu})$ was approximately equivalent to 90622-T in obscuring capability.

c. Ethyldiisobutylaluminum

Smoke agents, similar to TEA formulations, were prepared by using ethyldiisobutylaluminum, $\text{EtAl}(\text{i-Bu})_2$, as the active component. Again the aluminum alkyl was prepared by in-situ disproportionation:



This formulation, 44.7 wt % $\text{EtAl}(\text{i-Bu})_2$, was nearly equivalent to 90622-T in obscuring power in smoke tunnel studies.

d. Triisobutylaluminum Smoke

A series of triisobutylaluminum compositions similar to those containing TEA were prepared. In smoke tunnel studies, the best smoke agent of the series was 61 wt % TIBA which had the obscuring capability of about 70% of 90622-T.

e. TEA-Fluorocarbon Smokes

Several TEA-based smoke agents were prepared which contained halogenated hydrocarbons: Freon-114B2 (duPont's dibrometrafluoroethane) and Fluorolube FS-5 (Hooker's trifluorochlorovinyl polymer). In smoke tunnel tests, this agent is about equivalent to 90622-T in obscuring capability. Its composition is:

30 wt % TEA
12.4 wt % α -methylnaphthalene
37.6 wt % Neutral 75 oil
10 wt % Freon-114B2
10 wt % Fluorolube FS-5

Freon-114B2 has a boiling point of 47.5°C and was used as a component in two formulations in an effort to reduce initial flammability by sheathing the agent in a nonflammable gas. Fluorolube FS-5 has a boiling point of 50°C at 1 mm of mercury (about 230°C at atmospheric pressure) and is nonflammable. This was also used in an attempt to reduce the flammability of the candidate agents. In spite of this, two agents having 25 wt % TEA, 23.8 wt % TEA, respectively, containing high concentrations of Fluorolube FS-5, were pyrophoric. It is believed that, although the concentrations of TEA were not very high on a weight basis, they were quite high on volume basis (density of Fluorolube 1.87 g/ml vs Neutral oil's density of 0.8). It is also possible that at elevated temperatures TEA may be reactive with Fluorolube to form AlF_3 .

f. Higher Aluminum Alkyls

Tri-*n*-hexylaluminum and tri-*n*-decylaluminum did not form smokes when squirted into air. An effort was made by Ethyl Corporation to determine if 90622-T smoke capability could be enhanced and its flammability reduced by substitution of nonpyrophoric tri-*n*-decylaluminum (TNDECYL) for a portion of the diluent oil.

40 wt % TEA
 20 wt % TNDECYL
 12.4 wt % α -methylnaphthalene
 27.6 wt % Neutral 75 oil

By disproportionation, the actual composition of this agent became:

30 wt % TEA
 30 wt % $\text{Et}_2\text{AlC}_{10}\text{H}_{21}$
 12.4 wt % α -methylnaphthalene
 27.6 wt % Neutral 75 oil

It was reported that smoke tunnel studies indicated that the substitution severely reduced the obscuring capability.

3. Inorganic Chlorides

A number of inorganic chlorides provide white smoke by a direct volatilization recondensation process. In such cases, the substance does not decompose and the smoke consists of particles of the original chloride. In general, to provide the energy required for evaporation, a considerable quantity of heat must be supplied. The reaction may proceed further via hydrolysis if sufficient atmospheric moisture is available and, in this sense, these chloride smokes are similar to those discussed in previous sections. The metallic chlorides in this category include copper, aluminum, zinc, iron, cadmium and mercury. The TOP of these compounds is relatively low and, because of difficulties in providing the heat of transition necessary for their use for a liquid chemical smoke agent, is questionable. A possibility exists that such compounds might be incorporated as additives to intimate smoke mixtures where the pyrophoric constituent would serve both as a liquid vehicle carrier and pyrotechnic heat source. These metal chlorides are less corrosive than FM or silicon tetrachloride, but, being hygroscopic, must be kept from contact with moisture.

4. Sulfur Smokes

Sulfur smokes consist of small particles of elemental sulfur suspended in the air. Sulfur smokes can be produced by methods similar to those used for the production of oil smokes. In addition, sulfur smokes can be made by intimately mixing sulfur and a suitable fuel. Mixtures which have been used include sulfur, sodium nitrate and

charcoal; sulfur, potassium nitrate and charcoal; and sulfur, ammonium nitrate and charcoal. The sulfur is present in much larger quantities than in black gunpowder; the latent heat-of-vaporization and fusion of the sulfur absorbs the heat produced by the reaction and, hence, slows the burning-rate. The burning-rate for this type of mixture depends on the percentage of sulfur.

5. Mechanical Dispersions of Water

A technique which has been utilized in preliminary investigations is the production of fogs consisting of salt-water sprays, containing surface active agents via a spray nozzle. A report* indicates that fogs using 10% NaCl-water solution have TOP value of 6000. The practical difficulties of producing such sprays are considerable, requiring high velocity air streams and pressure heads in excess of 3000 psi. From tests at Edgewood, it was concluded that formation of smokes by spraying or atomizing of these solutions was not practical.

It should be noted that major changes have been made in the design of high pressure flight weight hardware, and in the development of efficient surface active agents capable of reducing the surface tension of water solutions. This technique might be adapted for use in air-borne systems in which the gas flow requirements are met by a modified ram jet inlet system. It is probable that this technique would not be suitable for ground base smoke generators because of the relatively high power requirements which are necessary to achieve high efficiency. For use with air-borne dispersion, this technique would not provide an adequate ground level cover.

E. Smoke Agents Requiring the Dissemination of Solid Particulate Matter

1. Solids

A number of materials have been used to produce military screening smokes based on the dispersion of particulate matter. To be persistent, these materials must have a uniform particle size in the size range between 1 and 10 microns in diameter. If the particles are much larger than this size, they tend to rapidly fall out. Because these particles usually do not react in any way with the atmospheric gases to

* Mechanical Formation of Smokes, G. G. Brown, NDRC Div. B
OSRD-153-Serial #91, October 18, 1941.

produce a larger quantity of bound material, the TOP values can be no greater than those obtained from the best oil fog agents. This places an approximate upper limit of about 1200 on such agents.

For the application with an aerial smoke dispersal technique, these materials have a major disadvantage in useage. In order to obtain an effective smoke screen near or at ground level, the material must be transported in some way from flight altitude to ground level. Because of extremely high drag coefficients for particles of this size, use of bursting-type dissemination devices cannot provide a uniform or effective distribution of powder over a wide area. Use of an inert pressurant can be effective, but leads to considerable mechanical complexity. Materials which have been considered for this purpose include Bentonite clays, talc, and polyethylene. Of these powders, it is probable that polyethylene spheroids such as Microfine could be used relatively effectively since an extremely uniform particle size can be manufactured. As yet, no positive results regarding the TOP for this material have been reported. A few of these agents were briefly investigated experimentally as a part of this program, but problems of powder compaction and agglomeration were encountered which negated the usefulness of the results. Major advantages of these agents is their inertness, being completely non-toxic and non-corrosive. The major problems are inherently low TOP values and difficulties in providing uniform dispersement at ground level.

