AD NUMBER

AD827272

NEW LIMITATION CHANGE

TO

Approved for public release, distribution
unlimited

FROM

Distribution authorized to U.S. Gov't.
agencies and their contractors;
Administrative/Operational Use; Dec 1967.
Other requests shall be referred to
Edgewood Arsenal, Physical research
Laboratory, Edgewood Arsenal, MD 21010. .

AUTHORITY

USAEA ltr, 14 Sep 1971

AD

Final Report

RESEARCH STUDIES ON THE DISSEMINATION OF SOLID AND LIQUID AGENTS

Contributing
Editors:

I. G. POPPOFF
W. C. THUMAN

This document has been approved
for public release and sale; its
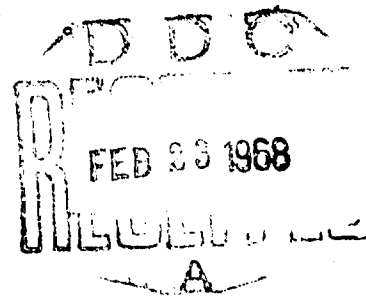distribution is unlimited

DECEMBER 1967

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Physical Research Laboratory
Research Laboratories
Edgewood Arsenal, Maryland 21010

Contract DA-18-035-AMC-122(A)

STANFORD RESEARCH INSTITUTE
Menlo Park, California

DDC

FEB 23 1968

STATEMENT #2 UNCLASSIFIED

DISTRIBUTION STATEMENT

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, Edgewood Arsenal, ATTN: SMUEA-STI-T, Edgewood Arsenal, Maryland 21010.

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.

DISPOSITION

Destroy this report when no longer needed. Do not return it to the originator.

UNCLASSIFIED

AD-827 272   15/2   7/4
STANFORD RESEARCH INST MENLO PARK CALIF

RESEARCH STUDIES ON THE DISSEMINATION OF SOLID AND
LIQUID AGENTS.   (U)

DESCRIPTIVE NOTE: FINAL REPT. APR 64-DEC 67,
      DEC 67   138P   POPPOFF,I. G. ;THUMAN,W.
C. ;
CONTRACT: DA-18-035-AMC-122(A)
PROJ: DA-1B522301A081; SRI-PAU-4900
TASK: 1B522301A08101

        UNCLASSIFIED REPORT
  DISTRIBUTION: NO FOREIGN WITHOUT APPROVAL OF ARMY
EDGEWOOD ARSENAL, ATTN: SMUEA-TSTI-T,
EDGEWOOD ARSENAL,MD. 21010.

DESCRIPTORS: (*CHEMICAL WARFARE AGENTS,
 DISSEMINATION), SOLIDS, LIQUIDS, AEROSOLS,
 EXPLOSIVE MATERIALS, ELECTROSTATICS, DETONATIONS,
 SHOCK WAVES, IGNITION, PYROTECHNICS, PYROLYSIS,
 OXIDATION, DEGRADATION, CONDENSATION, ULTRASONIC
 RADIATION, PNEUMATIC SYSTEMS, ENCAPSULATION,
 HYDROLYSIS, EQUATIONS OF STATE, ENTROPY,
 ATOMIZATION, POWDERS   (U)
IDENTIFIERS: POINT-SOURCE DISSEMINATION   (U)

    THE OBJECTIVE OF THE PROGRAM WAS TO PROVIDE BASIC
    INFORMATION NECESSARY FOR AN OVERALL IMPROVEMENT OF
    CHEMICAL AGENT DISSEMINATION TECHNIQUES. STUDIES
    WERE MADE OF EXPLOSIVE GENERATIONS OF AEROSOLS
    (MECHANICS OF EXPLOSIVE PROCESSES; DETONATION,
    SHOCK, AND REACTION PROCESSES; IGNITION PROCESSES;
    COMMINUTION PROCESSES); THERMAL AND PYROTECHNIC
    GENERATION OF AEROSOLS (THERMAL AND PYROTECHNIC
    PROCESSES; PYROLYTIC AND OXIDATIVE DEGRADATION
    PROCESSES; CONDENSATION PROCESSES); ULTRASONIC,
    PNEUMATIC, AND ATOMIZATION PROCESSES; ELECTROSTATIC
    PHENOMENA ASSOCIATED WITH AEROSOL PRODUCTION; THE
    APPLICATION OF MICROENCAPSULATION TO AEROSOL
    GENERATION AND ENHANCEMENT; AND NATURAL AEROSOL
    GENERATION. A CRITICAL SUMMARY OF THE PROGRAM AND
    RECOMMENDATIONS FOR FUTURE WORK IS FIRST PRESENTED.
    THIS IS FOLLOWED BY A DISCUSSION OF ACCOMPLISHMENTS
    AND RECOMMENDATIONS FOR FUTURE RESEARCH IN EACH OF
    THE STUDY AREAS LISTED ABOVE, WITH REFERENCE TO
    PROGRAM REPORTS (22 SPECIAL TECHNICAL REPORTS
    AND 13 QUARTERLY PROGRESS REPORTS) FOR
    DETAILS. (AUTHOR)   (U)

                              UNCLASSIFIED   /BECKS

Final Report

RESEARCH STUDIES ON THE DISSEMINATION OF SOLID AND LIQUID AGENTS

Contributing
Editors:

I. G. POPPOFF
W. C. THUMAN

DECEMBER 1967

FOREWORD

The work described in this report was authorized under task 1B522301A08101, "Dissemination Investigations of Liquid and Solid Agents (U)." The work was started in April 1964 and completed in October, 1967.

Acknowledgments

2

DIGEST

The objective of the program was to provide basic information
necessary for overall improvement of chemical agent dissemination tech-
niques. Studies were made of explosive generation of aerosols (mechanics
of explosive processes; detonation, shock, and reaction processes; igni-
tion processes; comminution processes); thermal and pyrotechnic genera-
tion of aerosols (thermal and pyrotechnic processes; pyrolytic and oxi-
dative degradation processes; condensation processes); ultrasonic,
pneumatic, and atomization processes; electrostatic phenomena associated
with aerosol production; the application of microencapsulation to aerosol
generation and enhancement; and natural aerosol generation.

A critical summary of the program and recommendations for future
work is presented first in this report. This is followed by a discussion
of accomplishments and recommendations for future research in each of the
study areas listed above, with reference to program reports (22 Special
Technical Reports and 13 Quarterly Progress Reports) for details.

3

CONTENTS

5

CONTENTS (Concluded)

ILLUSTRATIONS

TABLES

I
CRITICAL SUMMARY

I. G. Poppoff[*]

A. Introduction

1. Background

The successful development of effective chemical munitions requires a sophisticated technology. The many frustrating problems that are encountered in chemical munitions development are actually reflections of the state of knowledge of fields in which comparatively little basic information is available. As a result, many of the questions asked today

---

[*] I. G. Poppoff, formerly Chairman of Stanford Research Institute's Department of Atmospheric Sciences, was program manager of these studies from their inception on April 1, 1964 to his departure from the Institute on December 31, 1966. He then served as a consultant on the program until its termination on December 31, 1967.

bear a strong resemblance to questions asked 20 or even 40 years ago. In fact, in some areas so little basic information is available that it is difficult to judge whether chemical munition development is hampered because of limitations imposed by natural laws or because the laws are not being interpreted properly and exploited efficiently.

During the past several decades, a considerable amount of research and engineering has been done in the field of chemical warfare. A large body of empirical information has been compiled and many problems have been identified. However, the work has in general been directed toward limited objectives or short-range solutions to urgent problems. As a result, the information available has not been adequate to solve the problems and many promising developments have been frustrated to the point of stalemate or abandonment.

Leaning heavily on analogies with sophisticated technologies that have developed successfully during the past 20 years, such as nuclear weapons systems, chemical therapy, and solid-state electronics, it can be predicted that startling advances could also be made in chemical warfare--provided that a vigorous and balanced interdisciplinary effort is launched in this direction.

The program reported here is an effort along these lines. Although the effort is small compared with the magnitude of the job, it is demonstrated that definite progress can be made toward the solution of key problems if research is directed toward the exploration and understanding of basic processes.

2. Research Objectives and Scope

The basic objective of this research program is, simply, to provide basic information necessary for an overall improvement of chemical agent dissemination techniques.

Although the objective is simply stated, the scope of work is very large and the variety of problems is almost infinite. In considering the scope of work concerned with chemical agent dissemination, one is impressed not only with the complexity of the problem but also with the diversity of the scientific and engineering disciplines required to

10

advance the state of knowledge. Many interrelated processes are involved in the conversion of a bulk material into an effective agent aerosol. The role of each process, its importance, and its relationship to the other processes require delineation. The following brief examples illustrate the complexities.

In typical explosive dissemination methods, an explosive burster charge is surrounded by agent and enclosed in a container. The detonation of the burster generates a shock wave which traverses the agent; when the container bursts, the shock, the agent, and detonation products are injected into the ambient atmosphere. The questions that arise are: What are the detonation products and can they react with the agent? Can the shock degrade the agent, chemically or physically? How and when is the aerosol formed? Can the size of the particles and the extent of the cloud be controlled? Is there subsequent interaction between detonation products and aerosol particles? Do the detonation products react with air? Under what conditions will the aerosol ignite?

In typical pyrotechnic dissemination methods, the fuel-oxidizer formulation is mixed intimately with agent. The combustion of the pyrotechnic formulation provides heat to vaporize the agent, which subsequently condenses to produce the desired aerosol. The questions that arise are: Can an agent be degraded by the thermal environment? What _is_ the thermal environment? What combustion products are formed and can they interact with agents? Is the subsequent condensation homogeneous or heterogeneous? If heterogeneous, what is the identity and what is the concentration of the nuclei? Can the particle size and concentration of the aerosol be controlled?

3. Organization

Both a literature review and a research program were organized to provide answers to questions such as those listed above. Emphasis was placed on explosive and pyrotechnic processes because of their immediate importance in CW munitions development. Material pretreatment, atomization, electrostatics, and ultrasonic processes were also considered important and were included in the program; natural aerosol formation

processes were studied to determine if some aspects could be adapted to chemical agent dissemination requirements.

Accordingly, the program was divided into the following study groups:

A. Mechanics of Explosive Dissemination Processes

B. Shock, Detonation, and Reaction Processes in Aerosol Formation

C. Comminution Processes in Shocked Materials

D. Droplet Ignition Processes in Combustible Aerosols

E. Thermal and Pyrotechnic Aerosol Production Processes

F. Condensation Processes in Aerosol Formation

G. The Role of Oxidation and Pyrolysis in Agent Utilization

H. Formation of Aerosols by Atomization

I. Ultrasonic Aerosol Production Processes

J. Pneumatic Dissemination of Dry Powders

K. Natural Generation of Aerosols

L. Electrostatic Phenomena in Aerosol Dissemination

M. Encapsulation Processes and Their Application to Aerosol Generation

N. General Concepts of Forced Clouds

The first task of the program was to review the previous work as reported in the existing literature--this included not only the CW literature but also work in other relevant fields. This review was presented in a special technical report which, together with discussions with Edgewood Arsenal personnel, served as the basis for the ensuing research program.

The organization and direction of the research program were altered from time to time to attempt to provide close coordination between this program and the needs of Edgewood Arsenal. Additional and drastic changes were also necessitated as a result of two severe reductions in funding.

The work accomplished by each research group was published chronologically in 13 quarterly progress reports, compiled in the 22 special technical reports, and summarized in this final report. Titles, authors, dates of publication, and Defense Documentation Center (DDC) Accession Numbers of the special technical reports are given in Appendix A.

Reporting period, author, and DDC Accession Number of the quarterly reports are given in Appendix B.

B. Accomplishments

Over the span of the program (three and one-half years), the funds available for this work were severely reduced twice. As a result, several research efforts were terminated before satisfactory completion and the level of effort was significantly decreased in many others. Unfortunately, this caused a reduction in scope and depth of the investigation, and much of the work reported is necessarily incomplete.

In spite of these difficulties, a considerable amount of progress was made, significant new insights were achieved, and valuable new technology was acquired for future development. These accomplishments are highlighted below.

1. Explosive Dissemination Processes

The use of explosives to disseminate chemical agents provides two distinct advantages: quick production of agent clouds because of the rapid action of explosives, and long storage periods for munitions because of the separation of the agent and reactive components of explosives.

On the other hand, the use of explosives for dissemination has been limited because the size of the cloud formed with any single explosion is small, and agents disseminated explosively are sometimes degraded severely. Despite the relatively large effort that has been expended in explosive research, it was found that not enough was known of detailed explosive dissemination processes to delineate key problems and guide the search for solutions.

In this program, unique radiographic and photographic techniques were used to investigate the mechanical processes involved in dissemination. Detonation parameters were calculated by means of a numerical computer code for explosives compositions that have been used for dissemination or that are of interest for future use.

13

It was found that the interface between explosive products and liquid agent is remarkably stable during the early portions of the explosive process and that mixing among products, agent, and air occurs comparatively late in the sequence of events.

The rarefaction wave apparently converts the liquid into foam just before the agent container bursts. It is quite apparent that after the container bursts, the agent moves outward as an expanding shell until the disparity between internal and external forces becomes so great that the shell breaks up into streamers. The streamers subsequently erode into the droplets that form the agent cloud. It is evident that the hot detonation products, agent, and air can mix at this point in the sequence of events.

These observations contrast sharply with former theories that were based on the notion that the particles are formed by the breakup of spalled layers. None of the experimental results obtained in this program could be construed as being consistent with the spallation theory.

The droplet size of the agent aerosol is determined by the aerodynamical forces that prevail during the streamer phase; the chemical reactions that occur depend on the temperature, droplet characteristics, and detonation products that exist during the same phase. Hence, improvement or control of the explosive dissemination technique requires the ability to control or modify conditions that exist during the shell breakup stage.

The temperature and composition of the detonation products for various explosives were computed using a program that utilized the BKW equation of state and the RUBY code. By selecting the proper explosive mixtures, detonation parameters (pressure, temperature, etc.) and the combustibility of the products can be controlled while still maintaining the properties necessary for efficient dissemination.

An experimental and theoretical effort was pursued to determine the boundary conditions for droplet ignition. It was found that a characteristic lag-time for spontaneous ignition can be determined which is a function of chemical composition of the droplet, the temperature of the

14

oxidizing atmosphere, the droplet diameter, and droplet spacing; lag-time was relatively independent of the oxygen content of the surrounding atmosphere.

Experiments were conducted to discover conditions that prevent the combustion of agent in explosive dissemination. Flashing of agent clouds is prevented by a high degree of symmetry of the burster-agent configuration. The use of an additive to lower the flame temperature of the products increased the ignition lag-time of the detonation products and apparently lowered the probability of ignition of the agent cloud, but at the cost of some energy that would otherwise be available for the dissemination process.

The extent to which the agent may be heated during the dissemination process and subsequently degraded or preconditioned for degradation reactions was explored by both computations and experiments. The calculations show that as much as 30% of the energy released by the explosive is wasted by absorption in the agent. To determine the temperature to which an agent is raised by the waste heat, a partial equation of state (e-p-v) must be obtained. A complete equation of state for a liquid under the high pressures produced in explosions has never been determined. Therefore, a series of shock experiments was initiated to obtain (e-p-v) data for a nonreactive liquid; these data were then converted to a (p-v-t) relationship. Although the fund reduction made it impossible to complete the experimental program in its entirety, the work showed for the first time that such experiments are indeed feasible. Temperatures in the shock wave were derived (not completely free of assumptions but under more satisfactory assumptions than had heretofore been possible) over a restricted range of pressures.

The relative velocity that causes streamer erosion is limited by the outward air velocity produced by the air shock. Exploratory experiments have shown that this can be circumvented by enclosing the fill in hollow perforated beads. The momentum of these beads allows them to penetrate the shock and disseminate agent in smaller particles and over much larger areas. In fact, it seems that the cloud effectiveness could be limited by agent toxicity instead of by the shock wave characteristics.

15

Considering the observations given above on agent cloud ignition, it follows that agent stability could also be preserved by using perforated beads. Note that the perforated beads are "moving cloud generators"--one way of overcoming inherent limitations of forced clouds.

Radiographs revealed that initial breakup occurs very much sooner for powder fills than for liquid fills. Preliminary calculations also showed that the relative velocities produced in explosive dissemination are not sufficient to cause secondary breakup of powder aggregates; therefore, the powder must be divided into suitable particle sizes by the initial shock loading. A parallel study of comminution processes was then initiated in order to explore the potential of explosive methods for the dissemination of solids. Studies of dynamic loading character- istics of materials and the effect of containment were made to complement the dissemination tests being conducted at Edgewood Arsenal. It appears that the key to effective dissemination of solids is an understanding of the mechanisms of fracture and particle separation; systems can then be designed to maximize stress amplitudes, velocity gradients, flow diver- gence, etc., as needed. Preliminary results are very encouraging.

A considerable amount of consistency obviously exists among the several investigations--the temperature dependence, the lag-time, the containment of products within an expanding shell of agent, the condi- tions for droplet or solid breakup. The correlations and specifications are still semiquantitative at this point; however, the groundwork has been laid and the direction toward a solution has been determined.

2. Thermal and Pyrotechnic Dissemination Processes

Both thermal and pyrotechnic aerosol production processes involve the use of hot gases to disseminate agents. The distinction between the two types of processes is that contact between agent and motive gases occurs just before dissemination in the case of thermal techniques, whereas the agent and gas-forming chemicals are intimately mixed and evolve simultaneously in the case of pyrotechnics. Thermal techniques have the advantages of not subjecting the agent to pyrotechnic defla- gration and of not involving problems of storage compatibility between agents and gas-forming chemicals; on the other hand, pyrotechnic

16

techniques have the distinct advantage of convenience. Both processes involve the volatilization and condensation of agent. These techniques are of particular interest because they are at present the most successful methods of disseminating solid materials.

In the literature review it was found that little was known regarding the details of the complex processes involved in these techniques; therefore there was little basis for determining the inherent limits of these techniques and for determining the most profitable directions for significant improvements.

Studies were initiated of four aspects of thermal and pyrotechnic processes: characteristics of pyrotechnic combustion, the thermal and oxidative degradation of agents, the condensation of volatilized agents, and the development of rapid thermal dissemination techniques utilizing rocket motors.

For the pyrotechnic characterization studies, an assessment technique was developed in which all combustion products, agent, and agent degradation products were captured and a total mass balance could be made. This unique method eliminated the problems attendant on obtaining representative samples from a plume. Another unique procedure involved the placing of small thermocouples within the pyrotechnic unit to observe the deflagration wave; temperatures and their duration were measured for the first time.

These studies showed that many former ideas concerning the rapid heating and volatilization of agents were in error. From measurements of deflagration-wave characteristics, product composition, and agent yield, it was apparent that (1) the agent can spend a comparatively long time (several seconds) at elevated temperatures, (2) agent degradation does occur, and (3) equilibrium flame combustion theory (based on gas-phase reactions) cannot be easily applied because of the apparent involvement of rate-controlling solid phase and liquid phase reactions. Radiographic studies were also made of the functioning of a pyrotechnic unit; they showed that the burning surface is not homogeneous but is composed of discrete particles that spontaneously decompose. The radiographs also confirmed that as the reaction zone moves through the pyrotechnic,

17

a thick char bed develops through which the volatilized agent must pass; hence the agent dwell-time in a hot reactive char increases with burning time--presumably the efficiency of agent production decreases correspondingly, particularly for thermally unstable agents.

Many other important aspects of pyrotechnic functioning were studied-- activation energy, melting points, phase changes, reaction temperatures, high pressure combustion, the role of coolant materials such as kaolin, and the influence of agent loading on burning rate, temperature, and efficiency. Because it appeared that shorter action times (and consequently shorter agent dwell-times) were beneficial, studies were made of burning rate enhancement by variations of pyrotechnic density. Also, the functioning of larger units was explored; they were found to be feasible and efficient.

Pyrolytic and oxidative degradation of agents was investigated in two ways--by studying agent yield, retention, and loss in functioning pyrotechnic devices, and by studying decomposition rates of agent in laboratory systems without the added complications of a combustion-product environment. Unfortunately, the studies were not expanded to agents other than CS. However, some rather interesting conclusions were obtained. The laboratory studies showed, as suspected, that CS is a very stable material. Decomposition rates were so slow, it could be assumed that no detectable decomposition could occur during the reaction times encountered in a pyrotechnic device. However, mass-balance analyses of functional pyrotechnics indicated that an appreciable fraction of such a stable agent as CS was nonetheless decomposed. Although it was not possible to pursue this important aspect of the work to a satisfactory conclusion, the evidence indicates that thermal degradation processes should be very well understood if we wish to be able to predict the extent of pyrotechnic munition potential. The use of thermocouples to measure the heating characteristics of the pyrotechnic and radiographic studies of the burning surface provided new and significant information on the agent environment. However, it is still only possible to guess at the thermal experience of an agent in such complex processes. One possibility that was explored was to use a thermal tracer--a material

18

whose thermal stability is well known. Unfortunately, this study was terminated before positive results could be obtained.

The end result of all these processes is the formation of an agent aerosol with the physical characteristics necessary for effective chemical action. With pyrotechnic techniques, aerosol particles are formed by condensation. Thus, the physical characteristics of the agent aerosol are determined by the simultaneous kinetics of nucleation, condensation, and agglomeration. Little was known about the condensation processes in pyrotechnic jets except that the particles produced were very small, too small for maximum effectiveness. Previous work on condensation generally has been limited to water or metal vapors over a fairly limited range of conditions; theories are not well enough developed to use for predictions. During the course of this program it was realized that the vapor loading and quenching rate in pyrotechnic jets was sufficiently large to allow both homogeneous (caused by self-nucleation) and heterogeneous (caused by foreign nuclei) condensation to occur simultaneously; therefore, both kinds of nucleation were studied. It was found that the potential does exist for controlling particle sizes of aerosol particles produced by pyrotechnics. The effectiveness of various salts as condensation nuclei was demonstrated; both size and uniformity of the aerosol could be altered. It was shown that under controlled conditions, particles can be grown to sizes of several microns in diameter by the use of "giant nuclei" and/or coagulation chambers. Hence, one of the severe limitations of pyrotechnic dissemination systems can conceivably be bypassed. A considerable amount of information was also obtained on homogeneous nucleation processes; the state of development of the theory was advanced significantly. The work on condensation was terminated before it could be developed to the state necessary for efficient application.

Early in the program, while developing apparatus to study thermal dissemination processes, a rocket motor dissemination device was conceived that has great potential. In brief, the gas evolved by a burning rocket motor is exhausted through an expansion nozzle where the gas is both cooled and accelerated. Agent introduced in the nozzle is entrained in the exhaust to form a long, dense plume. Because of the rapid action

19

of the motor and the length of the plume, a large area can be fumigated
almost instantaneously. By varying the flow conditions and motor composi-
tion, the conditions to which an agent is exposed can be varied over a
wide range, and the mode of aerosol formation can be varied from atomiza-
tion to condensation. Further development of this rather versatile equip-
ment into either laboratory or field apparatus was terminated because of
funding limitations.

Although a multitude of problems must yet be explored before a satis-
factory understanding is achieved of pyrotechnic aerosol production pro-
cesses, a significant advance in the state of knowledge was made in this
program. Of particular consequence are the time-temperature characteris-
tics of pyrotechnics and implications regarding agent survival, the ex-
ploration of combustion characteristics generally, the role of condensa-
tion and possibilities for controlling particle size, and the preliminary
development of a new generation of thermal disseminators.

3. Atomization Processes

The subdivision of a bulk liquid is commonly called atomization.
Because atomization is one of the important processes involved in the
dissemination of liquid agents (or suspension of powdered agents), a
study was undertaken to critically review and evaluate the literature
pertaining to this field. Although this should have been part of the
early literature review to be consistent with the general organization
of the program, it was not started until after that review was in draft
form. Rather than delay publication of the review, atomization was
treated separately.

Although atomization has been reviewed many times, this review is
easily the most comprehensive. The results are presented in a form that
allows comparison of the works of the various investigators. This is a
particularly informative and useful report and will have wide application.

The comparison of results reported for simple nozzles suggests that
the effect of turbulence has not been properly considered and that the
assessment techniques were rather limited. The review also showed that
the effect of surface tension has not been resolved, although it is

important. Other shortcomings in the literature include insufficient knowledge of the effect of gas density, the effect of ultrahigh pressures, and the effect of high loadings.

4. Pneumatic and Ultrasonic Dissemination of Powders

Because of the importance of solid agents and the general difficulty of disseminating them, studies were made of pneumatic and sonic techniques for aerosolizing powders. Pneumatic techniques have proved quite effective for the dissemination of industrial and agricultural powders. However, power utilization and aerosolization efficiency are not as critical in industrial and agricultural applications as they are for chemical munitions applications. Therefore considerable emphasis was placed on the design of nozzles and on the use of additives to increase the ease of producing aerosols of small particles and to reduce the expended energy. The successful use of additives is noted later under "Pretreatment." The efficiency of breakup was found to be dependent on nozzle design. Curved nozzles which forced particle agglomerates to strike a surface during their passage produced much higher fractions of small particles than straight tubes; this is a confirmation of recently published Russian work. The work on pretreatment and nozzle design points the way to a considerable increase in pneumatic dissemination efficiency. A sonic disseminator was designed with a vibrating cavity in which powders were placed; almost instantaneous and complete dissemination was achieved. It was also learned that surfaces vibrating at sonic frequencies can rapidly erode compressed powders such as blackboard chalk. Unfortunately, fund limitations would not allow further work along these lines.

5. Ultrasonic Dissemination of Liquids

Ultrasonic aerosol production is simply a special case of atomization, but the basic mechanisms are not very well understood. Nevertheless, sonic methods have important potential advantages that are worthy of exploitation; they may be used for clandestine operations; they can process delicate agents without degeneration; and particle sizes can be controlled. The question is, can they be developed into practical and efficient devices?

21

The purpose of this investigation was to determine the potential limits and applications. The literature search revealed very little fundamental information that could be used for such evaluations. Therefore, both theoretical and experimental studies were launched in an effort to obtain the needed data. At the same time, prototype devices were developed, based on the limited knowledge available, in order to gain an understanding of present limitations. These devices were surprisingly light weight and capable of handling relatively high flow rates. The most successful was a circular wedge design. An attempt was made to analyze its operation analytically in order to be able to extend the design development. An experimental study was made of the effect of surface tension and viscosity of the liquid on droplet size; attempts were made to interpret these observations in terms of capillary wave theory. An experimental study was also made of cavitation in the thin film of liquid flowing over the sonic transducer surface.

Unfortunately, this ambitious and potentially fruitful study was terminated before the studies could be brought to a useful point.

6. Natural Aerosol Production Processes

A great variety of aerosols is produced naturally. Because of this profusion it is often felt that natural aerosol production must be very efficient. A short study was made to explore the possibility of adapting some of the natural techniques to chemical munitions.

It was found that no exciting breakthroughs could be achieved. The facts are that natural forces and quantities are so large that great efficiencies are not required for the production of seemingly staggering natural aerosol displays such as dust storms, fogs, and the spread of wheat rust.

The production of monodisperse spores is enhanced in nature by loose packing and the separation of spores by a matrix of filaments. There may be cases in which this concept can be adapted to agent dissemination, although volume restrictions are often also critical in munitions. Secondary production of aerosols by the explosion of small capsules containing only a few particles is also found in nature, and is consistent with

22

the miniaturized all-mixing element concept developed in other parts of the program.

7. Electrostatic Phenomena in Dissemination

Electrostatic forces have long been blamed for many of the difficulties encountered in the handling of aerosols and fine powders. On the other hand, the possibility of using electrostatic forces to disseminate powders has also been recognized, and occasional (but unsuccessful) attempts have been made to exploit this potential.

Qualitatively, the important role of electrostatics in dissemination was demonstrated again during the investigation of pneumatic powder-dissemination techniques in this program.

The potential uses and limits of electrostatic dissemination techniques were first explored theoretically and reported in the literature review. It was pointed out that unipolar charging of agents can result in marked improvements in the effectiveness of agent dissemination, that ambipolar charging could be beneficial under certain circumstances but was not very promising, and that precharging of powders before dissemination was not technically feasible. In the theoretical studies of forced cloud production, it was also shown that electrostatic techniques offered one of the few ways to avoid using most of the dissemination energy to move air; electrostatic methods would not require dilution by air as do explosive, thermal, and atomization techniques and therefore would not be as severely limited as to cloud size.

It is easy to demonstrate the qualitative aspects of electrostatic influence in dissemination, but it is very difficult to conduct controlled, qualitative experiments that can provide data suitable for the design and development of munitions. Therefore, the highest priority was given to the development of an instrument that could provide unambiguous, quantitative analysis of charged aerosols. Such an instrument was developed; it can be used to measure both average particle sizes and mobilities of charged aerosols. From the measurements, specific particle surface gradients can be computed.

23

Thus, the feasibility and potential of electrostatic dissemination techniques have been demonstrated theoretically, and key experimental instrumentation has been developed. Direct experimental studies can now proceed on a firm basis.

8. Pretreatment of Agent by Additives and Encapsulation

Special treatments of materials before dissemination have been suggested and tried, for the solution of a number of vexing dissemination problems. The use of additives to improve ease of powder dissemination has been explored by many groups; the development of special coatings has also been attempted for the same purpose. Although occasionally promising, the results were never clearcut.

An important activity in this program was to explore the problem again and to attempt to determine the potential usefulness of pretreatment techniques. The use of encapsulation technology for these applications appeared to be especially promising because of recent advances in that field.

It was determined that powder silicate additives were indeed as effective as previous workers had suggested, but that the additives were very specific as to materials they could affect. One of the important results of this study was that several powder characterization techniques were found that could be used to relate easily measured bulk properties to ease of aerosolization--which is difficult to assess. Thus, future research with additives can progress at a much faster rate.

The use of encapsulation techniques to modify the properties of agents was shown to be at least as promising as it was thought to be at the beginning of the program. Techniques were developed to prepare the agent CS in microcapsules less than 10 microns in diameter. By using various combinations of wall materials and encapsulation techniques, the release rate of agent was decreased substantially, thus increasing the potential physiological effects. It was demonstrated that agent characteristics can be altered so radically that essentially new agents are prepared. It was also shown that incompatible mixtures of agents and pyrotechnic materials can be made and stored by encapsulating either the

24

agent or the pyrotechnic grains; liquids can be encapsulated to further
extend the potential application of pyrotechnic dissemination techniques.

One of the results of the study of forced cloud production showed
that one way to overcome inherent restrictions on forced cloud volume
(and area coverage) is to project miniaturized air-mixing elements. A
very interesting way of producing miniaturized air-mixing elements was
developed with capsule technology. It required large capsules (~1 cm
diameter) filled with agent and coated with explosive. The technology
of producing large capsules was developed, as were techniques for coating
the capsules with explosive. It was demonstrated that liquid aerosols
could be disseminated very satisfactorily from the small units. In addi-
tion, it would be possible to fill the large capsules with small capsules
of specially modified agents.

Thus, encapsulation techniques can have a large impact on chemical
munition development; the results of this study indicate the magnitude
of the impact and provide the basis for efficient exploitation of encap-
sulation technology.

9. Formation of Forced Clouds

Dissemination can be considered to consist of three stages: the
initial breakup of material or formation of particles, the formation of
a cloud by utilizing the energy of the dissemination device to dilute
the aerosol with air, and lastly, area coverage through interaction with
ambient meteorological conditions.

Obviously, this research program was centered on investigations of
processes involved in the first stage. To the extent that the first and
second stages overlap, some of the work concerned second-stage processes
as well. Consideration of the third stage was limited to the effects of
meteorological conditions on natural dissemination processes. The pro-
cesses involved in the first stage are uniquely dependent on the dis-
semination technique under consideration, but as dissemination progresses
from the first through the third stage, the processes become quite similar
and the particular dissemination technique becomes less and less
important.

To explore the inherent limitations of cloud formation, a study was made of energy utilization in the second stage. A mathematical expression was derived for the volume of the cloud formed in the second stage. It was found that the volume is controlled by the portion of the cloud mass originating in the dissemination device and the kinetic energy imparted to that mass by the disseminating device. The particulate density of the cloud depends on the fraction of the initial mass which becomes particulate, the air density, and the kinetic energy.

General expressions were then derived to relate the maximum time during which the mass should be released at a particular velocity to form a specified cloud, the volume of the cloud, the average particulate density, and the form of the cloud. The expressions were derived for three groups of devices: explosive, gas atomization and pyrotechnic, and pressurized sprays.

It was shown that there are definite limits on the minimum particle densities that can be achieved as well as on the diameter of the cloud, and that a very large fraction of the energy released by a dissemination device is utilized to dilute the cloud but only a small fraction is utilized in the initial particle breakup processes. The mass of air in such a cloud typically exceeds 10^3 the mass of the particulates and the dilution occurs only by utilizing the energy released by the device.

An important conclusion is that the only way to overcome inherent limitations in cloud formation is to form a cloud composed of miniaturized air-mixing elements or to utilize electrostatic dissemination properly. Ways to form miniaturized air-mixing elements were noted in the preceding discussions.

C. Recommendations for Future Research

Significant progress toward the solution of key problems has been made in this program. As noted earlier, the magnitude of the job is very large and full return on the investment already made cannot be realized unless research is aggressively continued. It is strongly recommended that future work be conducted along the following lines.

26

1. Explosive Dissemination Processes

    (a) Complete the studies of streamer development and erosion, inasmuch as this appears to control the size distribution of aerosols produced by explosive techniques.

    (b) Continue the development of perforated beads for dissemination, since this is one of the few possibilities for overcoming the limitations of cloud volume inherent in the production of forced clouds.

    (c) Continue the shock comminution studies. This work was initiated late in the program; although the preliminary results are very promising, the work has not progressed as far as many of the other studies. In order to provide design criteria, further consideration should be given to shock strength and profile, static and dynamic mechanical properties of specimen materials, effect of presizing particles, preshock strength of particle bonds, choice of matrix materials, preshock compaction density, surface treatment of particles, and geometric configuration.

    (d) Develop an oxygen-balanced explosive specifically for dissemination, designed to take advantage of advanced formulation techniques now available. This would require the use of a computer code that is much more flexible than RUBY. The development of such a code, TIGER, has been completed at SRI and can be used with parallel experimentation to develop a new equation of state for explosive products, and subsequently for realistic calculation of the detonation and expansion of the products in the dissemination process.

    (e) Conduct experiments with oxygen-balanced explosives in order to arrive at suitable equation-of-state parameters. The constants presently used in the BKW equation were developed from explosives with negative oxygen balance.

    (f) Apply the principles of geometrical asymmetry and central initiation in the design of explosive chemical munitions to minimize "flashing" losses.

    (g) Complete the liquid equation-of-state studies in order to determine properties of shocked liquid agents.

    (h) Continue the experimental and theoretical studies of droplet ignition in order to clarify the precise relationships between ignitibility, oxidizer composition, chemical properties of the liquid phase, and the chemical kinetics of the droplet-oxidizer system. Although it was thought earlier in the program that the magnitude

27

of the ignition lag ruled out droplet ignition as an important process, the recent observations of increased lag between product and agent cloud ignition indicate that additional work is warranted.

(1) Continue the development of explosive capsules; they appear to represent a promising approach to the development of miniaturized air-mixing elements that can overcome the area coverage limitations of explosive weapons.

2. Thermal and Pyrotechnic Dissemination Processes

(a) Continue the attempts to develop physical or chemical techniques for the stimulation of burning rate in pyrotechnics. With presently available technology it seems that the development of castable compositions is the most promising approach. Castable compositions should allow more uniform processing and higher loading densities of agent; and ultimately, they should be adaptable for use with burning rate catalysis techniques.

(b) Continue the research to delineate thermal and chemical history of agents in pyrotechnic systems. This knowledge is vital in extending the scope of pyrotechnic chemical munitions to embrace new agents and new pyrotechnic formulations.

(c) Develop techniques of particle-size control for pyrotechnics based on present knowledge of condensation and coagulation, and continue to develop information on these processes to provide bases for further developments. The possibilities for particle-size control that are now apparent would provide powerful design tools if developed.

(d) Continue development of the rocket-nozzle injection technique for thermal dissemination of chemical agents. This is an opportunity to exploit rocket-motor technology for a rapid and significant improvement in dissemination capabilities.

3. Cold Gas and Ultrasonic Aerosol Production Processes

Liquid and powder dissemination by pneumatic or sonic aerosol generators has advantages of large throughput, minimum chemical degradation, and a relative lack of noise or smoke. These generators do not seem at present to have the advantages of portability and instantaneous action that appear to be controlling considerations in most military applications. Nonetheless, there are applications where they could be most useful, for instance in riot control, clandestine operations, and

28

dissemination of relatively fragile agents. Unfortunately, the state of development of these techniques is not very high and when it is desired to use them, it will be found that their usefulness is limited by a relative lack of research and development effort. Thus, although the highest priority might not be assigned to these techniques at present, research and development should be continued. Sophisticated chemical agent dissemination systems will undoubtedly require the utilization of such techniques eventually.

4. **Electrostatic Phenomena in Dissemination**

Continue studies of electrostatic dissemination techniques utilizing the analyzer developed during this program. Both mechanical and electrostatic techniques for the production of unipolar aerosol clouds should be carefully investigated. It should be remembered that this approach, although difficult to study properly, represents one of the few possibilities for overcoming the inherent limitations of forced cloud production.

5. **Pretreatment of Agent by Additives and Encapsulation**

Continue the development of capsular techniques to modify physiological effects of agents. Potential applications are nearly infinite for the utilization of such techniques (1) to allow the use of fragile agents, (2) to extend usefulness of standard agents, and (3) to provide operational systems capabilities designed to meet specific tactical requirements. To achieve this potential, the development of capsular technology should be closely associated with physiological research and the development of dissemination systems.

II

MECHANICS OF EXPLOSIVE DISSEMINATION

George B. Abrahamson, Director
Explosives Engineering

Explosive dissemination devices were first used in modern chemical warfare in World War I. They were introduced to reduce dissemination time and to improve geographical control of the agent cloud. The first devices were cylinders filled with agent that were projected toward the target by mortars or artillery. A central explosive charge detonated on impact to rupture the container, discharge the agent, and form a cloud. Spreading of the agent cloud to a maximum effective area (minimum effective concentration) was left to local winds.

Present explosive dissemination devices have the same purpose as those used in World War I and are of similar design (i.e., they minimize dissemination time and maximize geographical control, and they consist of an agent container with a central explosive charge which is projected to the target by mortars, artillery, or rockets, or is carried by aircraft). As with the original devices, spreading to a cloud of maximum effectiveness area is left to local winds.

Although explosive dissemination devices have been available since World War I, the processes by which the agent cloud develops have remained largely unknown. An understanding of these processes is essential to provide a basis for interpreting past experimental results and for planning new experiments to obtain information for the design of more effective devices. The lack of such understanding has greatly complicated weapons development programs and has resulted in the collection of a large amount of empirical information which for years has begged for interpretation.

Dissemination of chemical warfare agents occurs in three stages: (1) placement of the container in a favorable position; (2) discharge of the agent from the container; and (3) spreading and movement of the agent

cloud to cover a maximum effective area.* In the present context, placement consists of projecting containers into the target area and dischage consists of discharging the agent from the container with explosives. Spreading is required with all present dissemination systems, including explosive systems, and occurs by local wind action. For example, explosive dissemination systems produce initial clouds on the order of 25 times the size of the container, corresponding to a volume increase of 15,000. If the initial density of the agent in the container is assumed to be unity, the increase in volume required to reduce the density to the minimum effective concentration of 5 mg/m^3 (CS) is 2×10^8. This is 13,000 times the initial cloud volume achievable with explosive discharge, or about 24 times the initial cloud diameter. Thus, the maximum effective area of the cloud is about 600 times the initial area.

Since in all present systems spreading is left to local winds, dissemination systems differ only in means of placement and discharge. This part of the program has centered on developing an understanding of the processes involved in discharge as they occur in spherical explosive devices. The results of the program are documented in four major reports.[1-5] The first of these is a description of the state of knowledge of explosive dissemination as of 1965. The second is an interim report describing technical work on the present program through mid-1966. The second report was superseded by another report,[3] which is an attempt to provide a comprehensive description of the present state of knowledge of the mechanics of explosive dissemination (mainly discharge). Another report[4] and its supplement[5] describe some calculations undertaken to determine the fraction of the explosive energy which goes into the agent through shock heating. The following summary is based on References 3, 4, and 5.

---

* As usually defined, dissemination covers only stages 2 and 3. For lack of a better word to cover all three stages, here the definition of dissemination is extended to include stage 1.

Problem Breakdown

Spherical explosive discharge devices are usually 3 to 6 inches in diameter and are constructed of plastic or light metal about 1/16 inch thick. The agent may be liquid, compacted solids, or a slurry, and the central explosive charge is generally a common military explosive such as Composition B. The action of the explosive ruptures the container and projects the agent outward as an expanding sphere, as shown in Figs. 1 and 2. As it moves outward, the expanding agent sphere is transformed into many radial streamers. The subsequent development of the cloud is envisaged as the erosion of the streamers as they penetrate the surrounding air.

This model neglects the effects of possible chemical reactions of the agent with the explosive gases and the surrounding air. Inasmuch as chemical reaction of the agent must be prevented in any practical device, such an assumption is basically sound for a model of mechanical processes.

Cloud front measurements indicate that three force regimes occur during explosive discharge of chemical agents from spherical devices: (1) an initial ejection regime, during which the explosive forces tending to accelerate the agent predominate; (2) an intermediate transition regime, during which the explosive forces and the air-interaction forces are comparable; and (3) a final expansion regime, during which the air-interaction forces tending to decelerate the agent predominate. The ejection regime is limited to the first quarter or less of the motion, and the transition regime is limited to the first half of the motion. Since the first half of the motion involves only one-eighth of the cloud volume, most of the cloud is formed during the expansion regime. Hence, the characteristics of the cloud (particle size, distribution, cloud size) are controlled by the processes of the expansion regime.

The principal processes of explosive discharge are conveniently considered in terms of four phenomenological phases: (1) the detonation phase; (2) the shock phase; (3) the departure phase; and (4) the streamer phase. The detonation phase extends over the detonation period, i.e., until the detonation wave reaches the surface of the explosive. The shock
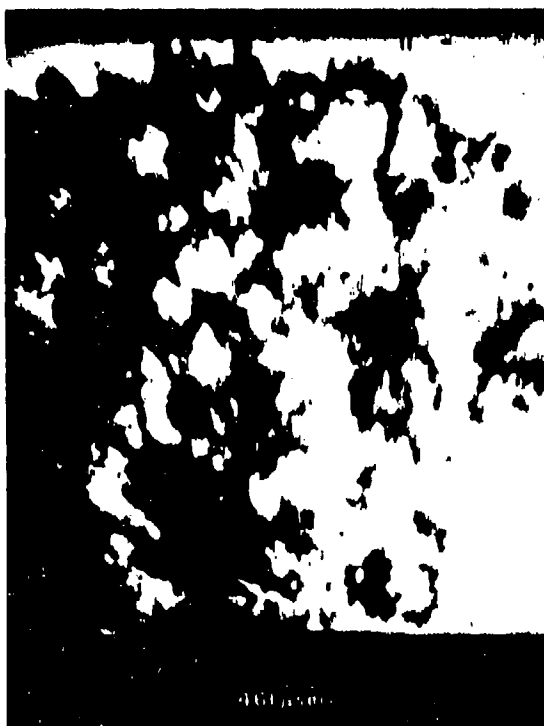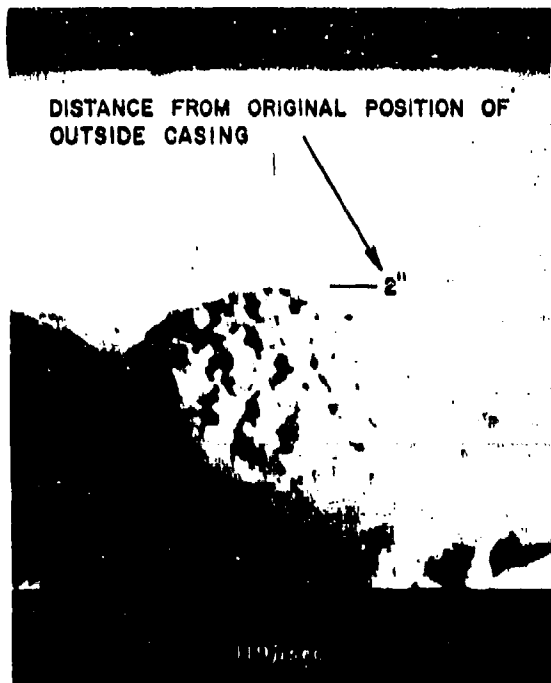
FIG. 1 PHOTOGRAPHS OF EXPANDING LIQUID FILL (ETHYLENE GLYCOL)
FROM A SPHERICAL DEVICE (3-inch OD, 1.4-inch-diameter burster cavity,
1/16-inch walls, charge 25 g Comp B, fill-to-explosive mass ratio A/B = 8).
Time is measured from detonation

DISTANCE FROM ORIGINAL POSITION OF
OUTSIDE CASING
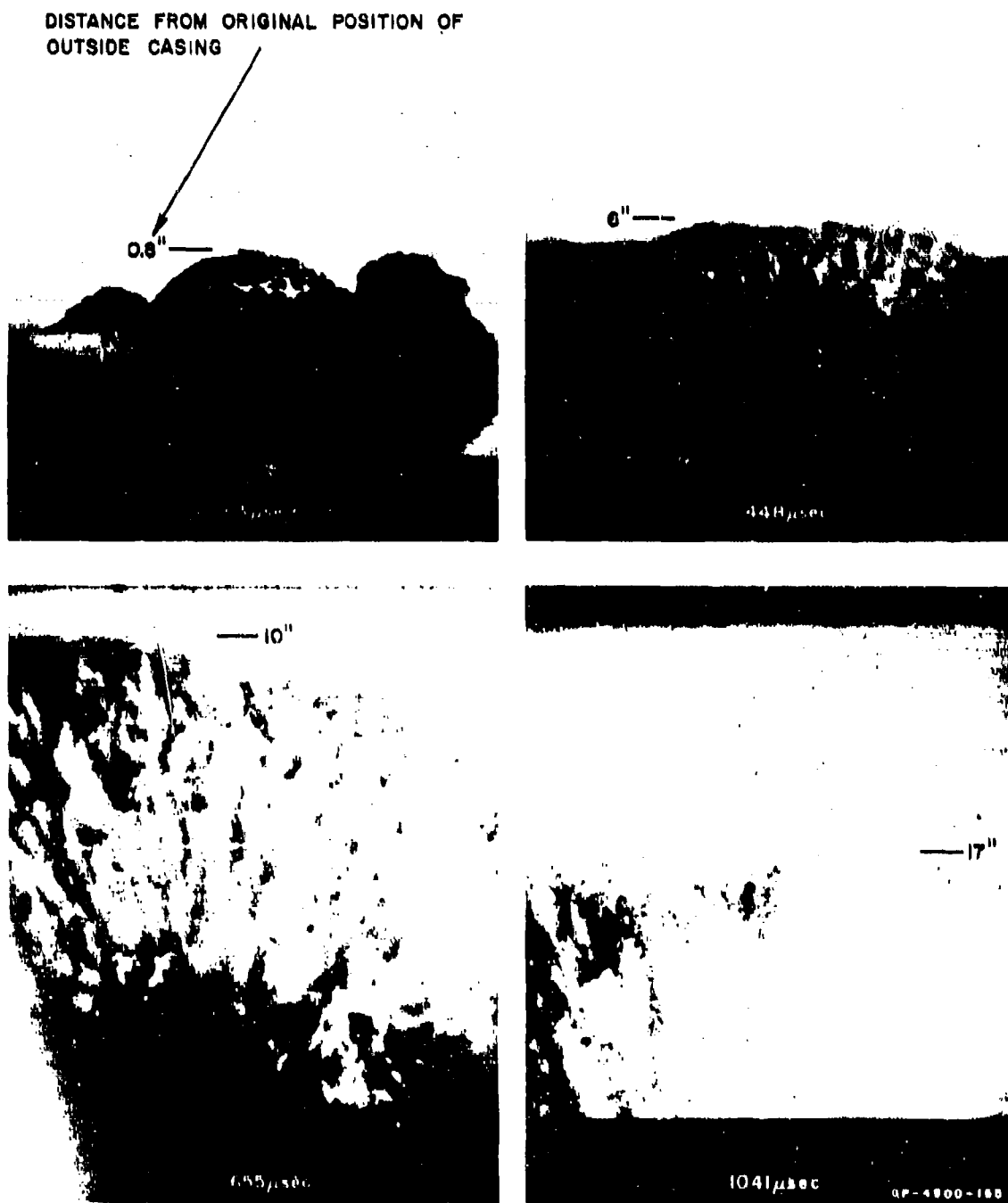
FIG. 2   PHOTOGRAPHS OF EXPANDING SOLID FILL (200 μ KI) FROM A SPHERICAL
DEVICE (3-inch OD, 1.4-inch-diameter burster cavity, 1/16-inch walls, charge 25 g
Comp B, fill-to-explosive mass ratio A./B — 13). Time is measured from detonation

phase extends from the time the detonation wave reaches the surface of the explosive until the shock waves in the explosive gases and the agent die out. The departure phase covers the period from the rupture of the case until the streamers form. Finally, the streamer phase extends over the subsequent period of cloud development. The relationship between the phases and regimes is indicated in Fig. 3.