2. Fcams

The use of foaming agents to provide military screening smokes has been reported by several investigators. These agents can be used to advantage for select ground based applications. The TOP capability is potentially high since it may be possible to form hollow spheres from a vacant foam-agent. Most of the agents investigated require both thermal volatilization and blowing from a high velocity air stream. This is not easily accomplished using airborne equipment if a ground cover is desired. Therefore, investigation on this contract investigating these agents was limited. It is possible that an effective IR scattering particle could be developed using very low density plastics.

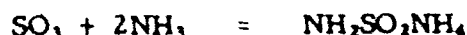
F. Dual Smoke Agents

Many smoke agents have higher TOP values and can be used to advantage if a second agent is also disseminated in conjunction with the first. The major disadvantage of using two agents is associated with

the increased hardware and handling problems. However, the advantages of improved smoke properties can outweigh these additional complications. The effectiveness of a smoke can result from either improved obscuration power of the combined system, or, from a reduction in the corrosion and irritation properties of the smoke. For example, the highly corrosive properties of FS can be substantially modified at no overall reduction in obscuration power, by the addition of a weak chemical base capable of combining with the dilute acids formed during the hydrolysis of the agent with moist air. This can be accomplished by using any suitable volatile base such as ammonia or amine derivatives. The irritation of the smoke is also reduced at the same time, resulting in considerable improvement in operational suitability to military missions. In addition to the neutralization of acids, some dual agents provide improved obscuration capability by the formation of fine particulate matter. Two general chemical mechanisms are used for this latter purpose. One is the formation of ammonium chloride from dilute hydrochloric acid droplets formed during the hydrolysis of metal chloride smoke agents, and the second is the formation of complex reaction mixtures consisting of sulfonated products of reaction formed during the neutralization of sulfuric acid and sulfuric acid chloride smoke agents with ammonia or amine derivatives. In spite of the additional logistics and dissemination problems, these dual systems offer some advantages. The principal difficulty in using mixed agents based on ammonia is the dissemination of ammonia at ground level. This is necessary in order to provide proper support for ground troops.

1. Sulfur Trioxide and Ammonia or Amines

The smoke is formed by supplying a reactive gas to sulfur trioxide at the time of dispersion. Ammonia and amines have proved successful, and other basic substances, such as hydrazine, hydroxylamine, etc., might be satisfactory. In the case of sulfur trioxide and ammonia the reactions are:



All three reactions occur more or less simultaneously. As far as can be determined, the smoke consists of particles of these products.

2. Chlorosulfonic Acid and Ammonia or Amines

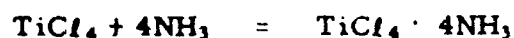
Ammonia and the amines react readily with HClSO_3 in much the same manner as with sulfur trioxide; other bases such as hydrazine, hydroxylamine, etc., probably could be substituted. The basic reaction is as follows:



Other reaction products might be formed in addition to the products indicated by this reaction.

3. Titanium Tetrachloride and Ammonia

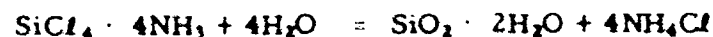
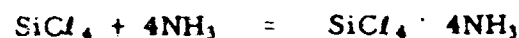
The reaction between titanium tetrachloride and ammonia is somewhat complex. First, an ammoniate is formed. This ammoniate is hydrolyzed by water vapor from the atmosphere. Ammonia reacts with the hydrochloric acid gas released during hydrolysis of TiCl_4 to give NH_4Cl . Therefore, the system without water vapor is less effective. The reactions for this process are as follows:



The smoke is a mixture of $\text{Ti}(\text{OH})_4 \cdot \text{H}_2\text{O}$, intermediate hydroxy chlorides of titanium, and ammonium chloride particles.

4. Silicon Tetrachloride, Ammonia and Water

The best proportions are two parts silicon tetrachloride, one part ammonia, and one part water, by weight. The reactions are quite complex; first, an ammoniated silicon tetrachloride is formed while at the same time hydrolysis of the silicon tetrachloride occurs to give SiO_2 , $2\text{H}_2\text{O}$, and HCl ; and finally, NH_3 combines with the HCl to give NH_4Cl . The reaction sequence is:



5. Hydrochloric Acid and Ammonia

The reaction of hydrochloric acid with ammonia is similar to the reaction of a metal chloride with ammonia. This two-gas system produces fine particles of solid ammonium chloride. The smoke formed is considered very visible. Gaseous hydrochloric acid is not very corrosive to metal containers when dry; however, when moisture is present; it is quite corrosive. The smoke, ammonium chloride, is not corrosive to metals. Hydrochloric acid gas is very irritating and, in moderate quantities, it is toxic. Ammonia gas is also toxic in moderate quantities however, the smoke, ammonia chloride, is harmless.

6. Sulfur Compounds and Ammonia

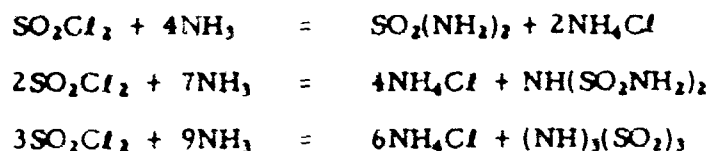
Sulfur compounds will also react with bases including ammonia and amines. These smoke-producing systems do not require atmospheric constituents to form the smoke particles and therefore, may be useful at high altitudes. Because of relatively low TOP values, these mixtures were not considered for this program.

7. Sulfur Chloride and Ammonia

This system has not been widely used. Little information is available as to chemical reactions of $S_2Cl_2 + NH_3$ or the handling properties and corrosiveness of this system.

8. Sulfuryl Chloride and Ammonia or Amines

Sulfuryl chloride will react with bases such as ammonia and amines to give a better smoke than formed with water vapor. The following reactions are for sulfuryl chloride and ammonia:



The first reaction gives sulfamide; the second, iminosulfamide; and the third, trisulfamide. Whether the smoke particles are these products or further reaction products is not known.

The dispersed phase will, therefore, consist of a mixture of ammonium chloride with sulfamide, iminosulfamide, and trisulfamide. Under

exceedingly humid conditions an additional product, ammonium sulfate, is observed. Because of relatively low smoke obscuration power, this agent has not seen extensive usage.

G. Discussion

This literature survey reflects the present state-of-the-art in military smoke technology associated with liquid smoke agents. It is descriptive in nature in that chemical agents are classified according to their gross behavior with atmospheric constituents, and their ability to produce aerosols having high TOP values. Very limited attention has been directed during this survey to the detailed chemical processes which are fundamental to the production and stability of such particles. This lack of detailed treatment is, in large part, due to the fact that the technical literature in this field has been primarily interested in the application of these agents to specific military goals. The exception to this lack of fundamental treatment is the description of the particle scattering coefficients as functions of particle size and the wavelength of incident light. In this latter field, the questions themselves have been fundamental problems of physics for many years and, therefore, theories have been developed capable of effectively describing most of the important parameters. Major advances in the field of military smoke agents, if they are to occur, will probably require a far more detailed knowledge of the chemical processes occurring in the intermediate phases of the reactions than is presently available. Unless some considerable knowledge of the reaction products and the paths by which these products are formed is available, a trial and error approach must be followed in the screening of chemical compounds for their smoke producing capability. Since many of the compounds which are possible candidates are available in research quantities, if at all, such a screening process must, of necessity, be incomplete.

The screening power of a smoke agent is evaluated in terms of either its total obscuring power or in terms of its density obscuring power. The screening power, therefore, depends on the weight of actual material available for forming the smoke particles, and the efficiency with which this material is used to form smoke particles of the greatest light scattering ability. The total weight of a smoke particle is composed of the weight of the agent used to form it, together with the weight of any atmospheric gases with which it might have combined. To be efficient, a prospective smoke agent must be able to extract a substantial portion of its total weight from the atmosphere through combustion and/or hydrolysis reactions. In addition, it is desirable that it form

particles with relatively narrow ranges of size in order to more effectively scatter incident light. These two requirements are independent and a smoke agent which can yield the greatest amount of actual particulate material may not be a satisfactory agent in some cases because of inefficient particle scattering coefficients or heavy particle fallout.

The ability of a formed chemical compound to extract material from the air is governed by the extent to which hydrolysis and combustion reactions can take place under the conditions present. Although oxidative combustion processes may occur under cold conditions, in general they take place during a deflagration between the smoke agent and air. A typical example of this type of reaction is the burning of phosphorus. Since a smoke agent which relies on a combustion process would tend to possess unfavorable properties in flash point, the use of a burning smoke was considered not as desirable as the non-burning types. A smoke which relies on the hydrolysis of a vaporized gas usually does not burn in the usual sense of the meaning of combustion processes. A relatively large number of compounds undergo strong hydrolysis reactions and it is in this class of compounds that one finds the inorganic chlorides, together with the derivatives of sulphurous and sulphuric acids. A discussion of the mechanisms that are important to the hydrolysis of these compounds has been given in the preceding sections for FS, FM, SiCl_4 , SnCl_4 and similar compounds.

An estimation of the effectiveness of the hydrolysis reaction in producing a smoke particle which has a substantial fraction of its mass obtained from atmospheric constituents can be made using thermochemical analysis of the enthalpy release for hydrolysis. The heat of reaction for the hydrolysis of a chemical compound at room temperature is a direct measure of the tendency of the reaction to proceed, and, therefore, the stability of the particle. Where the heat of reaction is high, it may be assumed that the particle will strongly absorb moisture. Also, if the physical state of the particle is such that the water absorbed can readily move through the particle to form bonds on all available sites, the maximum effect would be expected to occur. For solid particles the transport process is slow and the compounds must be heated or otherwise modified. This tends to favor the production of smoke from liquid particles. Since the free energy for the reaction is related to both the enthalpy release and the rate of reaction, a large change in enthalpy would tend to be correlated with a rapid absorption process; as a general rule, these considerations are reflected in the dessicant action. Therefore, one of the criterion which can be used to establish the suitability of a prospective smoke agent is the weight increase caused by

absorption of atmospheric moisture. Since there has been a large interest in the past in the use of inorganic chlorides for smoke agents, it is useful to divide the compounds into two separate categories; one involving the hydrolysis of inorganic chlorides, and the other consisting of the other compounds.

Metal chloride hydrates absorb between two and seven water molecules which are strongly bound by "weak" chemical bonds. Although these compounds can undergo further hydrolysis, the energy release for further dilution is small (to the point of being negligible) relative to the energy involved during the formation of these water adducts. As a first order approximation, the quantity of material which a metal chloride can absorb from the atmosphere is simply weight corresponding to these hydrate molecules. Table XI is a list of a number of chemical agents which add water directly to a metal chloride. All these agents can be expected to be hygroscopic to an appreciable degree. The underlined agents are those which have been used to produce military smokes. Missing from the group are several major smoke producing chemical agents including FM , SiCl_4 , and SnCl_4 . These do not form stable hydrates directly with the metal chlorides but, rather, undergo a complex series of reactions producing a mixture of hydroxides and chlorohydroxides. In this table is indicated the weight of water absorbed in grams per gram of the metal chloride for the direct hydrolysis reaction, and the total weight of the fully hydrated particle. As can be determined by inspection, the weight increase expected from the hydrolysis of a metal chloride varies between twelve and one hundred thirty percent for the compounds listed. The maximum smoke effectiveness of these chemicals can be calculated assuming that an optimum particle size can be produced which is similar in size to that found for fog oil droplets, and that the scattering coefficients are also effectively the same as for oil smokes. In this table a fog oil or sulphur dispersion mixture would have a rating of 1.0, corresponding to the fact that no material is added from the atmosphere. Since the maximum TOP that has been obtained from a fog oil is about 1200, a simple weight-increase ratio would indicate that a TOP of 2400 would be the maximum TOP which could be obtained from a metal chloride smoke agent, corresponding to a rating of 2.0. Of the metal chlorides listed there are four agents which might be considered to fall within this range. One of these agents, beryllium chloride, is not suitable because of toxicity and expense. The remaining three agents are lithium chloride, magnesium chloride, and calcium chloride. Table XII is a list of the physical properties of metal chlorides evaluated in Table XI. As can be determined, the physical state of the three agents under consideration is solid until quite

TABLE XI
METAL CHLORIDE HYDRATES

	<u>Water Absorbed per Gram Agent</u>	<u>Total Weight</u>
$\text{LiCl} \cdot 3\text{H}_2\text{O}$	1.30 gms	2.30 gms
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1.15	2.15
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1.00	2.00
$\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$	0.90	1.90
<u>$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$</u>	0.83	1.83
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.83	1.83
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	0.68	1.68
<u>$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$</u>	0.67	1.67
$\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$	0.66	1.66
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.57	1.57
$\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$	0.57	1.57
$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$	0.57	1.54
$\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$	0.50	1.50
$\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$	0.40	1.40
$\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$	0.39	1.39
$\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$	0.27	1.27
<u>$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$</u>	0.27	1.27
$\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$	0.23	1.23
<u>$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$</u>	0.19	1.19
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	0.17	1.17
$\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$	0.12	1.12