The detonation phase is concerned entirely with the detonation of the explosive. Hence, the processes of interest during this phase are the initiation and propagation of detonation waves in spherical charges.

The shock phase begins with the transmission of the initial shock wave into the agent. The amplitude of the shock is a maximum adjacent to the explosive, and due to spherical divergence, it decreases rapidly as the shock expands. When the shock reaches the outer case, a reflected wave is generated which propagates back into the agent. Although the reflected wave may initially develop as a shock, after a few wave transits through the case it changes into a rarefaction which relieves the pressure in the agent as it propagates inward, imparting an outward velocity to the agent. Subsequently, shock and rarefaction waves of decreasing amplitudes reverberate through the agent and the explosive gases.

The departure phase begins with the rupture of the case. During this phase the agent layer changes from a relatively well-defined material to a complex mixture of gas and condensed and vaporized agent of uncertain composition and properties. The reaction of the agent to the traversal by the initial shock and subsequent rarefaction and shock waves determines the composition and properties of the agent at the outset of the departure phase. The interaction of the expanding agent with the surrounding air results in the development of an air shock. Subsequent interaction with the explosive gases and the surrounding air may result in significant mixing with accompanying changes in composition, properties, and structure. The principal processes of the departure phase are the traversal of the agent by the shock and rarefaction waves, the development of the air shock, and the subsequent interaction of the agent with the explosive gases and the surrounding air.
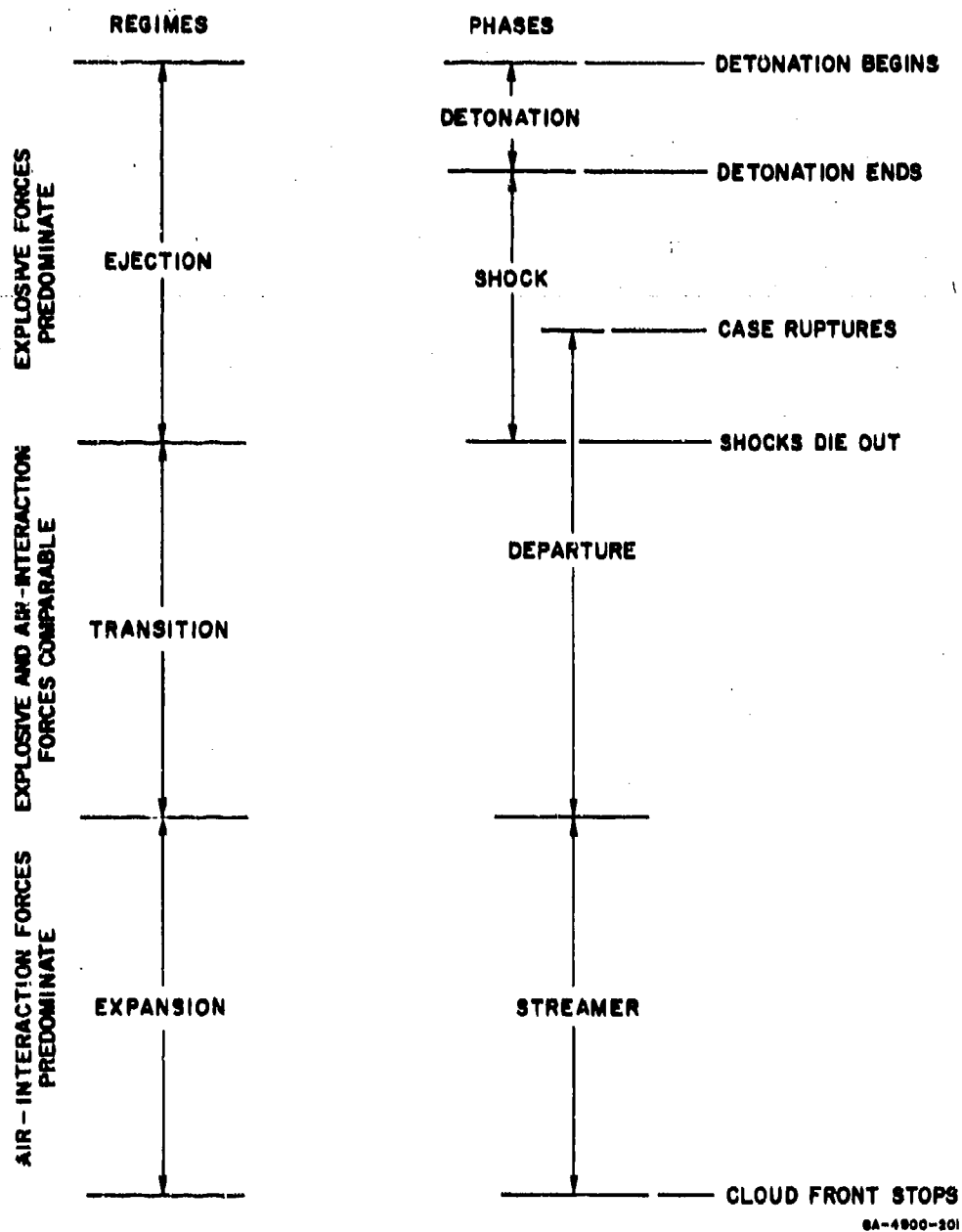
FIG. 3 RELATIONSHIP BETWEEN REGIMES AND PHASES

37

The beginning of the streamer phase is indicated by the change
in the appearance of the expanding agent from an essentially continuous
layer to many radial streamers. As the streamers penetrate the surround-
ing air, they erode to form the cloud. Thus, the principal processes of
the streamer phase are the formation and erosion of the streamers.

The main documentary report[3] touches on most of the principal pro-
cesses mentioned above and treats certain aspects in detail. The main
topics treated are reviewed below.

Detonation, Shock, and Departure Phases (Ejection Regime)

The main aspects of the detonation and shock phases considered in
Reference 3 are the calculation of detonation waves in spherical charges
and the peak pressure induced in the agent. In Reference 4, Duvall
employs an approximate equation of state to calculate the shock heating
that occurs on the first transit of the shock wave through the agent
using some representative materials (water, ether, glycerin). He finds
that about one-third of the explosive energy goes into shock heating.

Temperley's hypothesis that breakup of the fill into fine particles
occurs during the departure phase by spall is examined. Experimental
results are presented which show that only a small fraction of the fill
is affected by spall; hence it is concluded that spall is not a pre-
dominant mechanism. Possible effects of cavitation in liquid fills are
considered.

Fill Structure (Transition and Expansion Regimes)

A major aspect of the present program has been the utilization of
flash radiography to investigate the interior structure of clouds from
explosive discharge devices. The radiographs show that over a wide range
of conditions most of the fill material expands as a spherical shell of
increasing permeability. This observation, together with the observation
that the surfaces of expanding clouds viewed optically exhibit a streamer-
like appearance, is the basis for the cloud formation model adopted in
this study.

Fill Motion (Ejection, Transition, and Expansion Regimes)

In an attempt to understand the fill motion an investigation was undertaken of the motion of expanding spherical shells with various degrees of permeability. Two aspects were studied: (1) the sensitivity of the fill motion to the type of explosives used; and (2) the effects of permeability of the fill motion on the air shock. The results indicate that the type of explosive has little effect on the motion of the fill. Moreover, it is found that the air shock path is relatively insensitive to variations in permeability, but that the pressure along the shell and shock paths changes substantially.

Streamer Formation (Transition Regime)

An investigation was undertaken to attempt to determine the mechanisms by which the fill is transformed into radial streamers. Taylor instability was examined as a possible mechanism of streamer formation in liquid fill. It was found that this mechanism predicts instability during both acceleration and deceleration of the shell. Since instability is observed only during deceleration, we conclude that Taylor instability is not the dominant mechanism leading to streamer formation in liquid fills.

A mechanism of streamer formation for both liquid and solid fills is proposed which involves the interaction of the expanding shell with the surrounding air. The plausibility of such a mechanism is supported by the similarity of the streamers which develop for liquid and solid fills (see Figs. 1 and 2).

Streamer Erosion (Expansion Regime)

The process of streamer erosion was investigated in the laboratory using an artificial streamer consisting of an air stream with entrained liquid droplets which was directed against a larger diameter air stream flowing in the opposite direction. The streamer is turned around by the large-diameter air stream, and the shape of the tip which develops is similar to that observed in photographs of streamers from explosive devices. Two regions of flow involving the entrained droplet can be distinguished. The region of the streamer ahead of the interface between

the two air streams consists of small droplets which are able to follow the flow in the streamer air as it turns back. The region downstream from the interface contains larger droplets which cannot follow the streamer air as it turns back and penetrate the interface. The droplets which follow the air stream do not develop a significant relative velocity and are not subject to further breakup; however, those which penetrate the interface do develop significant relative velocities and may be broken up further. The essential conclusion from this study is that streamer erosion may result in further breakup of droplets and that this breakup involves individual particles.

Aerodynamic Breakup of Single Particles (Expansion Regime)

Aerodynamic breakup of liquid and solid particles is reviewed. For liquid drops, breakup is controlled by the relative velocity and the surface tension of the liquid. For solids, breakup is controlled by the relative velocity and the shear strength of the solid. Liquids with the surface tension of water (170 dyne/cm) and solids with a shear strength of 10 psi require a relative velocity of 2000 ft/sec to break up into particles of 15 microns diameter.

Device and Cloud Parameters

An attempt was made to establish a rudimentary relationship between device and cloud parameters. The initial velocity of the fill was related to the fill-to-explosive mass ratio using Gurney approximations. Using an approximation for the relative velocity and stability criteria for single particles, the mmd of the cloud was determined for a range of agent-to-burster mass ratios and for liquid and solid fills. It is concluded that although the essential elements for establishing a relationship between cloud and device parameters were present in the analysis, additional refinement is required before meaningful relationships can be established.

Dissemination from Beads

In conventional explosive discharge devices the relative velocity is limited by the outward air velocity produced by the air shock. To

40

circumvent this problem, some experiments were undertaken in which the fill was enclosed in hollow perforated beads which were projected from the device. The beads gradually discharged the fill as they traveled. With this scheme it is possible to spread an agent instantly over such large areas, and hence to such low concentrations, that the minimum effective concentration of the agent becomes the limiting factor.

Conclusions and Recommendations

The development of the spherical shell model for spherical devices presented in this report is a major step toward understanding the processes that occur in discharge from spherical devices. With this model, it is shown that breakup of the agent into fine particles occurs by erosion of streamers and involves aerodynamic breakup of individual particles due to the relative velocity which develops between the particles and the air. With spherical devices the relative velocity achievable is limited by the air shock produced by the expanding fill. This is a fundamental limitation which can only be overcome by circumventing the air shock. The limitations imposed on relative velocity by the air shock indicate that it will probably be difficult to increase recovery much beyond what has already been achieved. Moreover, with such devices, spreading will always have to be left to local winds.

The limitation on relative velocity imposed by the air shock can be overcome if fill is enclosed in containers such as hollow perforated beads. With such containers the agent can be dispersed to such low concentrations that the minimum effective concentration of the fill becomes the limiting factor. With such devices spreading occurs immediately and does not depend on local winds.

The next step in the investigation of discharge from spherical devices should be a study of the development and erosion of streamers (particularly the latter), as these two processes appear to control recovery. The next step in the utilization of beads for dissemination should be a field test of some type. Both of these investigations should be preceded or accompanied by system studies to determine the significance of possible advances.

41

CONTRIBUTORS

Contributors to this study include R. W. Gates, Chemist; S. V. Hanagud, Research Mathematician; G. M. Muller, Mathematician; G. E. Duvall, Theoretical Physicist (Consultant); and K. Schreiner, Mechanical Engineer.

REFERENCES

1. Special Technical Report No. 2. See Appendix A.

2. Special Technical Report No. 5. See Appendix A.

3. Special Technical Report No. 18. See Appendix A.

4. Special Technical Report No. 3. See Appendix A.

5. Special Technical Report No. 21. See Appendix A.

III

SHOCK, DETONATION, AND REACTION PROCESSES

Leslie B. Seely, Jr., Director
Fast Reactions

The program on shock, detonation, and reaction processes is based
on the conviction (developed in the literature survey[1]) that a fundamental study of early conditions in explosive dissemination will establish the pertinence of past flashing studies and indicate the direction
such studies should take in the future. The aim is to clarify events in
the dissemination process and thereby to determine the importance of various agent-degradation mechanisms that have been proposed. Some of these
degradation mechanisms occur in the early states (e.g., degradation due
to shock heating); others are directly affected by the early stages
e.g., combustibility of detonation products when exposed to air); still
others are affected only to the extent that any stage is determined by
preceding stages (e.g., droplet burning ut very late times). Whatever
the case, the early processes need definitive study.

In practical munitions, the production of aerosols by explosion
processes frequently results in some loss of the agent. No doubt many
mechanisms are possible. Among the causes of this degradation may be the
temporary high temperature when the agent is compressed by the explosion;
mixing and reaction with the detonation products; and burning at a late
stage essentially after dissemination has taken place. To assess these,
the following related tasks were undertaken:

1. Detonation calculations

2. Light emission studies

3. Studies of the temperature of shocked liquids

4. Boundary stability studies.

In this report we have used the term "flashing" when it can legitimately serve as a short name for light emission plus agent (or simulant)

degradation. It should be recognized, however, that uncritical use of the term has sometimes implied a one-to-one correspondence between light emission and agent degradation. We believe the term flashing should be avoided unless the correspondence can be demonstrated in fact. In simplified demonstration devices it is quite easy to establish that light can sometimes arise solely from detonation products. It is not clear that any agent degradation takes place in such cases. In complicated rounds it is difficult to establish in what component of the burst cloud the light arises; therefore it is hard to prove the precise connection between light emission and degradation. Finally, there are cases in which very little light has been observed but in which degradation of the agent (or possibly poor recovery) has been indicated. In spite of the convenience of the term flashing we have therefore restricted its use in this report to the emission of light accompanied by agent degradation.

Detonation Calculations

The actual behavior of practical explosive dissemination systems has been found to depend strongly upon the explosive. Hence, it is important to know the temperature, pressure, and composition of the detonation products. This requires calculations of detonation conditions with an appropriate product equation of state, and eventually will require estimation of product conditions during the subsequent expansion process. With such knowledge one may then ask with some confidence why the detonation products sometimes appear to be the main ignition source, why at other times they apparently are not, and why in some cases light-emission times do not correlate with loss of agent. Detonation product calculations carried out by Mader[a] and others have been available for several years for standard explosives and these results may be used for guiding experiments involving standard explosives.

Calculation of detonation parameters such as product composition and temperature has led to (1) a rational understanding of the role of the high explosive in the flashing process, (2) suggestions for explosive compositions for diagnostic tests of flashing or other degradation

mechanisms, and (3) suggestions for practical explosive compositions that will minimize flashing in munitions.

A working deck for the RUBY code, used to calculate products with the Becker-Kistiakowsky-Wilson (BKW) equation of state, was obtained from Lawrence Radiation Laboratory and was adapted to SRI's computing facilities. For many years, difficulties in calculating Chapman-Jouguet conditions have resulted from the complexity of the chemical reactions and from an inadequate equation of state. Computing machines have now overcome the mathematical complexities, in principle at least. On the other hand, difficulties with the equation of state are likely to remain for some time, since we are concerned with densities of "gases" higher than the normal crystal density of the explosive compounds. Pending a correct treatment of the equation-of-state problem from first principles, the empirical approach must suffice.

Results of detonation calculations depend on the form of the equation of state for the gaseous products, on the empirical constants used in this equation, and on certain other assumptions such as the identity of the constituents or the equation of state for solids. Within certain limits there is no sure guide as to what assumptions to adopt. But there is a point in being consistent within one set of calculations and in adopting skepticism about details that can be changed by assumptions within the permissible range. We have not affected our results by choosing the RUBY code over any of the other calculational schemes that may be available, since the methods are all basically the same. On the other hand, we have influenced the results by adopting the BKW equation of state, by adopting a particular set of constants for that equation, by assuming that carbon is produced in its amorphous form, and in general by following the lead of Lawrence Radiation Laboratory. We cannot claim to be absolutely correct, but we can hope to draw significant conclusions from a consistent set of calculations by skillful selection of large-scale trends among relative results for the explosive compositions studied.

The detonation calculations were reviewed in Special Technical Report No. 13.[3] The salient results were:

1. Calculations of 90/10 Comp B/oxamide explosive showed quite clearly what the effects of the oxamide are, and indicated that if this additive is to affect flashing, it will do so not because of the composition of the products, but rather because the temperature of the products has influenced their ignitibility.

2. The composition of the products of explosives that are oxygen-balanced to CO_2 remains unchanged over a wide range of loading densities. This allows considerable freedom in adjusting the pressure of such compositions.

3. Calculations were completed for 80/20 Amatol and 61/39 HMX/AP. Theoretically these are energetic compositions which, in addition to eliminating product-burn flashing, should be efficient in dissemination.

Our work with RUBY code has indicated several areas for continued progress and improvement of the calculations:

1. If work on oxygen-balanced explosives is continued, some experimental work on such compositions should be performed in order to arrive at suitable equation-of-state parameters. The present constants in the BKW equation of state have been determined from explosives with a negative oxygen balance.

2. The BKW equation of state in any of its forms is not suitable for expansion calculations. The high energy of intermolecular repulsion embodied in this equation and the complete lack of attractive terms are not physically reasonable when the density falls below 1 g/cm^3. Mader's expansion calculations may be used to indicate the qualitative way in which oxygen-deficient products change as they expand, but a quantitative treatment of expansion must await an improved equation of state for the products.

3. Developing an oxygen-balanced explosive specifically designed for dissemination requires a flexible code with which detailed compositions can be considered and problems of partial reaction can be studied as a function of particle size. Parallel experiments can then give answers to particle size and binder problems that will arise in developing a practical formulation.

46

4. The present RUBY code is too inflexible to permit the use of other equations of state than BKW,[*] which has serious theoretical short-comings and is unsuitable for expansion calculations. A very general computational code, TIGER, has now been completed at SRI. It is much more flexible than RUBY, and should be employed to develop a theoretically sound equation of state. The resulting improved code/equation-of-state combination should be used to optimize explosive compositions designed for the specific purpose of explosive dissemination.

Light Emission Experiments

Experimental work on the so-called "flashing" (light-emission) problem was the logical experimental extension of the calculation of detonation properties of explosives used for dissemination. Light-emission tests were run on dissemination of Bis (an agent simulant) in spherical bomblets containing a high quality, centrally initiated, spherical burster charge.

One of the aims of this task was to achieve an explosive system that displays the dissemination process in as unperturbed a form as possible, to obtain a quantitative measure of the efficacy of symmetry in avoiding light emission. The details of the tests were given in a special report.[4] At 1:1 fill-burster ratio, Fastax high-speed motion pictures showed no light emission (flashing) from the Bis cloud or from the detonation products of Comp B in a total of 15 trials.

The fact that no light emission (except the early detonation flash) was observed with any of these symmetrical rounds, even at so low a fill-burster ratio as 1:1, emphasizes the effectiveness of excellent symmetry, both in the geometry and in the detonation wave shape, in avoiding light emission and agent degradation due to combustion in the cloud. The importance of surrounding the burster evenly with fill has been suggested in previous investigations.[5,6]

In spite of 15 consecutive failures to find light emission, the statistical probability that light emission occurs in symmetrical rounds

---

[*] This also applies to Mader's "BKW Code," including the Fortran IV version.

(and might appear in subsequent tests) is still not negligible. This statistically indeterminate situation, which is apt to arise whenever a successful solution of the flashing problem is demonstrated, requires great reliance on statistics alone, because quantitative diagnostic measurements such as times to ignition are made impossible by the success of the solution.

The fact that the rounds did not emit light will permit positive testing for other types of degradation. Thus, if a similar round of PBX 9404 (which has the highest detonation pressure of any explosive now readily available) also fails to emit light, the possibility of degradation due to temperature in the shocked liquid may be put to a crucial test. Similar tests on mixing and lack of symmetry can also be conducted with modified test rounds.

The symmetrical round with central initiation was perturbed in various ways in order to induce flashing. It was clear from the results that severe asymmetry of the fill was necessary to produce a high probability of flashing. Apparently off-center initiation also increased the probability of flashing, but it was less clear that a high probability could be produced in this way.

The perturbed round that produced light most often was used for a test of the effect of oxamide in reducing light emission. Twelve such high-flash rounds were tested, six with Comp B bursters and six with Comp B/oxamide bursters. All six Comp B bursters flashed; five of the Comp B/oxamide bursters flashed. Quantitative statistical methods for testing for the equivalence of the Comp B and Comp B/oxamide results have not yet been developed—the difficulty arises from the fact that all six Comp B rounds flashed. However, light-emission time measurements were made on all 12 rounds; these indicated that oxamide had an effect and that this effect was of the type to be expected from the detonation calculations. The lower detonation temperature of the Comp B/oxamide results in a lower temperature of the products at each corresponding period of expansion. Since the ignition properties of the products are involved (rather than those of the agent) the results indicate once again the

48

important part the properties of the products play in the type of flashing observed in these tests.

We have positively identified only one flashing mode. It depends on the ignitibility of the detonation products in contact with air. The fact that burning of the detonation products occurs before burning of the Bis cloud in the type of flashing observed in this test program leads to several conclusions concerning properties of the products and the Bis cloud. The burning of the products is at the interface with the air; there is no evidence of a deflagration wave in a combustible mixture. Apparently, decomposition of the Bis takes place under the influence of radiation from the burning products and becomes self-sustaining only after the temperature of the cloud has been raised considerably. These facts suggest the following principles for avoiding flashing:

1. Keep combustible detonation products from coming in contact with air while they are hot. This can apparently be accomplished by using a symmetrical design.

2. Use explosives that give products whose temperature, when exposed to air, is low. This low temperature is apparently responsible for any improvement achieved by incorporating oxamide in Comp B. However, this method of avoiding flashing is of limited applicability, since adding very much of any energy-poor component will result in poor dissemination.

3. Use oxygen-balanced explosives with sufficiently small particle size that interzone burning will not continue after detonation. Pressed Amatol, a balanced mixture of ammonium perchlorate and cyclotetramethylene tetranitramine (AP/HMX), Bis(trinitroethyl)urea (BTNEU), mixtures of hydrazine mononitrate, and hydrazine ($N_2H_5NO_3/N_2H_4$) have been suggested. An energy penalty need not be involved in a balanced explosive.

The major results of this research may be summarized briefly:

1. Geometrical symmetry and central initiation will prevent flashing.

2. Oxamide in Comp B appears to reduce the probability of flashing. The increased time to ignition of the detonation products is evidence that the reduction is accomplished through cooling of the products by the oxamide.

3. Burning of the explosive detonation products is always the basic cause of flashing of the type studied in this task.

49

4. In view of the mechanism of this type of flashing, it is to be expected that an oxygen-balanced explosive would be an effective cure for many practical cases of flashing in munitions, provided the pertinent aspects of munition design and explosives engineering are complied with.

5. Statistical analysis shows that:

   a. Tests should involve a reasonable number of well-controlled rounds.

   b. In some cases, very simple analysis can show that results from an extensive series of tests are inconclusive.

   c. Any data obtained experimentally, even if they involve only a few tests, should be submitted to statistical analysis to discover--if nothing else--what has not yet been established.

From a practical point of view, symmetry can immediately increase the effectiveness of munitions such as scatter bomblets or chemical grenades. In other munitions where symmetry is impossible a carefully balanced explosive will stop product-burn flashing. A composition of ammonium perchlorate and HMX in a waterproof combustible binder is recommended for such cases.

Temperature of Shocked Liquids

The immediate effect of detonation of a burster charge is to send a shock into the agent. In a practical device this shock is followed by other pulses, and complicated reflections and interactions may cause agent degradation. Just as one needs a proper equation of state of the detonation products, so one needs a proper equation of state of the agent in order to achieve a complete and realistic picture of the dissemination process. The shock temperature in the liquid, either initially or in reflections, may cause agent degradation directly, or conditions induced in the liquid may influence later stages of the dissemination process-- for instance, shock reflections may influence bulk cavitation and in that manner influence agent degradation.

The problem of calculating the temperature of a shocked liquid involves determining a complete equation of state. The details of this problem have been reported in a special report.[7] An indirect method must

be used because experimental techniques for direct temperature measurement are not sufficiently fast or sufficiently sensitive to record temperatures in the range of interest in the short times involved. Since the mechanical properties of shocked liquids are the only ones measurable by shock techniques, one is forced to use them to determine a temperature-pressure-specific volume (T-p-v) equation of state. The temperature of a shocked state can then be calculated if its pressure and specific volume are known.

A combined theoretical and experimental attack on the liquid equation-of-state problem was carried out with the following results:

1. The theory for calculating liquid shock temperatures was formulated and the problem was defined thermodynamically.

2. Shock and free-surface velocities in the 300 kbar regime were measured for Silicone 210 liquid with the liquid at initial temperatures of -20°C, 25°C, 158.5°C, and 258°C.

3. Energies and densities of Silicone 210 were measured along the atmospheric isobar. The data were fitted to a Mie-Grüneisen equation of state with variable C_v and $(\partial p/\partial T)_v$. It was found that $(\partial e/\partial p)_v$ was a function of volume along the atmospheric isobar.

4. The shock and isopiestic data along the atmospheric isobar led to the adoption of the (e-p-v) relationship

$$e = pf(v) + g(v)$$

where $f(v)$ and $g(v)$ are arbitrary functions of volume. The two arbitrary functions were evaluated from the two sets of data.

5. Hugoniots and isentropes consistent with the data were calculated from the (e-p-v) equation, and the temperatures along the isentropes were calculated from the expression

$$T = T_o \exp - \int_{v_o}^{v} dv/f(v) \quad .$$

Where the isentropes crossed the Hugoniots the shock temperature was thus obtained. For example, at 53.5 kbar a temperature of 456.7°C was calculated for Silicone 210 liquid.

6. The independence of the (e-p-v) and the (T-p-v) equations of state was repeatedly demonstrated through the work. As a result of this independence shock calculations can be

performed to give a complete p,v history of a liquid through
a shock and subsequent isentropic expansion without specifi-
cation of the thermal terms. The excess enthalpy[6] of the
final expanded state (after shocking) is

$$h = h_o + \int_{v_o}^{v_e} \left(\frac{\partial h}{\partial v}\right)_p dv$$

and the final temperature in the expanded state may be deduced
from this and the heat capacity on the atmospheric isobar
without a knowledge of the temperature in the shocked state.

A truly satisfactory determination of the liquid equation of state
remains to be achieved, but the problem has been defined theoretically.
The importance of more extensive liquid equation-of-state work can hardly
be overemphasized in establishing the basic physical laws that govern ex-
plosive dissemination of liquids. The problem bears a direct relationship
to determination of an equation of state for detonation products, since
the density and temperature ranges in shocked liquids overlap those in the
detonation products.

Boundary Stability and Mixing

In explosive dissemination, thermal and chemical interaction of agent
with explosion products and air depends on the extent of mixing, and as
expansion proceeds the process of mixing becomes increasingly complex.
Early agent degradation may be directly affected by thermal transfer from
hot products to the fill, particularly if we are concerned with an unsym-
metric practical explosive dissemination device in which irregular expan-
sion, jetting, and stagnation play a prominent part. If droplet burning
occurs at a later time, it will be strongly affected by the composition
and temperature of the surrounding atmosphere and by the relative motion
of the liquid drops and gas, conditions which are a consequence of pre-
ceding states of the expansion. The complex problem can best be attacked
by studying several simpler aspects of the whole. Of first importance is
the basic stability of the product/liquid interface.

The purpose of our study of the instability of the explosive-product/
liquid and the liquid/air interfaces was to ascertain if simple theoretical

52

predictions are realized. The study was carried out with a Beckman Whitley Model 189 framing camera. Details of the experiments and results are given in a special report together with conclusions and practical implications.[9]

The experiments were run in a quasi one-dimensional geometry. Framing camera pictures of the interface between the explosive products and the liquid under the influence of motion imparted by an explosive showed that:

1. Some mixing occurs when the shock from the detonation enters the liquid. This early jetting apparently results from irregularities of the explosive surface.

2. If the jetting referred to above is pronounced, it is not prevented by thin metal walls between the explosive and the liquid.

3. For the geometry studied the product/liquid interface is quite stable in the period between entry of the shock into the liquid at the explosive/liquid boundary and its exit at the liquid/air boundary. (There is no acceleration during this period.)

As a result of these tests we conclude that mixing of the fill with hot detonation products is not likely to be a cause of extensive degradation. It appears that immediately after the shock enters the liquid the boundary is stable. If it later becomes unstable under the action of the rarefaction wave, cooling of the products will already have progressed far enough that degradation will probably be avoided in all but the most unstable agents.

Additional experiments were performed at a later time in the expansion process to observe acceleration of the detonation products under the action of the rarefaction reflected from the liquid/air surface. From high-speed framing camera pictures taken at these times it has been concluded that:

1. Rapid acceleration of the products takes place when the first rarefaction reaches the product/liquid interface. (This is a period when instabilities might develop.)

2. The rarefaction wave reflected from the liquid/air surface causes fine random cavitation.

53

There seems to be no further doubt that fine bulk cavitation takes place in liquids under the action of explosives. The existence of bulk cavitation must be recognized as an early phase in dissemination. It probably overshadows the highly idealized process of layered spalling and may also have a direct bearing on the agent degradation problem.

Summary and Recommendations for Future Research

The program to investigate flashing by means of a study of the early stages of explosive dissemination has resulted in a better understanding of the basic physics involved, and has indicated several principles for solution of flashing problems which should be reduced to practice as soon as possible. The decision to consider three subjects--the explosive detonation phase, the boundary stability problem, and the equation of state for shocked liquids--appears to have been reasonable (in that the three first processes taking place in explosive dissemination have been considered), and fruitful (in that conditions in these phases have been clarified and specific remedial action for flashing has been outlined). The light emission program in which flashing tests were run on Bis-filled spherical rounds served to confirm the importance of detonation calculations and a detailed consideration of the earliest state in the explosive dissemination process. These tests demonstrated the role of the products in flashing and somewhat surprisingly showed that the Bis cloud is hard to ignite. The tests indicate that study of agent/products/air mixtures are not pertinent to the real problem nor is study of detonable or deflagratable product/air mixtures; surface burning of products is involved instead.

There are two immediate practical recommendations:

1. Incorporate symmetry and central initiation in practical rounds where possible.
2. Develop a practical oxygen-balanced explosive based on AP and HMX.

Both of these recommendations involve further research and testing. For implementing the first, a program with modified test rounds is

required to see to what extent symmetry and central initiation can be compromised without jeopardizing the excellent performance of the idealized test rounds.

Most of the areas investigated in this research require further effort. Proposed future research may be listed in abbreviated form:

1. Development of a more flexible detonation code.

2. Improvement of the equation of state for detonation products.

3. Experimental determination of detonation properties of oxygen-balanced explosives.

4. Intensive computer study of formulations of AP/HMX and a binder to maximize performance and attain desirable practical properties.

5. Liquid equation-of-state studies should be carried on theoretically, distinguishing clearly between (e-p-v) and (T-p-v) problems.

6. Information on detonation product equation of state should be applied to the shocked liquid equation-of-state problem.

7. Bulk cavitation needs further study as a component stage of dissemination.

8. The possible relation between agent degradation and the collapse of cavitation should be investigated.

CONTRIBUTORS

Major contributors to these studies include Marjorie W. Evans, Director, Poulter Laboratory for High Pressure Research; M. Cowperthwaite, Senior Chemical Physicist; J. G. Berke, Physicist; J. Roth, Senior Physical Chemist; G. L. Stevens, Research Engineer; and J. Blackburn, Physicist.

REFERENCES

1. Special Technical Report No. 2. See Appendix A.

2. C. L. Mader, Los Alamos Report, LA 2900, OTS, U.S. Dept. of Commerce, 1963.

3. Special Technical Report No. 13. See Appendix A.

4. Special Technical Report No. 15. See Appendix A.

5. R. W. Gates, J. J. Howe, and S. A. Moses, "Explosive Dissemination of Liquid Agents," Stanford Research Institute Summary Report, Contract DA-18-108-CML-5510, September 17, 1957.

6. W. Haggarty, M. Markels, and G. von Elbe, "Research Study of Aerosol Flashing," Final Report, Contract DA-18-108-AMC-104(A), Atlantic Research Corp., August 1964.

7. Special Technical Report No. 14. See Appendix A.

8. S. R. Brinkley, Jr. and J. A. Kirkwood, Phys. Rev. 72, 1109 (1947).

9. Special Technical Report No. 12. See Appendix A.

IV

COMMINUTION PROCESSES

Ronald K. Linde, Director
Shocks and High Pressure Physics

Priority requirements currently exist for munitions to efficiently disseminate solid chemical agents in the form of aerosols with particle sizes on the order of 10 microns or less. Tests conducted at Edgewood Arsenal have provided evidence of considerable potential for ultimately meeting these requirements with explosive dissemination techniques; it is also evident that a much better understanding of the response of materials to dynamic loading (especially dynamic tensile loading) will be necessary before much further progress can be made. For example, under certain conditions an explosive event may result in fracture of a solid specimen into small particles, whereas under other conditions it may result in compaction of loose powders of the same material into a solid body. Of course, dynamic loading is not the only aspect of the problem in need of study; such questions as possible reagglomeration of particles in the aerosol may also be important. However, it is necessary first to produce an acceptable particle size distribution in the explosive event before such potential problems as reagglomeration can become limiting factors in performance.

The comminution studies were initiated midway in the program, and are being continued under another contract with Edgewood Arsenal.[*] Consequently, no special technical report was issued. A comprehensive discussion of these studies will be included in the final report on the new contract.

---

[*] Contract No. DAAA 15-68-C-0099, "Dissemination and Aerosol Behavior of Hydrophobic Powders."

The present effort has constituted a preliminary study of the fracture behavior of several brittle solids subjected to shock loading, in an attempt to achieve some understanding of the material properties which may be relevant for comminution processes. Although the brittle materials investigated in this initial study (mainly alkali halides and metal oxides) do not model agent materials as closely as possible, they were chosen for study at this point for two main reasons:

1. The fracture behavior of these brittle materials has been studied extensively under quasi-static conditions and a considerable amount of information is also available concerning their instantaneous response to shock compression; thus one has an opportunity to explore the relevance of various static and dynamic properties of a material in determining shock comminution behavior without incurring the considerable expense of measuring these static and dynamic properties for each material.

2. If any of these brittle materials evidences desirable comminution behavior, it may be suitable for use as an additive to the agent to form part of the matrix of a composite specimen. Such composites might allow dissemination of an agent which is difficult to comminute explosively into fine particles or which is easily degraded by temperature rise during shocking.

Experimental Techniques

It is evident that geometrical considerations affect compressive and tensile wave propagation, attenuation, and interaction, so that in order to separate the effects of material parameters from geometrical effects it is necessary to conduct experiments in a reproducible, and hopefully well-defined, geometry. Experiments at shock pressures above about 100 kbar were performed by inserting specimens in metal capsules which in turn were placed in momentum-trapping assemblies. The shock pulses were provided by plane-wave detonation of a high explosive in contact with the assembly. At shock pressures below about 100 kbar flat-plate impact experiments were performed; these are described below. The geometry was similar for experiments in both pressure ranges.

58

The flat-plate impact experiments all involved configurations similar (but not always identical) to those pictured in Figs. 4 and 5. The target was mounted on the end of a light gas gun barrel,[1] which was subsequently evacuated. The flying plate was attached to the cylindrical projectile body with epoxy resin so as to separate immediately upon impact with the target. The cylindrical body then did not hit the target, but flew through the low-density polyurethane foam supporting the recovery assembly. The thickness of the flying plate was nominally 3.2 mm, providing flat-topped shock pulses of 1 to 2 μsec duration, the precise value being determined by the shock and rarefaction velocities in the material used for the flying plate.
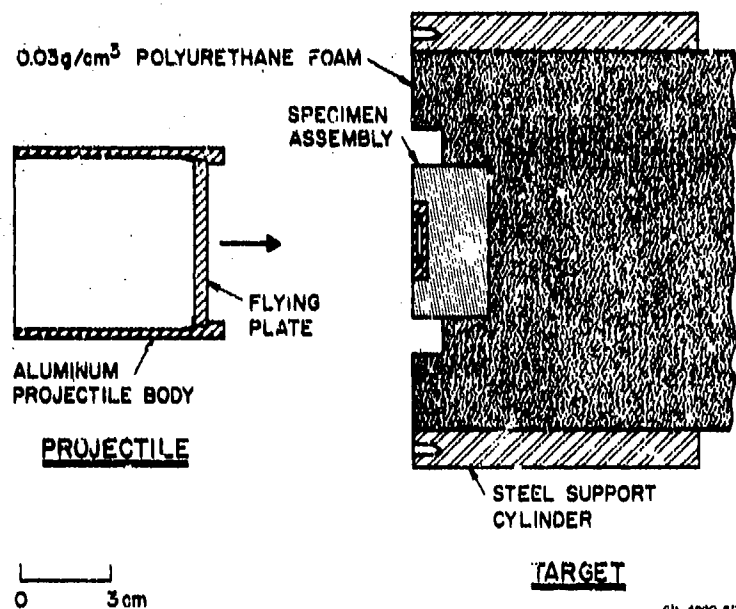
FIG. 4 RECOVERY TECHNIQUE FOR FLYING
PLATE EXPERIMENTS

SPECIMEN
METAL NEST
POWDER COMPACT
METAL INNER CAPSULE

TYPE I

SPECIMEN
SPECIMEN GUARD
0.03g/cm³ FOAM SUPPORT
METAL OUTER CAPSULE

TYPE II

0.03g/cm³ FOAM SUPPORT
SPECIMEN GUARD
SPECIMEN
METAL OUTER CAPSULE

TYPE III

0   3cm
48-4900-100
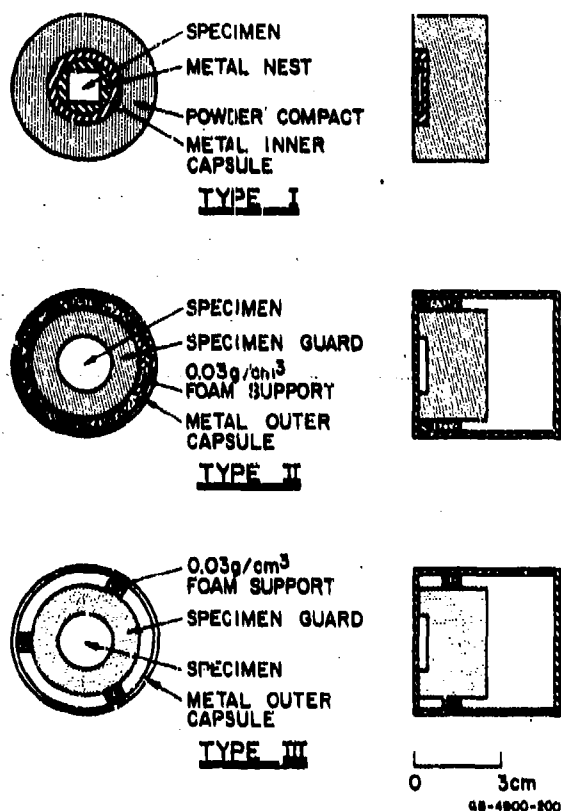
FIG. 5   DETAIL OF TYPICAL SPECIMEN
         ASSEMBLIES

For specimen assembly Type I (Fig. 5), the dimensions of the capsule were chosen so that rarefactions originating at free (or nearly free) surfaces always intersected in the region occupied by the powder compact, which served as a quasi-continuum of momentum traps. Controlled rarefactions and tension were allowed to enter the specimen by appropriate choice of material from which the metal nest and capsule were made. With specimen assembly Type II, the specimen was embedded in material of the same type as the specimen itself (specimen guard in Fig. 5), but the dimensions were again chosen so that tension formed by the intersection of free-surface rarefactions occurred in the specimen guard and did not propagate into the specimen. Tensions in the specimen could occur only as a result of imperfect interfaces between the specimen and the specimen guard. The outer metal capsule served to retain material for examination. In the case of alkali halides, the specimen guards were colored by radiation prior to shock, so that they could be distinguished from the specimens themselves. With specimen assembly Type III the specimen guard was not constrained, so that spalled fragments were free to fly in any direction. For Types II and III, the specimen and specimen guard were sometimes a single piece (i.e., a large specimen) rather than having a mated interface.

Results of Experimental Studies

Single-crystal and polycrystalline specimens of sodium chloride, potassium chloride, quartz, aluminum oxide, magnesium oxide, and titanium dioxide (rutile), as well as single-crystal specimens of germanium and

large polycrystals of silver chloride were shock-loaded to study their dynamic fracture behavior. In addition, composite materials consisting of hot-pressed and cold-pressed mixtures of various powders were investigated for their comminution behavior under dynamic loading. A summary of important results and conclusions drawn from this preliminary investigation is given below. (Where a material is not listed with a given item, no investigation of that particular point with respect to the material was undertaken.)

1. *Single-crystal NaCl, single-crystal KCl, single-crystal and polycrystalline SiO_2, polycrystalline Al_2O_3, polycrystalline MgO, composite materials:* Under certain conditions, some of which are outlined below, substantial fractions of particles in the size range from 10 to 50 microns were obtained after shock loading.

2. *Single-crystal NaCl, KCl, MgO.* These crystals, which normally undergo easy cleavage, were found in the dynamic case to still fracture predominantly along cleavage planes, regardless of the orientation of maximum tensile stresses produced. Furthermore, the cleavage cracks were of considerable macroscopic length.

3. *Single-crystal NaCl.* The fracture density and ultimate particle sizes are sensitive to the degree of external confinement of crystals but are relatively insensitive to variation in shock pressure, provided the shock pressure is somewhat above the dynamic elastic limit. The particle sizes achieved with specimen assembly Type III (Fig. 5) were roughly an order of magnitude smaller than those achieved with Types I and II, and while it is believed that some comminution resulted from flying particles impacting other flying particles and the outer capsule walls, examination of particle distribution suggests that this is not the predominant cause.

4. *Single-crystal and polycrystalline KCl and TiO_2.* The presence of a dynamic phase transition affects the ultimate crystalline size in recovered material but does not appear to significantly affect the macroscopic particle size or crack density. Single-crystal TiO_2, for example, initially had average crystalline sizes of 0.01 to 0.02 micron after shock.

5. *Single-crystal MgO.* Shock compression data indicate that this material loses all strength at 100 to 150 kbar,[2] but a specimen shocked to 120 kbar and below did not fracture into smaller particles than did materials which should retain their full

strength to much higher pressures, according to shock compression data. After shocking to 1000 kbar and allowing large tensions to enter the specimen, some millimeter-sized pieces of MgO were still recovered, but much of the specimen was lost and could not be examined. Experiments should be performed in the range from 150 to 200 kbar.

6. *Polycrystalline MgO and AL$_2$O$_3$.* These polycrystalline materials, which fractured predominantly by intergranular cracks under nonshock conditions, did so under shock-loading conditions also.

7. *Polycrystalline MgO, AL$_2$O$_3$, TiO$_2$, SiO$_2$, and composite mixtures.* Presizing of particles can produce a significant advantage under some circumstances. The effectiveness of presizing depends upon the materials involved and the bonding between particles. For example, specimens of 99.8% dense MgO presized with 20-micron <u>firmly</u> bonded grains were uniformly extremely friable into <u>approximately</u> 20-micron particles after shocking to 100 kbar. Under the same conditions, material of essentially the same density and having 5-micron <u>weakly</u> bonded grains was friable into some particles as small as 20 microns, but at least half of the material was not friable into particles less than a few hundred microns; essentially no particles in the 5-micron range were obtained.

A substantial bibliography on the fracture of solids has been compiled to serve as background for further studies.

Specimens Prepared for Explosive Aerosol Tests at Edgewood Arsenal

On the basis of promising preliminary tests performed at SRI, it was deemed worthwhile for Edgewood Arsenal to conduct dissemination tests on composite materials consisting of intimate mixtures of micron-sized powders of materials having considerably different shock impedances. Three pressed pellets containing different proportions of intimately mixed tungsten and NaCl powders, and three pellets containing different proportions of intimately mixed tungsten and C$_{12}$H$_{22}$O$_{11}$ (sucrose) powders, were prepared by SRI for explosive dissemination experiments to be performed by Mr. Craig Allan at Edgewood Arsenal. Because of the very high density of tungsten, the results of the explosive dissemination tests were inconclusive.

To circumvent the density problem, techniques were developed for preparing suitable specimens with magnesium oxide substituted for the tungsten. Twelve specimens, along with detailed specifications of their production, were delivered to Mr. Allan for testing. Results of these tests had not been reported at the time of this writing.