TABLE XII
PHYSICAL PROPERTIES OF METAL CHLORIDES WHICH FORM
STABLE HYDRATES

	<u>Melting Point °C</u>	<u>Boiling Point °C</u>
LiCl_3	614	1360
MgCl_2	712	1412
CaCl_2	772	1600
BeCl_2	440	520
AlCl_3	(190 a 2-1/2 atm)	180.2
NiCl_2	Subl.	973
CrCl_3	--	--
FeCl_3	315	--
CoCl_3	--	--
MnCl_2	650	1190
CrCl_2	--	1200d
NdCl_3	d	--
PrCl_3	823	--
CdCl_2	568	960
ThCl_4	820	--
PtCl_4	d370	--
CuCl_2	Subl.	1049
TlCl_3	37	100d
SnCl_2	247	623
BaCl_2	962	1560
AuCl_3	254d	Subl. 265

high temperatures are obtained. Therefore, if a successful smoke agent is to be developed using a metal chloride hydrolysis mechanism, a considerable amount of heat would be required to vaporize the agent. The heat for such vaporization can be furnished using a pyrotechnic mixture. However, this results in a decreased TOP because the additional weight of the added pyrotechnic components must be considered as dead weight. A possible method for the dissemination of a metal chloride would be to dissolve or slurry materials such as lithium, magnesium, and calcium chlorides into other agents in the hope of obtaining a mixed solution capable of effective dispersment of the active chloride agent in a liquid form thereby avoiding the necessity of evaporating a high melting salt. A possible approach to provide the necessary heat for evaporation would be to place a pyrotechnic coating on the surface of a small metal chloride particle and then slurry the particles into a stable liquid mixture. Solids loadings of up to ninety percent have been achieved for slurried rocket fuels and it is assumed that solids loadings of eighty percent are achievable for most solids of this type. Prospective coatings would include phosphorus and light metal alkyls. Phosphorus would be expected to have the added advantage of implementing the produced chloride smoke by the addition of a phosphorus smoke. The second approach might be accomplished by using a mixed agent consisting of boron trichloride and one of the more hygroscopic metal chlorides. Boron chloride itself is not hygroscopic in the sense previously discussed, but undergoes a reaction similar to the stannic and titanium chlorides upon air contact. The reaction is probably to form $B(OH)_3$ and HCl .

A second class of compounds consists of those undergoing strong hydrolysis reactions but not including the metal chlorides. These materials are desiccants and, unfortunately, are all normally solids at room temperature. This latter fact would imply that they would have to be disseminated as powders having extremely small particulate size. This would impose a number of technical problems in the VSE of these materials from airborne tankage. However, in some cases, it is possible that the desiccant agent could be formed by an oxidation reaction of the base material with air, similar to the manner in which white phosphorus becomes effective. A list of possible materials of this type is contained in Table XIII. Table XIII gives the product-to-reactant weight ratios corresponding to selected hydrolysis reactions. These ratios considered the hydrates which had the highest enthalpy of formation, restricted by the criterion that, where the free energy of formation was less than one-half kilocalorie per mole for the next highest hydrate, it was assumed that the reaction would be limited to the lower hydrate member. Table XIV

TABLE XIII
PRODUCT TO REACTANT WEIGHT RATIOS
FOR SELECTED HYDRATES

<u>Compound</u>	<u>Product/Reactant</u>
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2.05
$\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	1.8
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$	2.03
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.73
$2\text{La}(\text{NO}_3)_2 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$	1.5
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	1.5
$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$	1.64
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	1.95
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1.76
$\text{MgO} \cdot \text{MgCl}_2 \cdot 16\text{H}_2\text{O}$	3.16
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1.66
$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$	1.83
$\text{Mn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$	1.70
$\text{ZrO}_2 \cdot 5\text{H}_2\text{O}$	1.73
$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	1.80
$\text{BaO} \cdot 8\text{H}_2\text{O}$	1.94
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	1.94
$\text{LiOH} \cdot \text{H}_2\text{O}$	1.75
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	2.27
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	2.30
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	2.7
$\text{CaCl}_2 \cdot 3\text{CaO} \cdot 16\text{H}_2\text{O}$	2.03
$\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	1.71
$2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$	1.73

TABLE XIII (Cont)

<u>Compound</u>	<u>Product/Reactant</u>
$\text{SrO}_2 \cdot 8\text{H}_2\text{O}$	2.20
$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	2.20
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1.83
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1.50
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.57
$\text{Zn}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$	1.78

shows the same information for a series of hydrates which are similar to those in the previous table with the exception that the parent compound is an oxide which could also be formed by the combustion of the metal or one of its compounds with air. For this latter table, two P/R ratios are given corresponding to formation from the oxide and to formation from the metal. It is interesting that at least one of these hydrates is a strong desiccant producing a weight increase of the same order as phosphorus without the necessary requirement for combustion. In general, a fairly wide selection of materials exists which, theoretically, could absorb enough water moisture from the air to make a particle which has a weight two times greater than the starting material. For these materials, the major difficulty is that to have effective scattering the final particle size should be no larger than about 0.5 micron. This would imply the requirement that an initial particle no larger than 0.2 micron which must also be effectively and efficiently dispersed. Dispersion of particles of this size is difficult to achieve. It is, however, interesting to speculate that the corrosive effects on a sulfurous acid and a sulfuric acid based smoke agent might be substantially modified by the addition of a salt of sodium, magnesium, or aluminum to form scattering particles consisting of $MgSO_4$. Only a small effect on TOP for such additions would be expected, provided the weight of the anion component was light.

If a burning smoke can be tolerated, there are three potential smoke agents which could be considered to be candidates. These are the mixed calcium-boronoxide hydrate, the mixed magnesia-magnesium chloride hydrate, and the strontium oxide hydrate system. Each of these have the potential to have an obscuration capability greater than WP if the proper circumstances for burning and water absorption can be provided. One possibility which could be investigated is use of alkyl derivatives of strontium, calcium, and boron to determine their smoke effectiveness. With the lighter alkyl derivatives, it should be possible to provide a smoke agent having obscurational potential equal to WP.

One of the ways to modify a smoke agent's effectiveness is to reduce the weight of those parts of the molecule which are not used effectively for the production of smoke. In many of the proposed reactions explaining the hydrolysis of FM and $SnCl_4$, it can be inferred that the chlorine in these molecules does not effectively increase their smoke obscuration capability. A possible approach, then, would be to replace one or more of the chlorine atoms with a lighter group retaining the general range of liquidus properties. One way of accomplishing this replacement would be to exchange the heavy chlorine atoms for lighter

TABLE XIV
PRODUCT TO REACTANT WEIGHT RATIOS FOR SELECTED
HYDRATED METAL OXIDES

<u>Product Compound</u>	<u>P/R (Oxide)</u>	<u>P/R (Metal)</u>
BaO · 8H ₂ O	1.94	2.17
ZrO ₂ · 5H ₂ O	1.73	2.34
CaO · 3B ₂ O ₃ · 13H ₂ O	1.73	4.71
SrO ₂ · 8H ₂ O	2.20	4.32
MgO · MgCl ₂ · 16H ₂ O	3.16	3.45

alkyl groups. The lightest organic derivatives of titanium are the methyl substituted titanium chloride derivatives. These compounds possess favorable physical properties being liquids at ordinary temperatures. It would be expected that the products of hydrolysis would be no more corrosive or toxic than FM and the other parent compounds. Because the major difficulty in handling these compounds is associated with their characteristic polymerization reactions, resulting in extensive gumming of equipment, there is the possibility that a light alkyl derivative of FM would have favorable properties in terms of both smoke production and reduction of gum formation.

The parameters which are important to these combustion reactions for metal alkyls include the heat of formation of the parent compound, the heat of combustion to form the metal oxide and alkyl radicals, and an estimate of the dissociation energy for bond rupture. The rate of reaction is to a first approximation dependent on the activation energy necessary to cause bond cleavage. In this approximation, this energy can be correlated with the average bond dissociation energy. Thus, the lower the activation energy, the more easily bond schism occurs and the more rapidly hydrolysis or combustion reactions will proceed. The average bond dissociation energies for select metal alkyls is given in Table XV as $\overline{D(M-R)}$.

It has been reported that $Ti(CH_3)Cl_3$ is completely stable in the dark at room temperature. At higher temperatures, there is a tendency of this compound to undergo autocatalytic decomposition. Whether this decomposition is attributed to an autocatalyst or to impurities is not presently known. Whether dimethyl dichloro titanium $Ti(CH_3)Cl_2$ is stable is also not presently known. Uses involving this chemical have been reported in the chemical patent literature which would indicate this compound is stable. More recent work published in the open literature reports a half-life in the gas phase of about two hours. These reports are inconsistent, one with the other, and an additional evaluation of the thermal stability should be made for this compound. Very little data is available concerning the chemical stability of the last member of this series, titanium trimethyl monochloride.

The above compounds are reported as being liquids at $-40^\circ C$ or below. At room temperature, they are characterized as having an oily or viscous consistency. No reported work describing the properties of these compounds was available above room temperature. $TiCl_2(CH_3)_2$ is reported to have a vapor pressure of .2 mm Hg in the temperature range, 0 to $25^\circ C$.

TABLE XV
HEATS OF FORMATION OF SELECTED
ORGANO METALLIC COMPOUNDS

	$\Delta H_f^\circ (l)$	$\Delta H_f^\circ (g)$	$\overline{D(M-R)}$
Zn(Me) ₂	+ 6.3	+ 13.0	+ 41
Zn(Et) ₂	+ 4.3	+ 13.1	- 34
Zn(Pr) ₂	- 13.6	- 3.9	40
Zn(Bu) ₂	- 24.9	- 14.6	41
B(Me) ₃	- 34.8	- 30.1	89
B(Et) ₃	- 46.8	- 38.0	85
B(Bu) ₃	- 83.9	- 70.8	89
Al(Me) ₃	- 26.9	- 12.0	61
Si(Me) ₄	- 75.0	- 69.0	77
Sn(Me) ₄	- 21.4	- 13.6	53
Pb(Me) ₄	23.5	+ 32.6	35
Pb(Et) ₄	12.8	+ 23.0	31
P(Me) ₃	- 30.1	- 23.2	65
P(Ph) ₃	+ 54.3	+ 72.4	71
Sb(Me) ₃	- 1.4	+ 6.4	50

All members of this series react upon contact with either moisture or air. It is assumed that these reactions involve either a direct hydrolysis or air oxidation. Detailed results documenting the course of such reactions are not available.

It has been suggested that the titanium esters such as titanium tetraethylate and similar compounds may function as effective smoke agents. At this time, there have been no available numerical data concerning the effectiveness of these compounds when used for this purpose.

A prominent fact is the weight increase from atmospheric components in the case of white phosphorus results in a very effective smoke. For WP, the P/R ratio is 3.3, which is substantially larger than for other currently used smoke agents. An analysis of these values for SO_2 and FM indicates values of 2.1 and 1.45, respectively. This fact indicates that if a highly efficient smoke agent is desired, emphasis should be placed on modifications of white phosphorus. In addition, the smoke produced by WP and its derivatives is relatively noncorrosive and non-toxic. The major difficulty in using phosphorus as a smoke agent is its pyrophoricity. For certain solution (MIP), this is reduced considerably and, further, most phosphorus fires are readily extinguished by water. With the exception of WP, used either by itself or in conjunction with a plasticizer, there was little information in the literature concerning the smoke properties of phosphorus derivative. There are a number of techniques which can be used to provide a smoke agent containing relatively high amounts of phosphorus. These include the use of phosphorus in solutions, in mixtures, in slurries, and incorporated into selected compounds. Of considerable promise is the incorporation of WP into solutions and eutectic mixtures for the reason that high phosphorus loading can be achieved with retention of favorable physical properties. Because the work accomplished in this program has outlined a number of suitable agents, the discussion of phosphorus and its compounds and mixtures is more appropriately reserved for the experimental sections.

The effectiveness of a smoke agent has been correlated with the weight increase of the formed products of reaction during an air hydrolysis and air oxidation reaction. In previous discussions using this correlation, the statement was made without an indication of the basis for its validity. For four smoke agents, SO_2 , white phosphorus, titanium tetrachloride, and fog oil, verification is made in the following discussion. The smoke producing mechanisms of these agents can be summarized by the following reaction sequences.

- (1) $\text{SO}_3 + \text{H}_2\text{O} = \text{SO}_3 \cdot 5\text{H}_2\text{O}$
- (2) a. $\text{P}_4 + \text{O}_2 = \text{P}_2\text{O}_5$
 b. $\text{P}_2\text{O}_5 + \text{H}_2\text{O} = \text{H}_4\text{P}_2\text{O}_7 \cdot 1\frac{1}{2}\text{H}_2\text{O}$
- (3) $\text{TiCl}_4 = (\text{HO})_3\text{Ti-O-OH} + 4\text{HCl}$
- (4) Oil = Oil

As before, a criterion used to establish the extent of hydrolysis is the formation of a hydrate to the limit of 0.5 kilocalorie per mole energy increase. Products listed are those which would be expected from thermodynamic criteria. These are not necessarily those which have been discussed in the literature in which little or no experimental identification of species has been reported. Table XVI lists the measured TOP for these smoke agents as reported in the literature, together with the product reactant weight ratios for the assumed reactions. A calculated TOP is then obtained which was based on the assumption that the TOP of WP is 4800. As can be determined from this table, the calculated values of TOP tend to have a reasonable correspondence to those actually measured. Although there are a number of exceptions, it is useful to have a correlation of this type available for rough calculations. In general, the exceptions always result in lower calculated values of TOP, thus setting an upper bound to the obscuration power of untested smoke agents. The real difficulty in evaluating candidate smoke agents in this manner is to have sufficient chemical insight to be able to predict the actual reaction products. Thus, for example, in the case of FM, it would certainly be reasonable to assume that the HCl is ineffective and not to be considered or, alternatively, to postulate a mixed chloro oxide. The result of this analysis would tend to indicate that the HCl does not separate from the other reaction products in the formed particle.

At the beginning of this section, reference was made to the necessity for an effective smoke to have large scattering coefficients. The theoretical effects of changes in K_s on the obscuration capability of aerosols is well understood. The size of a particle is dependent thermodynamically on the surface tension of the exposed liquid. Where there are large solution effects—as is true for the hydrolysis of a P_2O_5 particle to form a dilute acid, it may be assumed there is also a considerable change in surface tension at selected stages of hydrolysis. Since this physical property can be greatly modified by small changes in the composition of the surface, it would be expected that the use of surface active agents to control particle size of the produced aerosol would be effective.