Allis-Chalmers Subcontract for Theoretical Studies

At the request of Edgewood Arsenal, Allis-Chalmers Research Division was awarded a subcontract (No. 11027) under which Dr. T. P. Meloy was to investigate the application of a statistical theory of comminution to the problem of explosive fragmentation of a brittle solid. The technical monitoring of the subcontract was performed by Dr. D. G. Doran of SRI. About midway in the program (in January, 1967) Dr. Meloy resigned from Allis-Chalmers, and the subcontract was therefore terminated.

The principal accomplishment of this incomplete study was the generalization of the Gaudin-Meloy theory so that, in principle, it might be applied to heterogeneous solids. This development was reported in detail in a quarterly report.[3] A detailed evaluation of the Allis-Chalmers study was reported in a later quarterly report.[4] As part of this evaluation, it was recommended that Meloy's statistical approach to the problem of explosively produced comminution not be continued at the present time.

Recommendations for Future Research

In order to optimize specimen preparation and experimental design, one should gain an understanding of the mechanisms of fracture under shock loading conditions. Explosive systems can be designed to maximize stress amplitudes, velocity gradients, flow divergence, etc. It should be determined what role these and other factors play in causing fracture and in separating fragments. The effects of strain rate should be understood so that quasi-static and dynamic data can be correlated. Interrelated with these configurational parameters is the effect of the condition of the specimen itself. In particular, when is preconditioning (e.g., presizing) effective? It is only after answers to such questions

63

are found that a theory of shock comminution might become quantitative and capable of being applied to the prediction of fragment distribution.

In summary, experimental variables worthy of additional consideration include shock strength and profile, static and dynamic mechanical properties of specimen materials, effects of presizing particles, preshock strength of particle bonds, choice of matrix materials, preshock compaction density, surface treatment of particles, and geometrical configuration. A full understanding of the effects of these variables should provide the design criteria for optimal explosive dissemination devices. Our state of knowledge has progressed to the point where shock studies on materials that closely model Agent CS should also be performed.

CONTRIBUTORS

Dr. D. G. Doran, Senior Physicist, was a major contributor to this study.

REFERENCES

1. Linde, R. K. and D. N. Schmidt, Rev. Sci. Inst. 37, 1-7 (1966).

2. Ahrens, T. J. and R. K. Linde, Proc. International Union of Theoretical and Applied Mechanics, Symposium on Behavior of Dense Media under High Dynamic Pressure, Paris (1967), in press.

3. Quarterly Progress Report No. 11. See Appendix B.

4. Quarterly Progress Report No. 13. See Appendix B

V

DROPLET IGNITION PROCESSES

Bernard J. Wood, Chemist

The aerosol cloud associated with a chemical weapon consists of a mechanical mixture of air, agent vapor, and discrete liquid droplets of agent. Flashing of such a cloud follows ignition by some mechanism. One possible route leading to flashing is spontaneous ignition of the liquid droplets in the cloud by exposure to hot gases generated in the detonation of a disseminating explosive charge. The object of this study was to elucidate the mechanism of spontaneous ignition of liquid droplets suddenly exposed to a hot, oxidizing atmosphere, and thereby to assess the relative importance of this process to the problem of aerosol flashing.

Theory and Experiments

A critical survey[1] of the literature on droplet ignition and combustion, carried out at the beginning of this study, showed that very little experimental work had been done on the ignition of freely falling, single, aerosol-size droplets. Theoretical analyses of such a system were meager also. The study, therefore, was directed along two parallel lines: (1) an experimental investigation of the effect of parameters such as dimension, velocity, composition, and temperature of single droplets and their gaseous environment on the ignition characteristics of the droplets; and (2) development of an analytical model to correlate the experimental facts and to use as a basis for predicting the ignition behavior of droplets under conditions other than those studied in the laboratory. Concurrently, R. L. Peskin (at Rutgers University) also carried out a theoretical analysis of droplet ignition[2] from a somewhat different point of departure, which complemented the theoretical and experimental studies at SRI.

The experimental investigation employed a specially designed furnace in which ignition lags and vaporization rates of freely falling, single, liquid droplets could be observed with photooptical techniques. With this apparatus, the effects on ignitibility and ignition lag of initial droplet diameter, droplet composition, oxidizer composition and temperature, and droplet-droplet spacing were evaluated. The theoretical study considered a liquid droplet as the center of a spherical shell of reactive vapor with the outer boundary at a higher temperature than the inner boundary. In such a model, the critical condition that arises when the rate of heat loss from the reactive shell is balanced by the rate of heat generation within the shell due to chemical reaction leads rapidly to thermal runaway--that is, to ignition.

In spite of the complexity of the ignition process, the results of the experimental study could be correlated qualitatively with both theoretical models, each of which seems to represent a reasonable approximation to the physical situation of a fuel droplet suddenly exposed to a hot, oxidizing atmosphere. The data indicate that a measurable quantity of practical interest is the ignition lag τ. This parameter depends strongly on the temperature of the atmosphere and on the droplet-droplet spacing, in addition to the chemical nature of the fuel, but appears to be only weakly affected by the oxygen concentration in the oxidizer. The ignition lag seems to be independent of the initial droplet size for droplets large enough to ignite at all. This trait insures that droplets with initial diameters D_o smaller than a characteristic value D_{cr}, given by $D_{cr} = \sqrt{\epsilon\tau}$, will not ignite during their lifetime. (The proportionality constant ϵ, termed the evaporation constant, is a parameter which depends on the chemical and physical properties of the liquid.)

Caution must be used in applying the results of this study of single droplet ignition to the ignitibility of an aerosol cloud. For instance, if an aerosol cloud is exposed to a strong ignition source such as a flame associated with the explosion that produces the cloud, then the quantity of interest is the aerosol concentration relative to the lower lean flammability limit. Under such conditions, spontaneous ignition of

individual droplets can be ignored. In the absence of a strong source, spontaneous droplet ignition is possible if the cloud is flammable and is exposed to a hot atmosphere, as from shock heating, for example. The character of the ignition will depend on the diameters of the cloud droplets relative to the characteristic diameter that corresponds to the given conditions. If the cloud contains droplets larger than the critical diameter, single droplet ignition of the type observed in this study is probable if the time of exposure of the aerosol cloud to a hot atmosphere is comparable to or longer than the ignition lag. The resulting single droplet flame can then spread throughout the cloud. Ignition and burning of single large droplets without flame propagation is still possible when the overall concentration of aerosol is below the lower lean flammability limit. Single drop ignition is favored by a high gas temperature, i.e., in the region where characteristic diameter is small. If the aerosol cloud does not contain droplets with diameters greater than the characteristic diameter, autoignition may occur only as a result of the formation of a flammable vapor-air mixture due to evaporation of much of the aerosol cloud. Such a condition is favored by a moderate gas temperature, i.e., in the region where characteristic diameter is large.

The complete results of this study are summarized and discussed in detail in Reference 3. A separate, detailed development of the analytical model has also been prepared for publication.[4]

Recommendations for Future Research

Although the results of this program suggest that spontaneous ignition of discrete liquid droplets is not a major causative factor in aerosol flashing under conditions of explosive dissemination, further experimental and theoretical studies would be of great fundamental interest. Still unclear, for example, are the precise relationships of ignitibility, oxidizer composition, chemical properties of the liquid phase, and the chemical kinetics of the liquid-oxidizer system.

CONTRIBUTORS

Contributors to this study include W. A. Rosser, Senior Chemist (now at AVCO Everett Research Laboratory), and Y. Rajapakse, mathematician.

REFERENCES

1. Special Technical Report No. 2. See Appendix A.

2. Peskin, R. L. and Polymeropoulos, C. E., "Theoretical Calculations of Fuel Drop Ignition and Extinction," Rutgers, the State University, New Brunswick, New Jersey, Presented at 1967 Spring Meeting, Western States Section of the Combustion Institute, La Jolla, California.

3. Special Technical Report No. 8. See Appendix A.

4. SRI Technical Report No. 20. See Appendix A.

VI

THERMAL AND PYROTECHNIC DISSEMINATION PROCESSES

C. E. Wooldridge, Senior Gas Dynamicist

Both thermal and pyrotechnic dissemination rely upon the application of energy from a heat source to vaporize and disseminate a chemical warfare agent. In thermal dissemination the agent is injected into a hot gas flow which has been produced by a separate combustion device, whereas in pyrotechnic dissemination the agent is intimately mixed with the fuel and oxidizer in the combustion chamber. In either case, the specific requirements to be met are:

1. Generation of an appropriately sized aerosol

2. Optimal distribution of aerosol in both space and time

3. Prevention of agent degradation in the thermal and chemical environments encountered

4. Prevention of agent degradation during long term-storage in contact with the pyrotechnic or propellant compositions

At the start of the program a literature review was undertaken to determine the current state of the art in the dissemination field.[1] Since the pyrotechnic dissemination of dyes and smoke additives parallels the dissemination of agents, this work was also included in the survey.

The review showed that in the generation of smoke or agent aerosols by pyrotechnic means, nearly all methods utilized a pyrotechnic based on potassium chlorate ($KClO_3$). The advantages of this oxidizer include its ease of ignition, its smooth burning, and its ability to maintain combustion at low temperatures and pressures.

Sugar, lactose, and other similar materials which oxidize easily at low temperatures are normally used as fuels. Sulfur is used predominantly in smoke-producing compositions. Its main drawback is the question of its shock sensitivity in combination with $KClO_3$; several accidents have been reported which have been attributed to the sulfur-$KClO_3$ combination.

Nitrocellulose (NC), often used as a binder, functions as a combination fuel-oxidizer Carbonates, bicarbonates, kaolin, and other coolants are added to absorb heat and to provide a uniform flame temperature and a suitable atmosphere for evaporation of agent.

The incorporation of burning rate catalysis has not been particularly rewarding in the pyrotechnic field. For example, incorporation of a palladium catalyst allowed 64% of methylaminoanthraquinone (MAA) to be disseminated without degradation when $KClO_3$ was used as an oxidizer, and the temperatures were reported to be very low. However, the cost of the palladium catalyst limits the use of such a system to the laboratory because relatively large quantities must be used to maintain combustion.

Gas generators commonly employed in the past for both laboratory and development studies of thermal dissemination have utilized propane and air, sodium chlorate and gilsonite, and ammonium nitrate and rubber as combustible combinations. The agent or simulant to be dispersed was injected into a low-velocity region where the material was converted to an aerosol principally by thermal energy. The process of thermal vaporization with subsequent condensation produces aerosols with volume-to-surface mean particle diameters (D_o) usually smaller than 10 microns.

The propane-and-air furnace has been used extensively for the generation of hot gas under controlled conditions. This allows the parametric study of the effects of important variables such as environmental temperature and gas velocity on both the yield and the particle size distribution obtained from hot gas atomization. An important result of these studies is the conclusion that aerodynamic forces contribute significantly to particle breakup when the gas velocity is sufficiently high that both thermal and kinetic energy must be considered.

The principal variable that must be controlled in any dissemination technique is the environmental temperature to which the disseminant is exposed, because high temperatures will produce excessive degradation. The principal advantage of hot gas dissemination is that is offers the possibility of a nearly inexhaustible range of gas compositions from the entire spectrum of solid propellants that have been developed for

70

propulsion purposes. In addition, any desired temperature is available in the exit cone of a nozzle, where the temperature is a strong function of area ratio. However, a complicating factor is that the nature of the carrier gas can influence the decomposition rate of the agent being dispensed. Additionally, solid particles of metallic chloride in the exhaust gas formed by the combustion of potassium chlorate or sodium chlorate are suspected of providing nucleation surfaces for condensing liquids, thereby affecting the particle size distribution.

The goals of the work carried out at SRI in the area of thermal and pyrotechnic dissemination were to develop an understanding of the processes involved in both dissemination schemes and to pursue in necessary depth those approaches that offer the highest probability of extending the state of the art and providing maximum usefulness of these techniques.

Thermal Dissemination

The results of research studies at SRI in the area of thermal dissemination with secondary injection into a supersonic rocket exhaust have been reported in References 2 through 11 and were summarized in a special technical report.[12]

As reported above, work done by other investigators has primarily been concerned with injection of the agent or simulant into a high temperature, relatively low kinetic energy, gas stream at Mach 1 or less. In contrast, SRI studies have considered injection of the disseminant into a gas stream which has been expanded to velocities on the order of five times the speed of sound. Since the gases are cooled upon expansion, the environmental temperature to which the agent is exposed can be controlled, and the aerosol can also be discharged with significant kinetic energy toward a chosen target. Typically when a gas expands from 1,000 psi to atmospheric pressure its temperature is reduced by half and its velocity is increased from zero to 5,500 ft/sec.

The technique developed at Stanford Research Institute utilizes a rocket motor with an integral tank that is filled with the fluid material to be aerosolized and pressurized by the chamber gases. Fluid is forced

71

from the chamber into the gas stream, which has been expanded through a De Laval nozzle. Nominal conditions which have been studied are 1,000 psia in the fluid chamber and 25 psia at the injection point, where the gas stream has a velocity corresponding to approximately Mach 5 with a temperature of approximately 1,200°F. The fluid stream is directed at right angles into the gas stream, resulting in a complex system of shocks accompanied by a very turbulent mixing region both in the nozzle and in the area immediately beyond the nozzle. Mixing in the plume i. enhanced by the ingestion of large amounts of air into the generated plume.

The composition of solid rocket propellants used for carrier gas generation may be varied to provide widely different combustion products and a wide range of operating conditions for the device. It was found that potassium perchlorate propellants were best suited to the current studies because of their high burning rates (leading to short action times) and their ability to suppress afterburning and consequent agent degradation downstream of the nozzle. That flaming was suppressed by propellants containing $KClO_4$ is not surprising, since potassium compounds have been used widely for flash and flame suppression. A further advantage or disadvantage (depending on the application) of using a potassium perchlorate propellant is the formation of solid KCl particles which are thought to act as nuclei for condensation of vaporized material. When liquid aerosol samples were collected on glass plates and observed through a microscope, approximately 90% of the droplets were observed to contain a particle of a solid thought to be KCl in the center.

Depending on the particular particle size distribution desired and the type of fluid being injected, very high injection ratios (weight of injected fluid to weight of carrier gas) may be feasible (>5:1). If, however, small particles (~1 μmmd) are desired, the injection ratio should probably be limited to the range from 2:1 to 3.5:1.

In tests carried out at a ratio of 2.5:1, measured recoveries of agent CS based on the ratio of CS to KCl indicated high efficiency, with associated action times of 1 sec. Particle sizes from 1 to 2 microns (50% pt on a weight basis) were measured.

72

The rocket nozzle injection scheme is particularly intriguing because many propellants are available for use, without development, which have been completely characterized, will provide a wide variety of gaseous products, and readily lend themselves to a wide latitude of design techniques. High-performance propellants are available to give initial higher thrust levels if they are desired. Solid rocket motors have reached a state of the art in which any size of "gas generator" can readily be designed with a very high degree of reliability.

Another advantage of the rocket nozzle injection technique is its ability to cover a large area in a short time. The direction of the cloud pattern can be controlled by the orientation of the nozzle, and the dissemination pattern is relatively unaffected by local meteorological conditions. The results of recent cloud growth studies at SRI have been reported in Reference 13.

Pyrotechnic Dissemination

The results of studies at SRI in the area of pyrotechnic dissemination were reported in References 2-11 and were summarized in a special technical report.[14] The effort was directed toward an understanding of the behavior of heterogeneous pressed systems. It was recognized that a broad spectrum of basic experiments was needed to advance the art of pyrotechnic dissemination beyond the purely empirical stage.

Adiabatic self-heating (ASH) measurements were made to provide values of activation energies and frequency factors. The value of the overall activation energy for a typical pyrotechnic formulation was found to be in the neighborhood of 80 kcal/g. In addition, separate measurements obtained from binary mixtures of pyrotechnic ingredients provided a method of comparing the relative oxidative stability of the agent and fuel components in the burning mix, since the reaction rate is proportional to the frequency factor.

Differential thermal analysis (DTA) measurements were made on various pyrotechnic components to provide data on melting points, phase changes, and reaction temperatures. The DTA is a versatile tool and provides significant information for a minimum of effort. Mixes which are experimental

73

in nature may be screened using this technique, and those which show an exotherm at a dangerously low temperature may be discarded before further effort is expended on their development. (A low-temperature exotherm is dangerous because of the possibility of explosion during storage.)

Since practically no literature information is available concerning the combustion of pyrotechnics above atmospheric pressure, burning rate measurements as a function of pressure were undertaken. A higher burning rate, if available, would reduce the residence time of the agent in the combustion zone and thus increase the dissemination efficiency. Pressure/burning rate data were obtained for pyrotechnics containing MAA and CS over a range of pressures from 14.7 to 750 psia. It was found that the pyrotechnic formulations obeyed the familiar solid rocket propellant burning rate expression, $r = cp^n$. The burning rate studies also indicated a tradeoff between reduced residence time and increased environmental temperature in establishing an optimal dissemination efficiency.

To support mathematical modeling studies of the combustion wave, thermal conductivity measurements were made on both the pyrotechnic ingredients and the pyrotechnic mixes. It was found that the value of the thermal conductivity was proportional to the density, which in turn depends upon the forming pressure. This implies that the burning rate should be independent of the forming pressure, as was found to be the case.

The efficiency with which an agent or its simulant is disseminated depends on its vapor pressure/temperature behavior. For this reason, vapor pressure measurements on the simulant MAA were undertaken at the direction of Edgewood Arsenal. The temperature corresponding to a vapor pressure of one atmosphere was found to be 416°C.

Considerable effort was devoted to the study of pyrotechnic combustion in canisters. In order to properly identify the critical processes that occur during combustion of a pyrotechnic, it is imperative to obtain a careful material balance before and after combustion. An experimental study of the combustion wave itself is also important because the product gases formed in the flame zone and in the ash bed provide the environment in which the agent must survive to become a useful aerosol. In the

74

SRI work it was decided to use a total sampling technique--capturing all of the output from a given pyrotechnic and performing suitable chemical analyses on it.

A complete material balance on the MAA pyrotechnic was only partially successful because of the amount and complexity of ash remaining after firing. In addition, the size, action time, and pressure variables are very significant contributors to the amounts of ash and its composition. The normal yield (i.e., percent of agent disseminated without degradation) obtained was approximately 75%. In the case of the CS pyrotechnics, yields obtained were on the order of 60%.

The following conclusions can now be drawn, based on the analytical results:

1. The kaolin used as a coolant loses only water and does not react or enter into the combustion process (the equilibrium computer program suggested Al_2O_3 and silanes might be produced.)

2. With water and HCl present in the gaseous products, the CS is effectively maintained in an acid environment during vaporization.

3. Considerable amounts of HCl are generated in association with water and may serve to provide nucleating sites for the vaporized agent.

If the gases from a conventional CS mix are bubbled through water, the water becomes acidic, and if the ashes from this same pyrotechnic are placed in water, the water becomes slightly acidic. On the other hand, the gases from an MAA pyrotechnic bubbled through water give a slightly basic response and the ashes dissolved in water are highly basic. Agent CS is very stable under acidic conditions and can be stored for months in highly acidic solutions without measurable degradation. MAA, on the other hand, is stable in basic solution but degrades under acidic conditions. The acid-base nature of the pyrotechnic by-products are thus an important factor in deciding which agents can be disseminated using a particular fuel-oxidizer-coolant combination.

Temperature profile measurements indicated that there is a significant preheat zone ahead of the combustion wave and that the char bed remaining

75

after passage of the wave can markedly influence agent decomposition. A correlation was found between dissemination efficiency and agent residence time in the pyrotechnic. This relationship indicates that pyrotechnics should be designed to function as rapidly as possible. Pyrotechnics of up to 3,000 grams were made and tested. There were no signs of a runaway reaction and it would appear that there is no limit to the size of a pyrotechnic which can be built to function satisfactorily if the design prevents severe buildup of heat ahead of the combustion zone. The larger the unit tested, the more effective it appeared to be. In terms of loading density (grams of agent disseminated/cc of pyrotechnic), the larger the pyrotechnic, the more effective it is.

Recommendations for Future Research

Physical and chemical methods of burning rate stimulation should be sought. The chances of finding a chemical technique of multiplying the burning rate by at least an order of magnitude are quite small because of the low temperatures involved and the restrictions imposed on possible reactions because of the presence of agent. However, a cast system instead of a pressed pyrotechnic system should be more adaptable to burning rate catalysis.

It appears that, in general, future gains in pyrotechnic performance will depend on the formulation of castable compositions which can be more uniformly processed and which will allow improved loading densities of disseminant. Although CS and BZ are far different chemically, they are physically similar. The use of binders for making castable compositions would provide some problems, since the compatibility difficulty is compounded for a dual system. It is felt that a castable pyrotechnic system could be developed for CS, BZ, and combination CS-BZ.

Results obtained from the thermal dissemination studies by secondary injection into a supersonic rocket exhaust indicate that significant amounts of CS can be dispersed in very short periods over large areas using rocket injection techniques. It was not possible to determine whether CS is broken up during injection or if it is vaporized and re-condensed.

On the basis of these successful trials of CS dissemination, it is suggested that tests with BZ and VX be considered to ascertain if thermal and oxidative degradation of these agents can also be minimized using this technique.

The design pressure used in all of the tests was approximately 1,000 psi. Efficiency of operation from the rocket performance standpoint is increased with increasing pressure, but it may be found that 100 to 200 psi may yield a more optimum system from the general design, operational, and handling standpoints. Thus, while these limited tests have demonstrated the feasibility of the rocket disseminator device, they have not explored the entire design spectrum.

CONTRIBUTORS

Mr. Lionel A. Dickinson directed these studies from their inception through February 1967, when he accepted the position of Director of Advanced Technology, Naval Ordnance Station, Indian Head, Maryland. Although Mr. Dickinson left the Institute prior to the writing of this report, the author wishes to give him full credit for the concepts and accomplishments described herein.

Other contributors to this phase of the program include John E. Baldwin, Chemical Engineer, Erwin L. Capener, Head, Propulsion Section, Roger J. Kier, Propulsion Engineer, Norman A. Kirshen, Physical Chemist, and Walter H. Johnson and Irving A. Illing, Engineering Assistants.

REFERENCES

1. Special Technical Report No. 2. See Appendix A.

2-11. Quarterly Progress Reports Nos. 1-10. See Appendix B.

12. Special Technical Report No. 4. See Appendix A.

13. Baldwin, J. E. and C. E. Wooldridge, Project RID (U), Final Report, Contract No. Noo123-67-C-0553, Stanford Research Institute, July 14, 1967.

14. Special Technical Report No. 16. See Appendix A.

VII

CONDENSATION PROCESSES

R. C. Robbins, Senior Physical Chemist

Pyrotechnic dissemination of liquid or solid agent is accomplished
by mixing the agent with the pyrotechnic material. The phase changes
in the process include volatilization followed by condensation of the
agent. The manner in which condensation occurs establishes the particle
size distribution of the disseminated material. The condensation pro-
cesses in pyrotechnic dissemination are complicated by the many kinds of
foreign nuclei that are present. Self-nucleation (homogeneous nucleation)
always occurs at some critical supersaturation of a condensable vapor,
but foreign nuclei will inevitably initiate condensation at lower super-
saturation values. The conditions of agent aerosol formation in pyro-
technic dissemination are highly specific, and a general model of vapor
condensation under these conditions would be meaningless. Condensation
involves nucleation, growth, and coagulation (agglomeration). The size
distribution of the agent aerosol involves the simultaneous kinetics of
nucleation, growth, and agglomeration.

In rapidly quenched jets there is considerable experimental evidence
that, in the presence of foreign nuclei, homogeneous and heterogeneous
nucleation occur simultaneously. Therefore, in order to understand con-
densation in pyrotechnic dissemination, it is necessary to study both
heterogeneous and homogeneous nucleation processes. Experimental studies
of both types of nucleation have been made in this study. Heterogeneous
nucleation was studied by using analog and actual pyrotechnic systems to
disseminate CW agent simulants. This work showed that it is possible to
modify the size and the size distribution of the disseminated material
by the deliberate addition of nucleating material to the system. Carried
to the ultimate degree of development, it would be possible to control
the particle size of an agent cloud. Homogeneous nucleation of a number

of compounds was studied in an attempt to understand its importance in actual systems.

Pyrotechnic Dissemination Analog Systems

Simple comparisons were made among pyrotechnic compositions containing potassium chlorate oxidizer, added potassium chloride, and other salts and salt-free compositions. The effect of the salts was always to substantially decrease the median particle size[1,2] of the thermally disseminated material.

A continuous vaporizer system was also used to determine the effect of salt nuclei on particle size distribution.[3] Agglomeration masked some of the results, but generally the effect was like those noted in the pyrotechnic mixes.

Reference Pyrotechnic Devices

Small pyrotechnic devices were made in a standard manner to study the effect of various classes of nuclei on particle size of the disseminated agent simulant, with selected "giant nuclei" being of particular interest. All of these devices were made by blending a mix of 10 g total weight and pressing the blended mix into aluminum cans at a pressure of 2,000 psi.

When mixes containing potassium chlorate oxidizer were used, the nuclei produced by the oxidizer controlled the nucleation of the agent simulant.[4] In order to examine the effect of material added to the mix as giant nuclei, an all-organic monopropellant--a triamino guanidine derivative (TAGGY)--was used. Blends based on TAGGY were partially successful in allowing the added nucleating material to control the condensation process, but the residual micronucleating effect of carbon remained a problem. It was then shown that for systems containing mixtures of very small carbon nuclei and the added giant nuclei, a properly designed coagulation chamber can produce a large, nearly monodisperse aerosol.[5]

Homogeneous Nucleation Studies

During our analog pyrotechnic dissemination experiments, we observed what we interpreted to be homogeneous and heterogeneous nucleation occurring together in the jet of condensing agent simulant seeded with foreign nuclei; there were two forms and two sizes of condensed particles. Buckle and Pouring report[6] that in the condensation of water vapor in subsonic jets, the concentration of foreign nuclei is indeed a critical function of the nucleation mode, droplet size, and size range; they observed both homogeneous and heterogeneous nucleation occurring simultaneously at intermediate nuclei concentrations.

In order to understand the nucleation processes in condensing jet systems, the role of homogeneous nucleation had to be assessed. This was undertaken by measuring the critical supersaturation ratios of a number of compounds as a function of temperature.

A unique apparatus utilizing two colliding gas streams was developed to make measurements of critical supersaturation ratios. The critical conditions could be produced and measured in the collision volume.[7] Much wider ranges could be studied than were heretofore available. A schematic diagram of the apparatus is shown in Fig. 6.

Homogeneous nucleation studies were made on water, benzene, carbon tetrachloride, carbon disulfide, n-hexane, cyclohexane, and chloroform. The critical supersaturation measurements on these compounds provided the basic data for the calculation of nucleation rates, critical cluster size of the nuclei, and the quantitative effects of molecular structure of these parameters--all, of course, as a function of temperature. A calculated index value which appears to be significant in correlating chemical structure with homogeneous nucleation parameters is the departure from bulk surface tension extrapolated to a critical cluster size of zero. These calculations are covered in detail in a special technical report.[8]
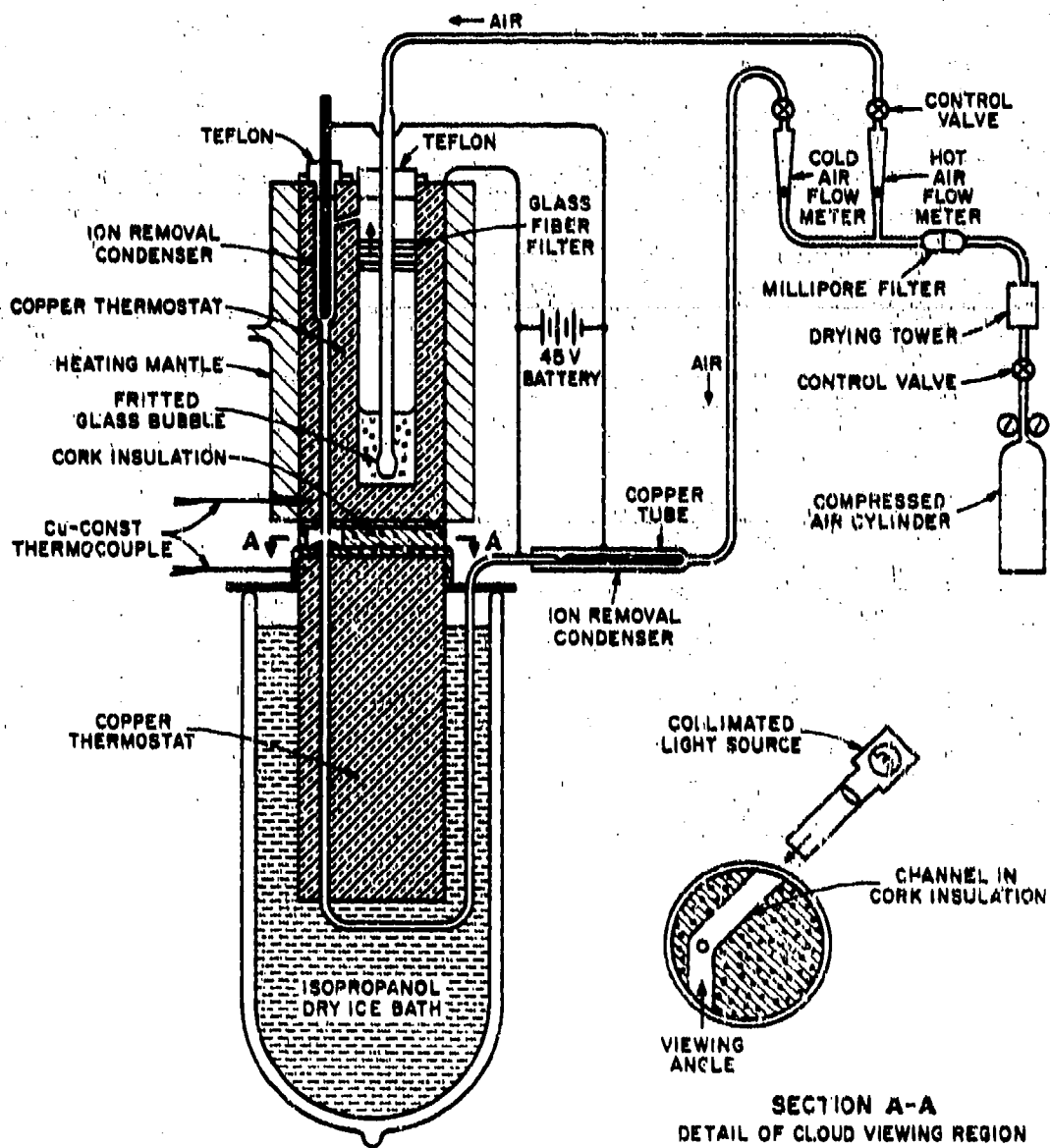
FIG. 6 APPARATUS FOR MEASURING HOMOGENEOUS CRITICAL
SUPERSATURATION RATIOS

While the homogeneous nucleation model developed during this study is of theoretical and practical importance in describing and understanding the condensation process, there is no mechanism at the present time for the utilization of this information in pyrotechnic dissemination involving simultaneous homogeneous and heterogeneous nucleation modes.

Recommendations for Future Research

A basic experimental investigation of the effects of composition, particle size, and concentration of foreign nuclei in condensation processes would aid in the general development of condensation theory and would also be of help in the direct application of the principles of heterogeneous nucleation to the design of pyrotechnic devices capable of disseminating homogeneous aerosols of extra-micron particle size.

CONTRIBUTORS

Mrs. Cecile Naar, physical chemist, contributed jointly with the author to these studies.

REFERENCES

1. Quarterly Progress Report No. 3. See Appendix D.

2. Quarterly Progress Report No. 5. See Appendix B.

3. Quarterly Progress Report No. 4. See Appendix B.

4. Quarterly Progress Report No. 6. Appendix B.

5. Quarterly Progress Report No. 9. See Appendix B.

6. Buckle, E. R. and A. A. Pouring, "Effects of Seeding on Condensation of Atmospheric Moisture in Nozzles," Contract No. Nonr 60947, February 1965.

7. Quarterly Progress Report No. 7. See Appendix B.

8. Special Technical Report No. 10. See Appendix A.

PYROLYTIC AND OXIDATIVE DEGRADATION PROCESSES

T. Mill, Chairman, Physical Organic Chemistry Department,
and G. R. Stevenson, Chemist

A long and successful history of dissemination of certain CW agents by means of pyrotechnic devices logically suggests extension of this technique to a variety of newer agents. A factor that might limit the wider use of pyrotechnic dissemination is thermal or oxidative degradation of the agent during the period of contact with the burning zone of the pyrotechnic. This phase of the program was concerned with a critical examination of earlier work in this area and with an experimental investigation of pyrolysis and oxidation of selected agents under conditions that would provide some fundamental information concerning these processes.

Previous Work

A critical literature review on oxidative and pyrolytic degradation of CW agents[1] summarized what other workers had reported from their studies of several agents at high temperatures with and without oxygen present. The results of the critical survey, already summarized in an unclassified abstract, are reported here for completeness.

The pyrolytic and oxidative rates of decomposition of GB,[2,3] appear to be inconsistent with the assumption that these reactions are homogeneous decompositions. More likely, both types of reactions are partially heterogeneous. Later work on the pyrolysis of GB and GD at moderate temperatures (200°C) indicates that these reactions are simple, unimolecular, ester elimination processes.[1] However, values for activation energy, Arrhenius A-factor, and the low-pressure limit all suggest that the reactions observed are in fact heterogeneous or complicated in some unsuspected way.

Observations by Sass and co-workers[4] concerning the degradation of BZ and other EA-series agents at 400-500°C are interpreted to mean that the reactions observed are ionic liquid-phase reactions catalyzed by

basic impurities. Some early experiments on the high-temperature oxidative pyrolysis of V-agent are of little value in understanding the primary kinetic processes responsible for decomposition of the agent.

Studies by the British and ourselves on the pyrolysis and oxidation of CS in the gas phase at 400 to 550°C are reported.[1] The results indicate that CS is very stable thermally and is so slowly oxidized that, even at 600 to 700°C, no significant loss should occur in dissemination devices.

A discussion of the factors important in degradation of agents during dissemination emphasizes the need for more accurate time and temperature data with respect to pyrotechnic processes.

Two kinds of experiments were carried out in this phase of the program. In the first, pyrolysis and oxidation of CS and a model compound for BZ were examined in static and flow reactors to learn something about the fundamental steps in the degradation of these materials. The second study was concerned with the use of thermally unstable azo-compounds and esters as molecular thermocouples for obtaining average kinetic temperatures within a burning pyrotechnic. Results of these experiments are considered separately.

Pyrolysis and Oxidation

A series of runs with $\sim 10^{-3}$ molar CS vapor alone on an admixture with one atmosphere of oxygen $(8-10^{-3}$ molar) was carried out in sealed Pyrex tubes at 410-500°C.[5] The disappearance of CS with time was evaluated as a function of temperature, surface coating, and the presence or absence of oxygen. The rate of pyrolysis of CS varies from 4.10^{-6} mole/liter/min at 410°C to 2.10^{-4} mole/liter/min at 500°C. At 410°C the reaction was sensitive to the history of the reactor wall, accelerating with time or with the presence of an initial coating of tar present from an earlier run. At 500°C the reaction displayed a reasonably good first-order rate despite heavy wall deposits. Only 10% to 15% of the unidentified pyrolysis products were volatile in the gas chromatograph; the major portion of material was converted to tar.

Not surprisingly, destruction of CS by oxygen was almost 100 times faster than pyrolysis. Initial oxidation of CS at 450°C gave mostly a dark residue which on further oxidation became white but yielded only small amount of O-chlorobenzoic acid, the expected oxidation product.

Kinetic parameters for the pyrolysis reaction were evaluated and found to give an A-factor of 102.2 and activation energy of 19 kcal/mole, much too low for a supposedly homogeneous unimolecular reaction; this indicated clearly that the destruction of CS in our system was at least in part a heterogeneous, wall-catalyzed reaction.

Despite the complexity of both kinds of reaction observed with CS, it is possible to develop some useful conclusions about the value of pyrotechnic devices for its dissemination. First, extrapolation of the data obtained in these experiments to temperatures thought to prevail in the burning pyrotechnic (800-1,000°C) indicates that CS will decompose only to a minor extent at short contact times, up to 10 to 20 sec. Second, the presence of very hot (possibly oxidizing) surfaces may contribute significantly to whatever decomposition is observed, and may perhaps catalyze the decomposition at a much higher rate than would be expected on the basis of these data. Exclusion of oxygen is obviously desirable.

In one sense, these conclusions are trivial because CS pyrotechnics are in fact quite efficient. However, the difficulty of extrapolating from one time-temperature regime to another is well illustrated by this example and is the principal reason why we sought to develop a flow system capable of providing very short contact times (on the order of seconds) useful in the temperature range from 600 to 800°C.

To this end, we constructed a stirred-flow reactor, first of Monel, then of Pyrex and quartz, designed to operate near one atmosphere total pressure.[6] Test experiments with ethyl acetate were carried out from 360 to 530°C with contact times as short as 4 sec. Arrhenius parameters for the unimolecular cleavage of ethyl acetate to ethylene and acetic acid

$$CH_3CO_2Et \rightarrow CH_3COOH + CH_2 = CH_2$$

87

compared favorably with those obtained by other workers using other techniques. At temperatures above 650°C and with contact times less than 0.1 sec, heat transfer became a severe problem. Redesign of the reactor to overcome this difficulty was considered but was not undertaken.

Ethyl acetate was chosen to provide a simple model compound for the ester elimination reaction that might be expected to occur in the gas phase with the more complex molecule BZ. Unfortunately, we had no opportunity to examine the pyrolysis of BZ in this reactor, since we were not able to secure the BZ before this part of the project was terminated.

If our assumption that BZ does undergo an ester elimination is correct, in all probability the reaction would proceed at a high rate under the conditions of pyrotechnic dissemination. A similar conclusion would apply to pyrolysis of other EA-series agents.

Molecular Thermocouples

Proper application of kinetic data for reaction of CW agents requires fairly accurate knowledge of both time and temperature characteristics of burning pyrotechnics. Volatilized agent will be exposed to a range of temperatures for varying periods of time; thus extrapolation of rate data to a new "average" pyrotechnic temperature as measured by thermocouples or similar devices would lead to significant errors in estimating yields.

We proposed to use the decomposition of a simple compound as a kind of molecular thermocouple for sensing the average kinetic temperature in a burning zone. In principle any unimolecular reaction with well defined kinetic parameters could be used provided that either products, reactants, or both could be analyzed. Reactions of interest are those that give 20% to 80% decomposition in the temperature range of interest. Possible examples are thermal decomposition of azoalkanes and esters. The former class of compounds gives nitrogen and alkyl radicals on decomposition.

To establish the feasibility of using such compounds as molecular thermocouples we examined the decomposition of two simple, substituted azoalkanes at 60, 81, and 100°C temperatures.[5] Both materials, solid at these temperatures, exhibited very slow initial rates of decomposition

88

(about one-thousandth as fast as in solution), followed by an acceleration in rate, typical for decomposition of solids. Observed rates bore little resemblance to those predicted from solution kinetic measurements.

A similar decomposition study of the Diels-Alder adduct of CS and cyclopentadiene indicated that at 400°C the half-life for decomposition was approximately 11 msec, much too fast to be useful in pyrotechnic systems.[8] Two experiments with ethyl p-hydroxybenzoate at 360°C and 510°C gave extensive decomposition of the ester to phenolic products, probably from subsequent decarboxylation of the first-formed benzoic acid.[7] Thus the ester cleavage is complicated at high temperature, making any estimates of average kinetic temperature unreliable.

Recommendations for Future Research

Pyrolysis of EA-series agents should be examined with some care to establish the actual mechanism of decomposition. The demonstrated sensitivity of this class of compounds to base-catalyzed cleavage[4] clearly indicates the need for careful purification prior to any kind of decomposition studies.

Recent improvements in the design and operation of very high temperature reactors (800-1,100°C) suggest their application to the measurement of kinetic parameters for pyrolysis of BZ-like structures.

Additional study of the temperature-time characteristics of burning pyrotechnics seems essential to defining the problem of agent degradation under these conditions. One approach worth considering is the use of the burning pyrotechnic as a flow reactor through which is diffused a volatile, moderately stable compound such as di-t-butylperoxide or t-butyldifluoramine $(t\text{-}BuNF_2)$. These compounds are relatively insensitive to base- or acid-catalyzed reactions but cleave to radical fragments with well known kinetic parameters. This approach, coupled with other kinds of temperature-time measurements, should provide a much firmer basis for prediction of the behavior of other new, possibly labile, molecules under the same conditions.

REFERENCES

1. Special Technical Report No. 2. See Appendix A.

2. Melpar, Inc., "Chemical Agent Warning and Detection Studies (U)," Third Quarterly Progress Report, Contract No. AD 18-035-AMC-104(A), Vol. 1, 1964.

3. Shell Development Company, "Potential CW Agents," Task 9, Vol. IV, May, 1954.

4. Sass, S. and P. M. Davis, CRDL Report 3232 (Draft), Edgewood Arsenal, June 1964.

5. Second Quarterly Progress Report. See Appendix B.

6. Fourth Quarterly Progress Report. See Appendix B.

7. Fifth Quarterly Progress Report. See Appendix B.

8. Sixth Quarterly Progress Report. See Appendix B.

IX

ATOMIZATION PROCESSES

C. E. Lapple, Senior Scientist

The subdivision of a bulk liquid is commonly termed atomization. Atomization may also be used to subdivide solids if they can be melted (as is the case with metals). Subdivision of a liquid or a solid may be desired for a number of reasons: (1) to permit distribution of materials throughout an area or space; (2) to expose a large surface for mass or heat transfer; (3) to provide desired flow, packing, optical, insulation, deposition, or other properties.

Because atomization is one of the processes involved in dissemination of liquid agents of solutions or suspensions of solid agents, a critical review and evaluation of the literature pertaining to this field was undertaken. The first phase of this study was an exhaustive survey of the literature.

Although the literature survey revealed many reviews of the field of atomization, none was considered adequately comprehensive, nor were the results of various investigations presented on a particularly comparable or usable basis. The second phase of this study was therefore concerned with a detailed and critical analysis of the results of those investigators whose work appeared to be most important. This analysis had the objective of summarizing available knowledge in the field of atomization in a self-consistent form, to permit a direct comparison of the results of various investigations and to aid in the design of atomization equipment. The detailed analysis was limited to certain mechanical atomization techniques (hydraulic or pressure, pneumatic or two-fluid, and rotary or spinning disk). Some techniques (vibrational, explosive, and electrostatic) were reviewed during other phases of the program, while others (gravitational and film bursting), although of importance in nature, appear to have capacities that are too limited to be of interest in dissemination.

To completely identify the performance of an atomization device it is necessary to specify the following items as functions of the operating conditions: (1) average size and uniformity (size distribution) of droplets produced; (2) power consumption; (3) liquid spraying capacity; and (4) operational considerations such as erosion or clogging. This study has been concerned primarily with the first of these, although the second and third items must be taken into account, if only indirectly. Certain general conclusions can be drawn concerning the relative merits of the various atomizing techniques from the standpoint of energy or power consumption. Capacity and operational considerations, however, are too intimately related to specific applications to permit generalized comparisons.

The work discussed here covered only the intrinsic mechanical capabilities of techniques for producing fine drops. Any further reduction in drop size that can occur as the result of evaporation was beyond the scope of present considerations, since it involves other properties specific to each liquid.

Results

The results of this study are all contained in a special technical report.[1] The literature survey yielded 955 pertinent references which were summarized together with abstracts where available.

A detailed evaluation of the most important investigations in the literature (covering hydraulic, pneumatic, and rotary atomizers) was made. The investigation was presented in the form of correlations relating mean particle size generated by the atomizing device to fluid properties and operating conditions, all correlations being manipulated into a comparable format. A comparison was also made of the drop size which each correlation would predict for an arbitrarily chosen set of standard fluid property and operating conditions.

For the standard properties and conditions, the sizes predicted by the various relationships for similar atomizers cover a twofold and threefold range for the most part, with an extreme range of over tenfold in some cases. There are also very marked disagreements in the magnitude of the role played by each variable, with some investigators reporting

inverted roles (i.e., particle size decreases with an increase in the variable in one case and increases in the other case) for similar atomizers. The best argument is shown by the data for hydraulic swirl nozzles, for which the most extensive data are available. Good agreement exists for data on rotary or spinning disks, but these data are relatively limited in extent. The greatest discrepancies are present in the data for simple hydraulic nozzles.

Some of the discrepancy can be attributed to the following factors: (1) many investigations covered only a narrow range of a variable, and hence had limited precision in assessing variations due to that variable; (2) some investigators did not actually investigate a variable but introduced it in the correlation for either rational or arbitrary reasons. The large discrepancies found with simple hydraulic nozzles suggest that turbulence, which is never reported or controlled directly, may be an important factor. It is believed, however, that a large part of the discrepancy is probably due to shortcomings in the drop-size analysis techniques, including sampling.

Recommendations for Future Research

Although resolution is needed in most areas, data are particularly scarce on the following matters: (1) effect of gas density on atomization, especially pneumatic atomization; (2) effect of turbulence on atomization; (3) effect of compressibility in pneumatic atomization; (4) effect of ultrahigh pressure in hydraulic atomization; and (5) effect of high loadings (i.e., representative of production capacities) on performance of rotary atomizers.

Surface tension is an important variable, but its effect on atomization is not sufficiently resolved. This is partially due to the small range (threefold) of variability in surface tension available with ordinary liquids. Although much larger surface tensions can be obtained by the use of molten salts and metals, very few investigators have employed them.

Despite the spread in available data, an attempt at correlating the available basic experimental data on a unified basis (as distinguished from comparing correlations of data presented by various authors) appears to be in order. This would present the data in their most usable form and should reveal more directly whether the discrepancies in the data are due primarily to the measurement techniques employed.

CONTRIBUTORS

Contributors to the survey include D. E. Blake, Chemical Engineer, J. P. Henry, Jr., Chemical Engineer, and R. G. Murray, Chemical Engineer.

REFERENCES

1. Special Technical Report No. 6. See Appendix A.

X

ULTRASONIC AEROSOL PRODUCTION PROCESSES

C. W. Smith, Physicist

Sonic dissemination of agents has a number of unique attributes. The dissemination process is clandestine and harmless, and chemically delicate agents are not degraded by the process.

An investigation of the generation of aerosols by ultrasonic techniques was begun, but a reduction in funding forced a severe cutback in the effort and the work could not be completed. Both experimental and theoretical studies were undertaken in an attempt to (1) obtain a clearer understanding of the basic mechanism of sonic aerosol formation, and (2) fabricate prototype disseminators capable of high flow rates.

Theoretical and Experimental Studies

An extensive literature search of material associated with the problem of sonically generated aerosols was completed, and a comprehensive historical review of work in this field was written.[1] Although the main interest concerned a usable device--its feasibility and its associated problems--it was also recognized that adequate theoretical treatment of ultrasonically produced aerosols was far from complete.