TABLE XVI
COMPARISON OF PRODUCT TO REACTANT WEIGHT RATIOS
TO RELATIVE TOP VALUES

	<u>TOP</u> <u>(Reported)</u>	<u>P/R</u>	<u>Relative</u> <u>TOP</u> <u>(Calculated)</u>
WP	4800	3.3	4800
SO ₃	3000	2.1	3200
FM	1900	1.47	2100
Oil	1200	1.0	1400

In summary, a review of the literature indicates that only two single-component smoke agents have a total obscuring power greater than that of FS. These agents are sulfur trioxide and white phosphorus. Sulfur trioxide has the same disadvantages that are characteristic of FS, namely corrosivity, irritation, etc., with the additional disadvantage of having a low boiling point necessitating the use of pressurized containers in order to properly store the agent. White phosphorus has a high TOP, nearly twice that of FS, but is normally a solid melting at 44°C. A major disadvantage of WP other than its physical properties is that it is pyrophoric with air. This pyrophoricity causes handling problems, particularly for airborne dissemination applications.

Dual Agents

The use of dual smoke agents can provide TOP values in excess of 2500. However, the additional complication of equipment would tend to nullify the advantages of higher obscuration power, lessening of corrosivity, and reduction in irritation. The agent ordinarily used to neutralize the acidic vapors is ammonia which, because of its low boiling point, would require substantial gas pressurization equipment together with relatively heavy flight-weight hardware. For a rapid development program, the use of dual agents could be used to provide substantial improvements in airborne military screening smokes. Only limited use of present tankage could be made for the dissemination of these dual agents. The minimum modification schedule would include the development of airborne mixing manifolds and the fabrication of ammonia tankage. There is a possibility that other less volatile amine agents could be used, but relatively little work has been done outlining their effectiveness.

Modifications to Titanium Tetrachloride

It is perhaps possible to modify agents possessing TOP value less than FS to improve their smoke obscuration and handling properties. The logical agent to consider is FM. One method by which modifications of this agent could be implemented is to synthesize different chemical compounds which are derivatives of titanium tetrachloride. The choice of possible derivatives of titanium tetrachloride which could be considered for this program is quite large and, because of program limitations, it is necessary to select relatively few for further study. Necessarily, this selection must be based on an analysis of the effective chemical mechanisms governing the extraction of atmospheric moisture to form the aerosol particle. Unfortunately, a critical examination of the

literature tended to indicate that the chemical hydrolysis mechanisms usually proposed are, in general, quite speculative. Apparently, very little detailed knowledge exists concerning the precise nature of the products of the gas phase hydrolysis reactions. For example, as a tentative hypothesis, it is possible to assume that replacement of a chlorine atom in titanium tetrachloride by a lighter alkyl group might provide some improvement in smoke properties. The basis for this hypothesis is the assumption that the first chlorine atom is easily removed during the initial hydrolysis step, and that it is ineffective in producing an increased weight in the smoke particle. Replacement of the chlorine atom by a methyl radical would allow a potential weight reduction in the weight of the molecule of the order of forty percent. If all other factors are the same it would then be possible to improve the smoke obscuration power of this modified titanium compound to a value approximating 2800. It is reasonable that replacement of chlorine atoms, one at a time, by methyl groups should result in a smoke agent with intermediate properties. The limit to the size of the alkyl group would be to the propyl radical which is somewhat greater in weight than the chlorine atom. A replacement of the Cl atom by a higher alkyl derivative would, in this view, be detrimental. There is, however, some preliminary evidence, as is discussed in the experimental section of this report, that the dissociation of a compound composed of higher molecular weight alkyls may give rise to an oil smoke formed by the gas phase recombination of alkyl radicals. It was observed that alkyl derivatives of phosphorus and tin both exhibited higher TOP values for butyl than for methyl replacements. This is contradictory to the above hypothesis and further work is needed to clarify the problem.

Phosphorus Derivatives

One of the prominent facts which is apparent from the literature review is that the physical and corrosive properties of a white phosphorus smoke are good and that the TOP of phosphorus based smoke agents is considerably in excess of that of the reference standard FS. The two major disadvantages of white phosphorus are its relatively high melting point and its pyrophoricity. Because the TOP of WP is high, it is possible to make substantial modifications of WP by compound formation, dissolution, slurries, and incorporation in mixtures. These modifications are not restricted to high concentrations of the active agent, since a fifty percent dilution of the WP would still provide a smoke agent having an obscuration power in the range of 2500. One problem which is difficult to overcome is the pyrophoricity of the smoke agent. However, it is possible to use fire retardants to slow the combustion rate

and provide mixtures that can be safely transferred by decantation in air. This has been done under this contract using EWP-MIP mixtures. Since the most likely prospect of developing a liquid smoke agent having good properties and a TOP of 2000 or greater appeared to require the development of a phosphorus based smoke agent, a considerable technical effort was expended on this area. The work performed is more fully described in the experimental sections.

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APPENDICES

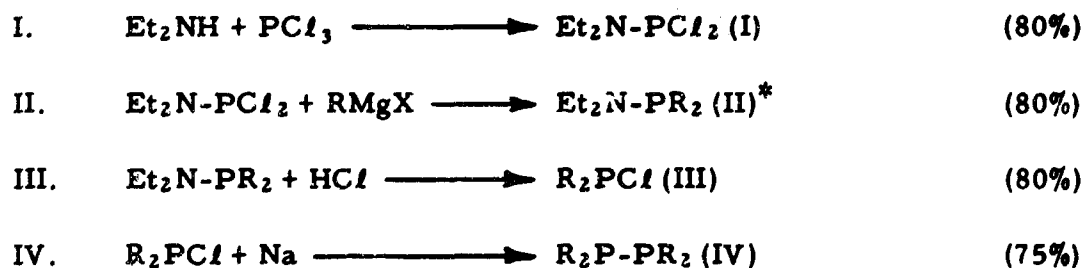
APPENDIX A

SYNTHESIS OF PHOSPHINE AND DIPHOSPHINE DERIVATIVES

By

Harry Babad, James B. Wood, and William H. McLain

Routes to the tetraalkyldiphosphines, for screening as possible smoke agents, were sought. Although compounds of this type have been reported previously,^{1,2} their synthesis has been but poorly described in the literature. The method of Issleib and Seidel³ was chosen as the most direct route to the desired compounds. This synthesis is outlined below:



Issleib and Seidel claimed an overall yield of 40% in the conversion of phosphorous trichloride to tetraethyldiphosphine or tetra-n-butyldiphosphine. In our hands, this synthesis leads to irreproducible yields of 0-30% of products in steps II and III. Drastic modification of the procedure of Issleib and Seidel, enabled us to obtain reproducible (70-80%) yields of the diethylaminedialkyl phosphines. Modifications included a drop in reaction conditions from -20 to -70°, substitution of a lithium reagent for the organomagnesium compound and elimination of the inverse addition of the organometallic to the diethylamino-phosphorous dichloride. These results are tabulated below:

Compound	Literature	RMgX	RLi
Me ₂ PNEt ₂		Less 25%	55%
Et ₂ PNEt ₂	65% ³	13-20%	55-60%
n-Pr ₂ PNEt ₂		30%	77%
n-Bu ₂ PNEt ₂	58% ³	29%	81%

* R = ethyl, n-butyl, etc.