Two novel ultrasonic disseminators were designed and fabricated.[2] These light-weight devices were capable of handling a high flow rate of liquid. The more successful of the two was a circular wedge type of atomizer,[3] weighing about one pound, occupying about 8 cubic inches, and capable of disseminating up to 22 gallons per hour of a water-like liquid. Since adequate design parameters for this device were lacking, theoretical work was undertaken to attempt to understand the motion of this circular wedge device.[3] The location of normal modes of vibration was sought but mathematical difficulties hindered a complete solution. A simplifying approximation yielded some partially useful results.

Because of the lack of a satisfactory theoretical treatment, we attempted to determine experimentally the relation between physical parameters of the liquid and the size and velocity of the aerosol droplets produced by sonic techniques. Information of this type would be useful in assaying the ability of a disseminator to handle agents of varying physical properties. A photooptical technique was developed[3] in which a thin stream of aerosol was photographed at right angles to the motion of the droplets. A multiple photoflash technique permitted determination of droplet velocity. Preliminary data were gathered[3] on the aerosol droplet size versus the parameters of surface tension, viscosity, and flow rate. Also, droplet velocities were measured at varying distances from the disseminator.

Theoretical work was pursued to determine the capillary wave forms in a liquid layer flowing over an oscillating reed.[3] This model was chosen because of its relevance to the high-flow sonic aerosol production devices. The free-liquid surface was found to grow through resonant instability. Pressure extremes occurred at the free surface and it was found that a cavitation mechanism for aerosol formation would occur near the free surface. Some correlation between aerosol droplet size and capillary wavelength was obtained.

Independent of this theoretical analysis, experiments were performed to investigate basic mechanisms in the formation of sonically generated aerosols.[3] The transition from capillary waves on a thin liquid layer to the emission of an aerosol from this layer was examined extensively, and a possible explanation for this transition has been suggested. It has been shown that cavitation plays a role in the production of an aerosol, and that the relative balance between the cavitation and the capillary wave mechanisms is quite likely governed by the viscosity of the liquid.

The photooptical technique can provide basic information on aerosol droplet size and velocity as functions of the physical parameters of the liquid. An extensive knowledge of this type of information would allow one to examine the physical properties of an agent and be able to make rough predictions of a disseminator's ability to handle an agent.

The successful use of the phenomenon is greatly enhanced by sound, viable theoretical understanding of the basic processes involved. A major step has been taken toward developing a basic theory which now needs experimental confirmation. The theory must also be tied to the experimental observations on the transition of the capillary waves on the liquid surface to the actual emission of the aerosol from the surface.

Because of its unique attributes, we feel that a sonic aerosol disseminator has useful potential. Several prototype devices have been constructed. It has been learned that successful development of the necessary design parameters for these vibrationally complex devices is greatly aided by a theoretical understanding of their vibratory patterns. The reported work, although necessarily incomplete, has shown that devices of this type are practical and should be developed.

CONTRIBUTORS

Contributions to this study were made by J. C. Martner, Physicist, D. R. Grine, Chairman, Sonics Department, V. Salmon, Senior Research Scientist, C. M. Ablow, Staff Mathematician, G. V. Hanagud, Research Mathematician, E. M. Spurlock, Physicist, and J. S. Arnold, Physicist.

REFERENCES

1. Special Technical Report No. 2. See Appendix A.

2. Quarterly Progress Reports Nos. 2, 4, 5, and 6. See Appendix B.

3. Special Technical Report No. 9. See Appendix A.

XI

PNEUMATIC DISSEMINATION OF DRY POWDERS[*]

P. L. Magill and D. Pon
Metronics Associates, Inc.

The object of this study was to obtain basic data on the dissemination of bulk powder into airborne primary particles ranging from 1 to 10 microns in diameter. The initial effort was a critical review of the literature.[1] The review showed that particles in this range adhere firmly to their neighbors in the bulk powder. The adhesion may be the result of any one or a combination of forces resulting from (1) electrostatic attraction, (2) adsorbed liquid films, or (3) van der Waal's forces. The smaller the particles are, the greater is the difficulty of producing an aerosol of individual particles.

Methods for making an aerosol from dry powder were examined. The methods fall into one of the following four categories, in which: (1) powder is fed into the intake of a rotary air blower; (2) powder is caused to flow through Venturi throats or capillary tubes; (3) loose or compressed powder is exposed to a sudden burst of gas with or without impaction on a solid surface; and (4) loose or compressed powder is eroded from a powder bed surface by high velocity air jets.

In terms of the surface energy of the particles, the power efficiencies of aerosol devices used were very low, perhaps as low as 0.001%. However, this value has little meaning because most of the energy is used for diluting and transporting the aerosol. At some stage between the time that the particles exist as a bulk powder and the time that they are sufficiently dilute to prevent agglomeration, energy must be used for mixing

---

air. The only concern for energy is that it be large enough and effectively coupled with the powder mass to produce forces that break bonds between individual particles.

Several methods of assessment of aerosols were reviewed. Complete assessment is a formidable task and several presentations of the practical and theoretical problems are given in the literature. No single method appeared to offer a complete solution to the problem.

Considerable effort was devoted to review of bulk powder modifications. Changes in properties such as tensile strength, shear strength, angle of repose and flowability were measured in attempts to correlate these measurements with improvement in aerosolizability. The assessment methods used gave data on the comparative efficacy of several modifications. Except for a few instances, no dramatic improvement in aerosolization occurred as a result of powder modification.

It was apparent from the literature review that the following aspects of powder dissemination should be included in this research program:

1. A wide range of powder types should be employed to obtain data on the effects of chemical composition, particle size, size distribution, and various powder treatments.

2. Additional investigations should be made of the effectiveness of powder treatment with additives to improve the ability to get individual particles suspended. This had not been clearly demonstrated in previous work and new observations were needed.

3. A simple and workable assessment procedure should be developed.

4. A simplified dissemination system amenable to mathematical analysis and capable of operation over a wide range of energy should be employed.

5. New observations should be made of the subsidiary phenomena and difficulties that are encountered during powder dissemination, including electrostatic effects.

6. The scientific principles controlling the production of individual particles should be identified.

Accomplishments

Details of this study are given in a special technical report.[2]
Powders differ markedly in their behavior in bulk and in the ease with
which the individual particles can be converted to an aerosol. A general
study of powder dissemination must therefore examine many kinds of pow-
ders. In this program, 17 powders and 16 additives were used in various
combinations. The powders had a wide range of properties and the addi-
tives were used to modify the bulk properties and to improve the dissemi-
nation of the powder particles.

Flowability, viscosity in aerated state, adhesion, and the angle of
repose were measured to characterize the behavior of the powder and
powder-additive combinations. The adhesion measurements revealed only
general trends, but the other three methods gave data that, in general,
correlated with ease of dissemination. For powders susceptible to improve-
ment by use of an additive, 0.5-1.0% hydrophobic Philadelphia Quartz
(PQ 2340) gave the best results in terms of flowability, angle of repose,
and reduction of viscosity of fluidized powder. Additives in excess of
1.0% were less effective. The effects of additives are highly specific
to the powder and additive combination. For example, glass beads, zinc-
cadmium-sulfide, and saccharin were benefited by use of an additive, while
quartz and aluminum powders were only slightly improved. The viscosity
of a fluidized powder is believed to most nearly reflect the properties
of a powder associated with its ease of dissemination.

Aerodynamic dissemination methods were employed which permitted con-
trol of breakup forces over a wide range of values. These included
(a) subjecting a small pile of powder to a gentle "puff" of air for low
energy application; (b) aspirating an air/powder mixture through straight
tubes over a range of velocities for soft impact at the tube wall; (c) as-
pirating an air/powder mixture through a curved tube at up to sonic velocity
for hard impact.

Some of the larger particles (12-18 μ) were almost completely dis-
seminated at the lowest energies used. The smaller the particle size,
the greater was the difficulty of obtaining complete dissemination. The

101

most complete dissemination of the smaller (1-10 μ) particles was obtained by aspirating powder with air at sonic velocity in a coiled tube to insure "hard" impact on solid wall surface. Other results were:

1. The effect of additives was dramatic for some powders not only in improving flow properties but also in improving dissemination, although the measured adhesive forces between particles were reduced only one-half to one-third by the use of an additive.

2. Irregularly shaped particles disseminated more completely than smooth, spherical particles of the same size.

3. Small ratios of powder/air in the aspirating system resulted in less reagglomeration following dissemination.

4. Reagglomerated aerosols can result in agglomerates having a greater mass than a single particle of the same material and yet having the same aerodynamic properties. The implication of this result is that control--not elimination-- of agglomeration may be the most desirable approach to dissemination of powders into an aerosol with suitable aerodynamic properties.

5. Theoretical considerations show that impact of agglomerates against solid surfaces is a necessary feature for successful pneumatic dissemination of particles in the 1-10 μ size range.

6. The reagglomeration observed could not be explained on the basis of collision and adhesion resulting from turbulent mixing, but was most likely caused by electrostatic attraction between particles.

7. Electrostatic effects were observed frequently during the dissemination tests. They affected dissemination, caused reagglomeration, and complicated assessment procedures. Additives were used to alter the charges generated on powder particles during dissemination. Injection of gas ions with the disseminating gas also altered electric charges on particles, and with further development may provide a technique for more efficient dissemination.

A laminar flow settling system was developed for assessing aerosols. This was used in conjunction with microscopic observation and photographic recording of settled particles. Microscopic observation alone did not permit distinction between agglomerates and single particles of irregular shapes. Particles settled from air can land sufficiently close to each other to make it uncertain whether they existed in the air as an agglomerate or as single particles. A method of correcting for this coincidental

settling is presented. The use of multiple techniques permitted the acquisition of data not obtainable by any single assessment method.

Recommendations for Future Research

There is no aspect of the study of powder dissemination followed in our program that could not profitably be extended, with benefits resulting from new knowledge. Some judgment must be employed to limit the number of recommended items for future work. Any such list will include some individual preferences, and ours are given below. One recommendation is for a fundamental study of triboelectrification and the other pertains to applying what we now know to the design of a scaled-up model of a pneumatic powder disseminator.

1. Triboelectrification of Powder Particles

The scientific principles that control electrical charging of powder particles when they separate from each other or from solid surfaces (contact charging or triboelectrification) have not been developed. Of the phenomena that affect dissemination and reagglomeration of powder particles, the electric charging of particles is probably the least understood.

When the scientific principles of triboelectric charging of powder particles are understood, it should be possible to minimize their detrimental effects and perhaps utilize them to advantage. A fundamental study of triboelectrification is therefore recommended.

2. Development of a Pneumatic Powder Disseminator

We have shown that successful pneumatic dissemination of a powder can be best accomplished by shattering agglomerates by wall or target impact. Reagglomeration can be minimized, even with some electrostatic charging, by dilution with primary air.

The work conducted in our program was designed to define the principles of dissemination without regard to constructing an integrated dissemination device. The scale of dissemination was deliberately small, to accommodate laboratory facilities. There are design problems associated with the development of larger scale devices. These include

103

powder-feeding mechanisms, configuration of flow channels and/or anvils to obtain powder impact, minimizing power requirements, and confining the system to a reasonable size envelope.

The design, construction, and evaluation of an integrated device using what we now know for disseminating 10 to 50 grams of powder per minute should provide useful data for still larger devices. The success-f ʼʼ construction of a powder disseminator will make available useful devices for large-scale laboratory and small-scale field tests in which active chemical agents can be evaluated.

REFERENCES

1. Special Technical Report No. 2.   See Appendix A.

2. Special Technical Report No. 19.   See Appendix A.

NATURAL GENERATION OF AEROSOLS

E. Robinson, Chairman, Environmental Research
and Engineering Department

It has sometimes been speculated that the aerosol dissemination processes incorporated in a variety of natural systems are unique and more efficient than are the dissemination systems conceived by man. Such speculation is often based on (1) the large volumes of the atmosphere which can be affected by some natural dissemination processes, (2) the large distances some natural aerosols are known to travel, (3) the often severe infectious or allergic response to natural aerosols, and (4) the small amount of energy that some natural systems seem to have available for aerosol dissemination.

The purpose of this study was to examine various natural dissemination processes to see whether there were any unique or previously unrecognized features which could be applied to agent dissemination processes. In this context, a "natural" dissemination process is one in which the mechanics and forces necessary for dissemination are available in the natural environment. Three major aspects of natural dissemination were analyzed: wind dissemination of dust clouds, formation of marine aerosols, and spore and pollen dissemination processes.

Dust or sand clouds in the atmosphere can result from the movement of wind across a particular area, but the nature of the cloud--and even whether or not one is actually formed--depends on interrelationships among the wind, the sand and dust particles, and the ground surfaces.

One feature of some natural dust o sand clouds which has attracted attention is their tendency, sometimes, to be physically limited to the lower few feet of air above the ground surface. If such a dispersion limitation could be made part of an agent dissemination system, it would obviously be advantageous; thus, this limited cloud depth characteristic was investigated in some detail.

A number of research studies have analyzed the mechanisms by which a very shallow surface cloud may be formed. There is general agreement that this results from the bouncing (saltation) movement of relatively large wind-driven sand grains (800-1000 μ diameter) across a generally uniform, nonvegetated, well-weathered surface. There is no indication that forces on the sand grains other than the wind and gravity are important. The depth of the cloud is determined by the height to which the sand grains rise as they bounce along with the wind. This limited depth of the cloud will be visible only when it is not obscured by fine dust, and over a well-weathered surface a dust cloud will not be produced.

Formation of fine dust clouds (particle diameter less than 50 μ) from an undisturbed surface generally requires the saltation movement of larger particles of rock or sand to dislodge the fine particles from the surface. Wind forces alone are not sufficient because of the shielding offered by stagnant air right at the ground surface. The characteristics governing the wind movement of fine dust particles would also apply to the reentrainment of chemical agent aerosol particles. Thus, in undisturbed areas where saltation movements are restricted, the reentrainment of agent aerosols would not be expected.

Marine aerosols are primarily made up of sea salt left airborne after the evaporation of sea water droplets. For aerosol-sized particles the droplets originate primarily in the bursting of air bubbles on the sea surface rather than in the entrainment of large spray drops from wave crests. In a bursting bubble there are two sources of droplets. The fragments of the bursting bubble film can form a relatively large number of evaporated salt particles in the 0.1 μ-diameter size range. A bursting bubble also produces a few large drops from the central cavity jet. The size of the jet drops is dependent on bubble size. Experiments have shown that sea salt particles in the range from 2 to 25 μ will result from the evaporation of the jet drops.

If there is a layer of organic material on the sea surface, the bursting of clusters of bubbles will cause the organic material to be incorporated in the resultant aerosol. Similarly, material such as

plankton suspended in the water may also become part of the aerosol. However, there does not seem to be any readily apparent application of marine aerosol production mechanisms to agent dissemination, nor any unique mechanisms to agent dissemination, nor any unique mechanism involved in the process.

Most observers of natural spore dissemination processes are impressed with the fact that a very effective particle dissemination is carried out with a relatively small amount of available energy. An analysis of spore dissemination was made to determine whether chemical agent systems could incorporate any unique properties of the spore discharge mechanism, the characteristics of individual particles, and the atmospheric transport mechanisms.

None of the spore discharge mechanisms seems to be directly applicable to chemical agent systems because most of them deal with release mechanisms tailored to individual particles in a complex biological system. However, in some of the dry spore systems (such as in puff balls), the spores are held in a matrix of capillitium threads which prevents compaction and permits some air circulation through the mass. Because of this matrix, a small air circulation is able to carry relatively large numbers of spores out of the puff ball and into the open atmosphere. Minor amounts of energy--the impaction of a single rain drop, for example--are sufficient to disseminate numerous spores from a mature puff ball. Other spore discharge mechanisms are described in a special technical report,[1] and these might suggest further interesting approaches to aerosol dissemination problems, especially in the area of encapsulation tricks whereby a number of small particles might be released from a single larger capsule.

Studies were made of some of the characteristics of lycopodium spores to determine whether there was some feature which made them especially easy to disperse. It was determined that these particles, although they are generally known for their good flow characteristics, did not act significantly better than similar manmade particles with good flow characteristics. Agglomeration is a factor to be considered with the lycopodium, as it is with all aerosol particles.

107

Part of the dissemination process for spores and pollen is windborne travel through the atmosphere until they are deposited on some sort of surface. Atmospheric propagation of pathogens has been analyzed to try to determine whether there are any unique aspects of the particles which contribute to this process and which could be adapted to the dissemination of chemical agents. Some spores which have been studied have been found to be capable of causing infection at relatively large distances (100 to 200 miles) from the source area. The cereal rusts, i.e., black rust (Puccinia graminis) or crown rust (Puccinia coronata), white pine blister rust (Cronartium ribicola), and the smuts, i.e., corn smut (Ustilago zeae), have provided excellent examples of infection propagation by airborne pathogens.

However, on the basis of an analysis of observed settling characteristics and diffusion patterns it is concluded that spores and pollens behave in a fashion similar to other aerosols and that the observed long travel distances are apparently not due to any unique aerodynamic properties of the aerosol. The ability of spores to transmit infection across long distances can doubtless be attributed to the extremely large number of spores (as many as 10^{12} or 10^{13}) which can be liberated by what might be assumed to be a minor infectious source.

Further details of this analysis of natural dissemination processes are given in Reference 1. In brief, this analysis shows that the reason these processes seem especially efficient or effective is that the sources involved in these natural systems are very large compared to typical chemical agent sources. It is relatively easy to overlook or seriously underestimate the magnitude of these natural sources and to ascribe the apparent dissemination effectiveness to some unrecognized property of the system. A careful review of these dissemination processes showed that the various mechanisms were quite well explained in the physical and biological science literature, although very little attempt had been made to generalize from the description of the systems.

Although neither the dust nor marine aerosol systems seem to have any features which are applicable to chemical agent systems, it may be useful at some future date to try to adapt certain features of some spore dissemination processes to a microcapsule system, primarily in terms of packing and anti-agglomeration aspects.

CONTRIBUTORS

C. F. Schadt, Physical Chemist, assisted the author in these studies.

REFERENCES

1. Special Technical Report No. 2. See Appendix A.

XIII

ELECTROSTATIC PHENOMENA IN DISSEMINATION

C. E. Lapple, Senior Scientist

Electrostatic phenomena are important in dissemination because (1) they can affect the behavior or properties of the materials being disseminated, (2) they can have modifying influences on all dissemination processes, and (3) they may be utilized as a direct means for dissemination. In order to more clearly elucidate the roles that electrostatics could play in dissemination, an exhaustive literature survey was undertaken. The most important articles we.e then analyzed in detail and a critical review was prepared, aimed at either quantitatively establishing the specific roles of electrostatics in the dissemination process or establishing areas where further research is necessary to permit this to be done. Subsequent work was to be aimed at resolving these areas.

Fundamental to any investigations involving charged particles is a rapid and reliable means for measuring the electrostatic charge distribution in aerosols. While many such techniques have been developed, the more reliable ones have involved measurements on a particle count basis and are relatively laborious. For CW agent dissemination a charge distribution on a mass basis is more realistic, and, although a conversion from a count to a mass basis is theoretically possible, there are many practical limitations to such a conversion. Consequently, an investigation was undertaken to develop a device for measuring charge distribution. This device was to incorporate the best features of available devices, with any indicated modifications to extend the scope of the measurement without undue complexity, and to be readily adaptable as a tool for field assessment.

111

All the work conducted in this area has been completely described in specific special reports which supersede any information previously recorded in monthly or quarterly progress reports.

Results of Literature Survey

The results of the literature survey are completely summarized in a special technical report[1] in which 1,028 references are cited, mostly with abstracts. The review of the role of electrostatics in dissemination is given in another special technical report.[2] This review was based on a critical analysis and coordination of the information contained in the more important references found in the literature survey.

The following broad conclusions were reached as to the role of electrostatics in CW agent dissemination in general:

1. Unipolar charging of agents can result in marked improvement in the effectiveness of agent dissemination and ultimate deposition. There is an optimum charging level, however, corresponding to a specific particle surface gradient, ϵ_{ps}, of the order of 1 volt/micron. Much higher charging levels will result in undesirably fast cloud expansion rate. Charge levels corresponding to values of ϵ_{ps} less than 0.01 volt/micron will usually not exhibit any significant electrostatic effects.

2. Ambipolar charging of agents can have both desirable and undesirable effects. Deposition rates may be larger due to electrostatic image forces, but aerosol dispersibility may be reduced and flocculation rates may be increased. It is believed, however, that normally the magnitude of effects due to ambipolar charges will be of secondary interest because of compensating effects.

3. Precharging of agents to significant charge levels prior to dissemination is not technically feasible. Any charging must be done during or after dissemination.

4. Direct dissemination by electrostatic techniques (as distinguished from electrostatic modification of other techniques) would probably have the lowest energy requirements of any known technique. Details of such

techniques, however, remain to be developed, especially in the area of powder dissemination. These techniques also have the drawback of requiring comparatively elaborate auxiliary equipment.

5. Unipolar charging to desirable levels is technically possible by direct contact charging as well as by either field or diffusion charging in the presence of gas ions generated by a corona discharge. Interface alteration (as in frictional charging) is also capable of producing charges of the desired level; however, the mechanisms in such cases are often quite complex, and control as to both magnitude and sign of charge is uncertain. Charging by thermionic emission is of no great consequence unless temperatures exceed $2,000^\circ K$.