As can be seen by the above results, the substitution of a lithium reagent for a grignard drastically increases the yields. The major problem in the grignard synthesis seems to be complexes involving the phosphorous compound with the magnesium halide. Step III, the addition of a gaseous HCl to a solution of dialkyl-diethylaminophosphine also proved irreproducible (0-30% yields). For the synthesis of the n-butyl compound, treatment of II, with acetyl chloride followed by distillation resulted in a fair yield (60%) of di-n-butylphosphorous chloride, but this synthesis could not be applied to the lower members of this series because of interference of the acetamide of diethylamine which leads to separation difficulties. The dimerization of the dialkylphosphorous chloride with sodium was not studied in sufficient detail to determine whether it too suffered from the failings of low yield and irreproducibility. Further work in characterizing these and other phosphorous alkyls is being undertaken, and the synthesis for these materials in good yields should make these available for other studies.

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APPENDIX B

SOLUTIONS OF WHITE PHOSPHORUS

One approach to increase phosphorus content of a smoke agent has been to try to dissolve high weight concentrations of white phosphorus in different solvents. The difficulty with this approach is that, with the exception of carbon disulphide, the reported solubility of phosphorus in most common solvents is too low to provide an effective smoke agent. Since it would be desirable to find other liquids which might also act as suitable solvents for phosphorus, an analytical approach was developed to predict possible new solvents for phosphorus. The analysis was based on theoretical work involving the theory of regular solutions as developed by Hildebrand et al for non-associated liquids. The central parameter in this theory involves the internal cohesive energy at constant volume, which is also commonly denoted by the term "solubility parameter." This parameter relates the relative solubility to the molecular interactions and is defined as the square root of the energy of vaporization per cubic centimeter.

$$\delta = \left(\frac{\Delta E^v}{v} \right)^{\frac{1}{2}}$$

A number of methods are available for calculating this parameter using data obtained from pure liquids. Since molar volumes are readily available for most liquids, the problem of determining values of the solubility parameter is resolved into evaluating the cohesive energy, (ΔE^v) at vaporization. Thermodynamically, this energy is given by:

$$\begin{aligned} \Delta E^v &= \Delta H^v - P\Delta v^v \\ &= (\Delta H^v_{app} - RT)Z \left(\frac{v_g - v^c}{v_g} \right) \\ &\approx \Delta H^v_{app} - RTZ \end{aligned}$$

where Z is the compressibility factor. For many substances the compressibility factor is < 1 and, as a first approximation, the solubility parameter becomes approximately equal to:

$$\delta = \left(\frac{\Delta H^v}{v^c} \right)$$

The heat of vaporization can be evaluated in several ways using: (1) calorimetric heats of vaporization; (2) vapor pressure data; (3) estimation from the Hildebrand rule, or; (4) solubility data. Where measured experimental data is not available, the use of the Hildebrand rule is applicable. This is an empirical rule of the form:

$$\Delta H^V_m \text{ (Cal/mole)} = -2950 + 23.7 T_b + 0.020 T_b^2$$

or: $\Delta H^V_b \text{ (Cal/mole)} = 17.0 T_b + 0.009 T_b^2$

which is applicable to non-polar liquids. An additional useful relationship is that associated for mixed solvents as given by:

$$\delta_m = \frac{\phi_1 \delta_1 + \phi_2 \delta_2 + \dots}{\phi_1 + \phi_2 + \dots}$$

The master equation relating the solubility parameter to the mutual solubility of non-associated liquids is given by thermodynamic relation:

$$\ln a_2 = \ln x_2 + \frac{v_2 \phi_1^2 (\delta_2 - \delta_1)^2}{RT}$$

where:

- a is activity
- x is mole fraction
- v is partial molal volume
- ϕ is volume fraction

in which the subscripts refer to components 1 and 2, i.e., the solvent and solute, respectively.

Rewriting this equation, it is obvious that the mole fraction of solute is related to a free energy function diminished by the quantity involving the second term in the above equation. Thus, as the difference between solubility parameters decreases, an increase in solubility of the solute into the solvent should be expected. In the limit, this term goes to zero for completely miscible solutions.

The general usefulness of this approach stems from the fact that, although it is at best semi-quantitative from a theoretical point of view, the relation of empiricals holds for a large number of different types of compounds. For example, for chloroform, the value of the solubility parameter is 13.1. Table 2.1 contains a list of selected values for the

TABLE B-1
SOLUBILITY PARAMETER FOR SELECTED
POSSIBLE SOLVENTS

Substance		Solubility Parameter	Molal Volume	$\delta_2^2 - \delta_1^2$
<u>Phosphorus</u>		<u>13.1</u>	<u>70</u>	<u>0</u>
CCl_4	Carbon Tetrachloride	8.6	97	20
SiCl_4	Silicon Tetrachloride	7.6	115	30
SiBr_4	Silicon Tetrachloride	8.8	127	18
SnCl_4	Tin Tetrachloride	8.7	118	18
SnI_4	Tin Tetraiodide	11.7	151	2.2
S_8	Sulfur	12.7	135	0.16
I_2	Iodine	14.1	59	1.0
Br_2	Bromine	11.5	51	2.6
$\text{n-C}_5\text{H}_{12}$	n-pentane	7.1	116	36
$\text{n-C}_8\text{H}_{18}$	n-octane	7.5	164	31
C_6H_6	benzene	9.2	89	16
C_8H_{10}	xylene	9.0	121	16
C_8H_8	styrene	9.3	116	14
C_6F_{14}	perfluro-n-hexane	5.9	205	52
C_6F_6	perfluoro-cyclohexane	6.1	170	49
CS_2	carbon disulfide	10.0	61	9.6
CH_2I_2	methylene iodide	11.8	81	1.7
CHBr_3	bromoform	10.5	88	6.8
CH_3I	methyl iodide	9.9	63	10
CH_2Cl_2	methylene chloride	9.8	64	11
$\text{C}_2\text{H}_5\text{I}$	ethyl iodide	9.4	81	14
$\text{C}_2\text{H}_5\text{Br}$	ethyl bromide	9.9	75	18
$\text{C}_2\text{H}_5\text{Cl}$	ethyl chloride	8.3	74	23
CCl_4	carbon tetrachloride	8.6	97	20
CHCl_3	chloroform	9.2	81	15
$\text{C}_2\text{H}_4\text{Cl}_2$	ethylene chloride	9.9	79	10
$\text{C}_2\text{H}_4\text{Cl}_2$	ethylene dichloride	9.1	85	16
$\text{C}_2\text{H}_4\text{Br}_2$	1,2 detromoethane	10.2	90	8
C_2Cl_4	tetrachloroethylene	9.3	103	14

solubility parameter for a number of classes of compounds. To determine the relative solubility of phosphorus in different solvents, a "zero order" approximation can be made using the criterion that the difference of squares between solubility parameters should be minimized. This quantity is given in column three of Table B-I. The substance underlined has a relatively low value of this parameter indicating that, in these series, the solubility of these substances should be high.

Of these substances, bromine, iodine, sulfur, methylene iodide, and tin tetraiodide appear most promising as solvents. The elements bromine, iodine, and sulfur tend to form stable compounds with substantial exothermic heats of reactions. Tin tetraiodide has a high melting point (150°C) indicating that even with a strong eutectic lowering the formed solution would freeze well above -40°C. A solution of WP in methylene iodide is most promising from this point of view.

APPENDIX C

OPTICAL PROPERTIES OF PARTICULATE CLOUDS⁺

Particles, suspended in a gaseous medium, scatter, reflect, and absorb radiation in a manner depending on the nature, size, shape of the particle, and the wavelength of the incident radiation. These factors, in turn, determine the effectiveness of a smoke for screening and its visibility when used for signaling or similar purposes.

The scattering of light by a particle can be treated as the interaction between the electromagnetic waves and the particle. When light strikes a particle which is comparable in size to or smaller than its wavelength, reflection and refraction, in their normal sense, no longer occur. Interaction between the radiation and particle results in energy being removed from the wavefront. Some of this energy is degraded to heat but much is re-radiated as scattered radiation. Each particle becomes, in effect, a self-luminous source.

The theory of scattering by spherical particles was developed from Maxwell's equations by Gustave Mie.* For spherical particles which are small compared to the wavelength of light, this theory gives results which are in complete agreement with the results obtained from the less-general Rayleigh theory, which states that the amount of radiation scattered is inversely proportional to the fourth power of the wavelength. As the particle radius increases in size to approximately the wavelength of the light, the scattering becomes a very complex function of the particle radius, the refractive index of the particle, and the wavelength of the incident light. The scattering coefficient, i. e., the scattering per unit cross-sectional area of the particle, is an extremely complicated function of the parameter r/λ (where r is the radius of the particle and λ is the wavelength of the incident light), and exhibits one or more peaks before approaching the limiting value of 2 as is shown in Figure C-1. The peak of this curve for maximum scattering moves toward smaller radii as the refractive index of the particle increases. For screening smoke made from fog oil, which has a refractive index of 1.50, the maximum scattering of visible light will occur when the droplets are about 0.3 micron in diameter.

⁺ This part of the discussion is abstracted in part from Evans, R. W., Pyrotechnic Handbook (1966) (In Press).

* G. Mie, Ann der Phys., 25, 1908, p. 377.

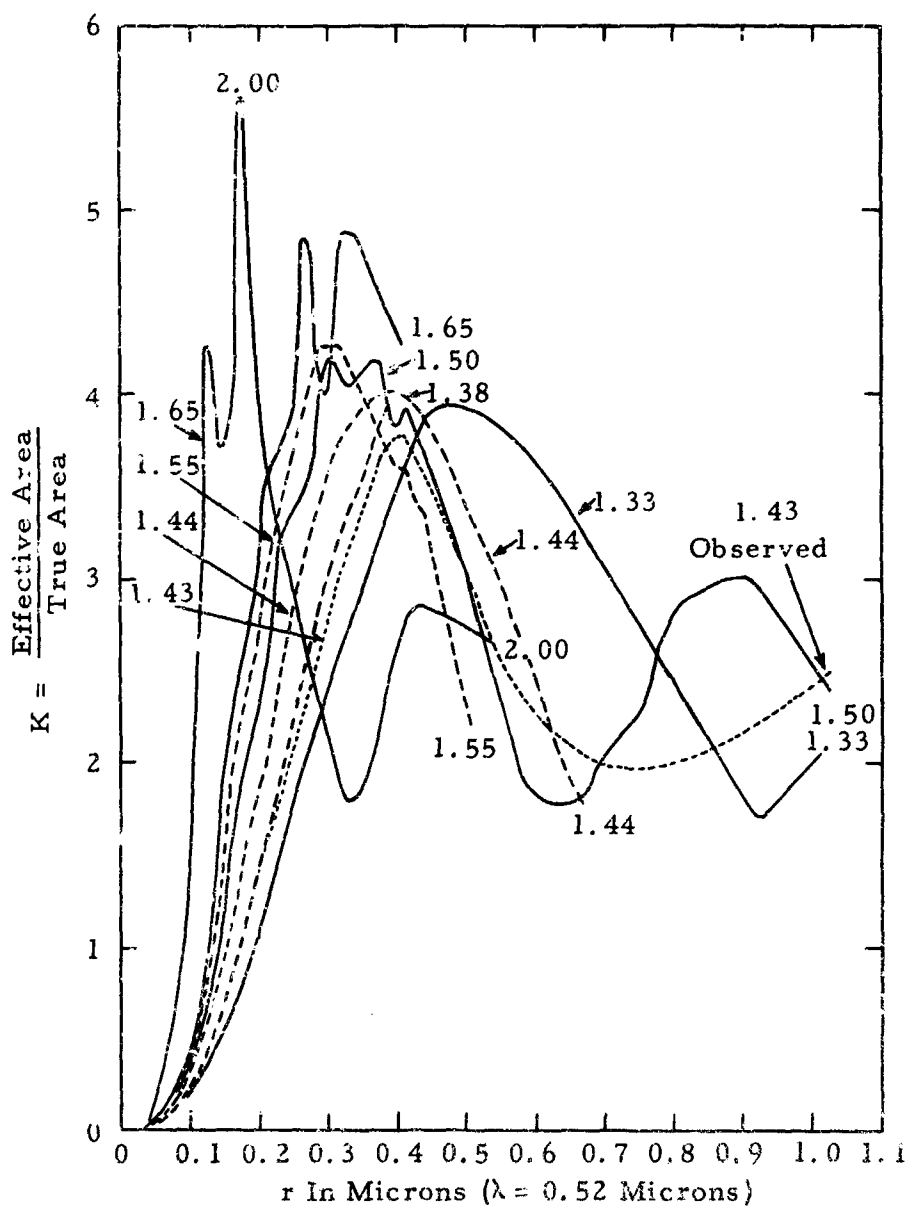


Figure C-1. Scattering Coefficient for Spherical Particles. K versus a , r and λ

The angular distribution of the scattered light is also a function of r/λ . For Rayleigh scattering by small particles, as much light is scattered backward as is scattered forward. With an increase in the particle radius, the forward scattering becomes much greater than the backward scattering. For a particle whose radius is equal to or greater than the wavelength of light, this factor may be 1000 or more.

Smoke clouds, which have a distribution of particle size, exhibit the scattering which would be observed for a mixture of a large number of uniformly-sized particles mixed in varying proportions. No completely satisfactory analysis of the amount of scattering that may be expected from such a poly-dispersed smoke cloud has been made.

The theoretical treatment of the scattering of light by particles which also absorb is a difficult problem, especially when absorption is selective. When the incident light is white, the scattering by each of the particles will remove some of the light selectively absorbed so that the light finally scattered by the cloud will be colored. Similarly, for a monodispersed system of selective particle size, scattering resulting in colored smokes may result.