Development of Aerosol Charge Analyzer

A technique has been developed for measuring the electrical mobility distribution of an aerosol and the average effective size at each mobility level. Details of this development are given in a special technical report.[3] A view of the mobility channel and charge analyzer is shown in Fig. 7. With this technique, an aerosol is passed through a purifier and a narrow mobility channel (1.5-inch spacing between collection electrodes, 10 inches wide and 15 inches long). The purifier removes charged particles from all but a thin central stream that enters the mobility chamber halfway between the electrodes. Particles are deposited on an insulating surface according to their mobility. The total charge distribution on the walls is determined by a special scanning probe. The mass distribution is determined by chemical or colorometric analysis. Tests carried out to determine the mobility distribution of a uranine aerosol generated by atomizing and evaporating a dilute water solution yielded reasonably consistent results. Although no absolute basis of assessment was available, the results were consistent with expected magnitudes. Average particle diameter (volume-to-diameter mean) was 0.8 micron, and particle charge levels ranged from 0.05 to 1 volt/micron specific particle surface gradient. Remaining problem areas are listed and suggestions are given for improving the technique and extending its usefulness.
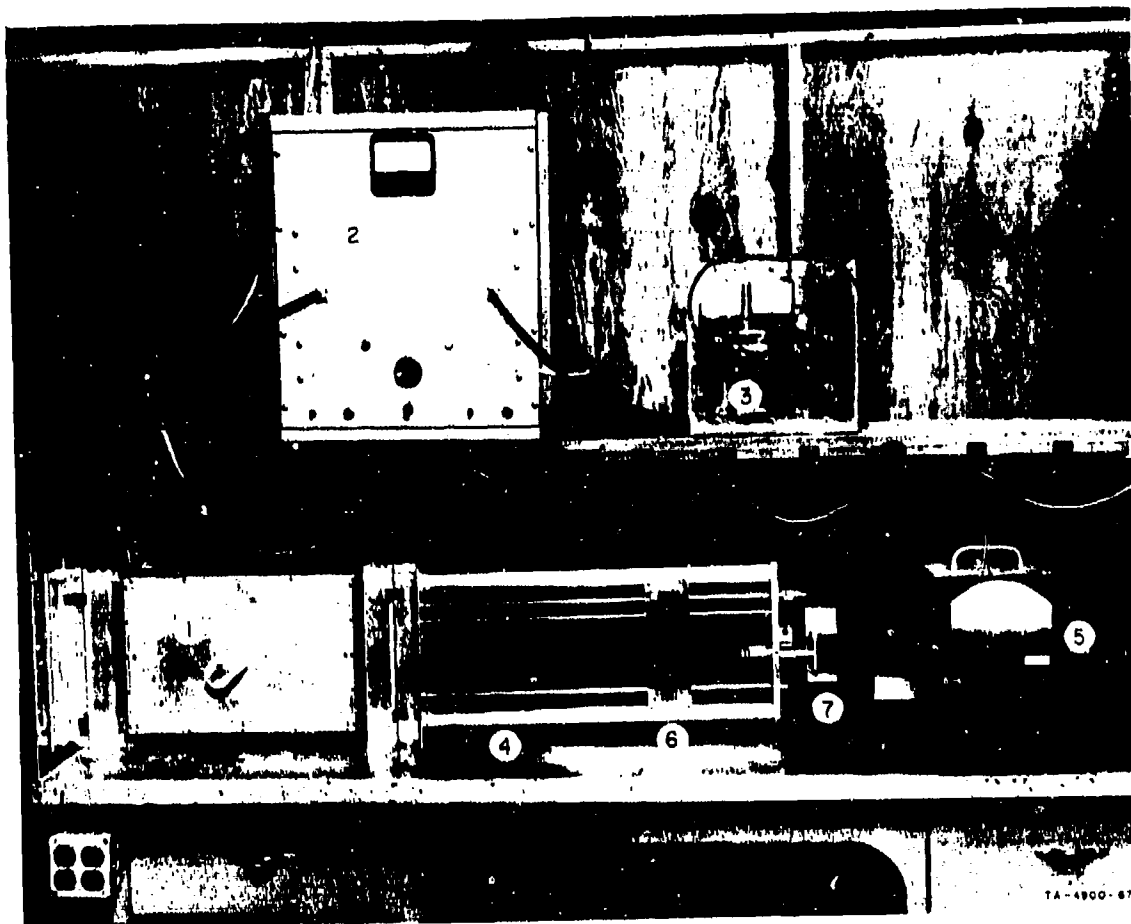
1.   MOBILITY CHANNEL (WITH FRONT ELECTRODE IN PLACE)

2.   HIGH VOLTAGE POWER SUPPLY

3.   HIGH VOLTAGE MICROAMMETERS

4.   CHARGE ANALYZER IN PROCESS OF BEING INSERTED IN MOBILITY CHANNEL

5.   ELECTROMETER

6.   SCANNING PROBE AND CARRIAGE

7.   CARRIAGE DRIVE MOTOR AND CONTROL

FIG. 7   CLOSE-UP VIEW OF MOBILITY CHANNEL AND CHARGE ANALYZER

Recommendations for Future Research

Although there are many areas in which further basic knowledge of electrostatic phenomena would be desirable, the following areas are considered to be those which will prove most fruitful for purposes of improving the effectiveness of CW agent dissemination.

1. **Controlled and predictable dissemination and charging of liquids and powders by electrostatic fields.** In the light of present knowledge, the best control is attained by exposing the liquid or powder to be disseminated to known electrostatic fields, with or without corona. Unipolar charge levels of the proper magnitude are attainable by this means. Many investigators have demonstrated the feasibility of these techniques for liquids. However, much of the effort in this area has been concerned with ion propulsion and has concentrated on attaining predetermined charge-to-mass ratios. It is still not possible to predict electrostatic field gradients, nozzle sizes, and currents required to achieve a specific dissemination capacity and particle size. The principles governing the dissemination of powders by this means are known to an even lesser extent. From the standpoint of application to agent dissemination, the primary objection to this technique is the need for the presence of appropriate high voltage generating equipment at the point of dissemination.

2. **Controlled and predictable dissemination and charging of powders and liquids by mechanical means.** Mechanical action (e.g., pneumatic conveying of powders) on particle interfaces can produce charges of the desired level on solids but the attainment of adequate levels on liquids by this means alone is questionable. While this method would permit the use of simple field equipment, the state of knowledge in this area is considerably more confused. Although unipolar charging is technically possible, there is considerable question as to the feasibility of achieving significant levels of unipolar charging without extensive, simultaneous ambipolar charging when dealing with collections of particles at feasible particle concentrations and dissemination capacities. Despite the fact that this area of electrostatics as applied to aerosols or powders has received much attention during the past 50 years, it still

115

remains one of the most confused areas of knowledge. The various anomalies that have been reported suggest that this mechanism is associated with a complex combination of phenomena that in turn may be sensitive to secondary influences or contaminants.

A potentially attractive concept would appear to be the blending, after separate mechanical dissemination, of CW agent and of a charge-control material. The charge-control material would be of very small particle size (1 micron or smaller) which can be charged to high levels (say ϵ_{ps} = 20 volt/micron) by mechanical or pneumatic means. Such a material would be separately disseminated at low rates compared to the agent dissemination rate (say 1 wt % of the agent rates). Upon subsequently blending the two aerosols (agent and charge-control material), the fine charge-control particles would coat the agent particles by flocculating with them and bring the average cloud charge level down to a predetermined optimum unipolar level of the order of ϵ_{ps} = 1 volt/micron. In such a case, the agent would preferably be treated to minimize charging during dissemination, and the same charge-control material could probably be used with any agent.

3. **Principles governing the maximum stable charge on fine particles.** Although the maximum stable charge is considerably above the levels considered optimum for dissemination, this may be an important factor in evaluating questions of particle adhesion during dispersion by other techniques. There are no known data in this area dealing with the particle size range below 10 microns. Previous discussions of this problem have been based on extrapolation of results from much larger geometries.

4. **Force of adhesion between particles.** This force is one of the controlling influences in the behavior, handling, and dissemination of powders, yet our knowledge in this area is quite meager. It is suggested that measurements of forces on charged particles may offer a promising approach for measuring forces of adhesion between fine particles or between fine particles and surfaces.

116

5.   Cloud expansion controls. The charge on particles constituting an aerosol cloud can be an important or controlling factor in determining the rate of cloud expansion as well as in augmenting the rate of deposition of the particles on a surface exposed to the cloud. Although there is little basis for questioning theoretical predictions, there is little in the way of a direct full-scale demonstration of potentials in these directions. To make such a demonstration requires the development of a practical concept for applying a significant unipolar charge to particles existing in a relatively concentrated form. This would essentially partake of elements discussed under items (1) and (2) above.

CONTRIBUTORS

D. E. Blake, Chemical Engineer, K. G. Dedrick, Research Physicist, A. P. Brady, Senior Physical Chemist, G. L. Pressman, Senior Research Engineer, R. L. Kiang, Research Engineer, P. M. Newgard, Senior Research Engineer, and B. A. Wolfe, Senior Technician-Model Maker, participated in these studies.

REFERENCES

1.   Special Technical Report No. 1.   See Appendix A.

2.   Special Technical Report No. 2.   See Appendix A.

3.   Special Technical Report No. 11.   See Appendix A.

XIV

MICROENCAPSULATION

A. G. Brown, Director
Chemistry and Chemical Engineering Laboratory

The technique of microencapsulation, as employed in this study, is the art of enclosing small particles of a solid, droplets of liquid, or bubbles of gas in a coherent shell or wall of natural or synthetic polymers formed in situ by a variety of processes. Of the many processes available, those selected for this study were the coacervation-based systems, developed largely by The National Cash Register Company (NCR), because of their demonstrated capability for very large scale-up (as for "NCR--No Carbon Required" multicopy business papers).

Prior to the present work, personnel at Edgewood and elsewhere had considered that microencapsulation might provide solutions to a variety of dissemination or CW systems problems, including protection of agent during storage of pyrotechnic compositions (CS had degraded in some mixes), protection of agent from light or other hostile environments before or after dissemination, ablative or other protection of agent from degradation during pyrotechnic dissemination, prepackaging of agent in predetermined desired size, reduction in handling hazards of CW agents generally, and the need for controlled or sustained action agents (particularly in the case of CS). Nonetheless, only incidental studies of encapsulated agents or simulants had been made.

The present study was initiated to provide a comprehensive and systematic exploration of the capabilities and limitations of microencapsulation for solution of these and other problems, to develop generic approaches to adaptation of encapsulation processes to new agents, and to provide quantitative data on the characteristics of capsular materials and the effects achievable in specific CW systems. In addition, as the work progressed, the desirability of extension of capsular technology to very

119

large and very small capsules became evident; such studies were undertaken to provide the desired materials and systems capabilities. Finally, the inherent value of encapsulation as a means to develop completely new or more versatile CW systems was recognized and the study of large-explosive-coated, self-disseminating capsules was undertaken as a generic concept of this kind. Complete details of these studies are provided in a special technical report.[1]

Major accomplishments of the project included significant extensions of encapsulation technology, successful evaluation of several applications of capsular materials in dissemination systems, and development of new CW systems concepts based on capsular agents.

More specifically, techniques were developed for extending capsular technology, for the first time, to large-scale, mass production of large capsules of agent in sizes to 1 cm or more in diameter. Techniques were also developed for the first time for extending capsular technology to large-scale, mass production of agent capsules as single particles in the size range less than 10 microns, fully controllable in respect to wall thickness and wall characteristics for both gelatin and polyvinyl alcohol as wall materials.

Techniques were developed for using polyvinyl alcohol as an effective new material for capsules of all sizes, but particularly in the <10 μ range, with special advantages of very low permeability and ease of drying to provide readily disseminable single capsule particles.

Several examples of generic, systematic procedures were worked out and documented for adaptation of gelatin (and to a lesser extent polyvinyl alcohol) encapsulation techniques to new internal phases. Limitations of gelatin as wall material were identified (permeability to polar compounds, degradation by acids from phosphorus-containing agents, disseminability difficulties) and possible solutions to these difficulties were suggested.

Together, these several technological advances provide Edgewood Arsenal with broad new capabilities for development of capsular CW systems and a flexibility of design permitting tailoring to specific tactical requirements.

120

In application studies of capsular materials in pyrotechnic and related systems, the compatibility of gelatin capsules in pyrotechnic mixes was demonstrated. Particle size effects on capsule integrity in pressed pyrotechnics were evaluated and the new <10 μ capsules were indicated as having potential for permitting press-filled rather than cast or dry-filled munitions even with liquid agents. The new propellant-based hot-gas disseminator was suggested as an efficient way to disseminate capsular agent with intact walls, and was recommended for further study.

The concept of large-explosive-coated self-disseminating capsules was conceived as an example of the inherent capabilities of encapsulation for developing new CW systems tailored to meet special tactical requirements. The technology for production of such capsular materials was developed and the basic feasibility of the concept was evaluated. Results showed that, for a liquid agent, droplet sizes of aerosolized material could be somewhat controlled from mass-mean particle sizes of >50 μ to <20 μ with dissemination efficiencies apparently significantly greater than for normal explosive dissemination. Applications of these and other large capsule products were suggested for achieving a flexibility of delivery and dissemination patterns not otherwise obtainable, area denial systems with agent release by the activity of undesired entry into the area, volatile agent systems with delivery and dissemination less dependent than previously on meteorological conditions, impact pellet systems for short or long range delivery of critical dosages of cutaneous agent, and others.

Major applications studies were directed to the feasibility of achieving controlled and sustained or prolonged release inhalable agent capsules in the size range <10 μ. The new small capsule technology developed on the project was adapted to the successful production of <10 μ capsular CS with both gelatin and polyvinyl alcohol walls. Laboratory experiments demonstrated that capsules could be tailored to provide release rates of agent (CS) into aqueous media varying from close to those for CS itself to nearly two orders of magnitude less. Accidental exposure of laboratory personnel to one of the gelatin-based capsular CS

121

materials indicated prolonged effects had been achieved, and this approach was confirmed by plethysmographic tests on mice in another laboratory.[2] These latter tests also indicated that delayed onset of effects could be induced by encapsulation, a potential advantage in certain tactical situations. Evaluations with volunteers at Edgewood[3] on highly retentive polyvinyl alcohol-based capsular CS having one-fifth the release rate of CS itself showed that five times the dosage was required for this capsular material to produce the same effect as unencapsulated CS. Implications of significant reduction of handling hazards of agents by this particular wall material are clear and such capsules should also be highly useful in mechanism of action studies. Overall, these studies on capsular inhalables, if fully confirmed by further evaluations, have provided a new incapacitating agent with the advantages of CS and with much more prolonged effects which can be uniquely tailored, by admixture of unencapsulated CS and capsular CS materials with controlled wall characteristics, to meet a wide variety of tactical requirements. The capabilities for such tailoring can be seen in Fig. 8.

Experimental Program

A critical review of the literature in the encapsulation field was carried out at the initiation of the project as a preliminary basis for assessing contributions to CW dissemination systems that might be made by microencapsulation.[4] This literature study reviewed the state of the art of the various encapsulation methods with respect to their advantages, limitations, and uses. No references were found which covered applications of microencapsulated agents or other materials in dissemination. The review defined a number of areas in which the encapsulation process might be used advantageously; these include reduction of handling hazards, presizing, stabilization by isolation, protection from light or other hostile environments, sustained release, and impaction capsules. Most (but not all) of these areas involve the application of encapsulation capabilities to existing concepts of dissemination. The review pointed out that real capsule properties might limit the contributions desired for existing systems and that considerable effort should be devoted to

122

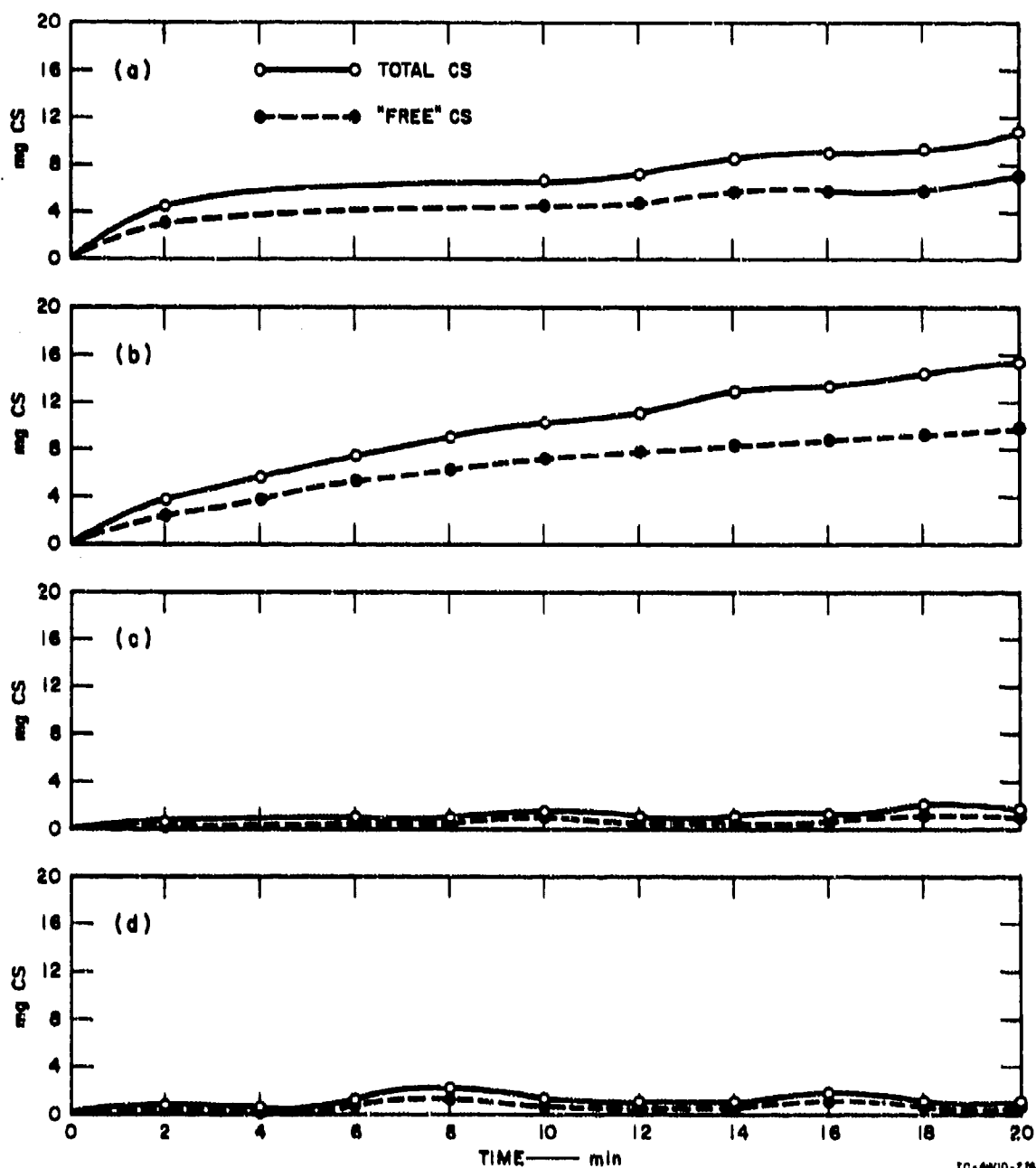FIG. 8 RELEASE OF CS ENCAPSULATED IN POLYVINYL ALCOHOL INTO AN AQUEOUS MEDIUM, pH 7.6, CONTAINING WETTING AGENT. Wetting agent, 0.1% sodium 2-ethylhexyl sulfonate; liquid volume, 500 ml. (a) Sample 7498-66A, PVA, air-dried, 0.1615 g (b) Sample 7498-66B, PVA, 5% celkate-T-21, air-dried, 0.1566 g (c) Sample 7498-72B, PVA-Cold method, 1% Cabosil, air-dried, 0.1004 g (d) Sample 7498-72A, PVA-Cold method, air-dried, 0.1043 g.

123

applying real capsule properties to development of capsular products which might be the basis for new or novel dissemination weapons systems. Large, explosive-coated capsules which might be rendered self-disseminating were suggested as an example of such a concept.

The experimental portion of the work reported here was directed toward applications of capsular materials in both new and existing dissemination systems and concepts. Preliminary studies were broadly based, to identify problems in encapsulation technology or capsular characteristics and to indicate where extensions of technology might be desirable, as well as to provide a background for application to current systems and for development of new concepts. During the work, the desirability of extending technology to provide efficient production of very large (0.5-1.5 cm) and very small (1-10 μ) discrete capsules became evident. A subcontract with NCR was most successful in providing effective approaches, and also new wall materials, for the 1-10 μ range;[5] conditions for large capsule production were developed as part of the SRI work. In most of the research, aqueous gelatin systems were employed, but some exploratory studies with nonaqueous polymer solutions were also included. In late stages of the work, the very useful polyvinyl alcohol encapsulation procedures became available as a result of the NCR subcontract developments; these were adapted at SRI for encapsulation of a range of active and inactive liquids and solids.

Adaptation studies made up a very appreciable part of the work, since each new material to be encapsulated has different physical and chemical properties and the encapsulation processes are sensitive to such properties. Optimum conditions, for example, are different for each of the four basic gelatin procedures, for different capsule size ranges for a given method, and for different materials to be encapsulated. Adaptation of coacervation encapsulation methods generally required determination of the effects on wall formation of such parameters as pH, temperature, agitation, and concentration of encapsulation solutions. For a variety of reasons, optimum values of each of these parameters may vary for different stages of the encapsulation process. Optimum programming of each variable through the various processes was therefore required, and was determined for

124

several materials and processes to provide a sound generic base for obtaining the best capsular products. Details of such programming were provided in a special technical report.[1]

Drying methods, which also play an important role in capsule properties, were the subject of considerable study. Methods employed included solvent drying, rotating screen, fluidized bed, air drying, freeze drying, and spray drying, as well as use of particulate and other additives as drying assists. Capsules greater than 100 μ in diameter presented relatively few problems if the encapsulation itself was effective. However, problems (especially of aggregation) increased with decreasing capsule size. Spray drying appeared to offer solutions to most of the problems but time did not permit complete studies of this approach. Drying problems were minimal for the special polyvinyl alcohol capsules; this ease of drying makes the polyvinyl alcohol encapsulation processes specially attractive.

Quantitative assay and evaluation were employed in a variety of forms throughout the study, both to assess the developing technology and to provide basic data. Included were routine measurements of internal phase, wall ratios and wall integrity, assessment of storage stability of capsular products and evaluation of thermal and chemical effects, mechanical properties of walls and sensitivity to rupture in pressing operations on pyrotechnics, capsule size determinations, measurements of agent degradation in dissemination from self-disseminating explosive capsules, the droplet size distribution in dissemination of liquids by such capsules, and measurements of release rates of capsular products into aqueous media. Of special significance was the development of methods for the simultaneous assay of CS and its hydrolysis products in aqueous media because of the importance of this effect in understanding biological mechanisms of action and agent design.

A number of applications studies were carried out in a flexible program responsive to changes in emphasis by the Physical Research Laboratories. Limited efforts were concerned with the use of capsular materials in pyrotechnic compositions, especially with effects of capsule

125

size on capsule integrity in pressed pyrotechnics. No incompatibility of gelatin capsules with selected pyrotechnic compositions was observed in storage tests at elevated temperatures, and no degradation of encapsulated material occurred in such tests. In the pressing studies it was clear that capsule sizes less than 20 μ would be required to avoid appreciable capsule rupture, at least with a liquid internal phase, in normal pressing operations and pressures. The new processes for producing capsules <10 μ in diameter are suggested as a probable solution to the capsule integrity problem. The work was not extended to studies of effects of encapsulation in actual dissemination because of changes in emphasis, but possible effects are discussed, including ablative protection of agent and decrease in flame temperature. The new propellant-based, hot-gas disseminator developed on this contract[6] was suggested as a potentially highly effective alternate to pyrotechnics for efficient high speed dissemination of intact capsules.

Large, explosive-coated capsules for possible self-dissemination uses were studied broadly. Conditions for efficient production of large capsules (to 1.5 cm or more in diameter) were first identified; these are described in detail. Lead azide was selected as the experimental explosive, though other less hazardous materials may be usable, and techniques for overcoating the capsules with this material were developed. Detonations of single capsules, capsule arrays, and capsule masses were carried out for a variety of capsule sizes and explosive loadings to provide data on dissemination efficiency for operations research evaluation. Individual capsules produced aerosolized clouds up to 5 feet in diameter and a mass median particle size of aerosolized liquid (di-2 ethylhexyl phthalate) less than 20 μ in diameter was shown to be possible. Dissemination efficiencies of at least 50%, based on total munition weight, appeared to be possible. Novel tactical potentials of these and related large capsule materials were presented.

Major efforts were devoted to production and study of sustained release, inhalable capsules (1-10 μ diameter), particularly in respect to possibilities for prolonged-effect CS. Considerable extensions of technology were found necessary for this size range and were accomplished

126

for both gelatin and polyvinyl alcohol as wall materials. Time did not permit optimization of all parts of the procedures, particularly drying techniques (spray drying appeared best), but appreciable samples of the best state-of-the-art capsular CS in this size range, with both gelatin and polyvinyl alcohol as wall material, were provided to the Physical Research Laboratories for further test and evaluation. Delayed release of the encapsulated CS into an aqueous medium was demonstrated in the SRI studies. A decrease in release rate of nearly two orders of magnitude was found with certain PVA capsules and release could apparently be tailored to any value within this range. Accidental exposure of laboratory personnel to one of the gelatin-based capsular CS samples indicated prolonged effects had been achieved. Initial tests on volunteers carried out at Edgewood Arsenal[3] indicated that PVA capsular CS was less effective than straight CS and produced no prolonged effects. However, plethysmographic tests on mice, carried out elsewhere,[4] using SRI capsular CS samples with both gelatin and PVA walls appeared to confirm the previous observation that capsular CS could produce prolonged effects. Prolonged effects may not be related as much to release rate as to adhesive properties of the wall material. The studies, if confirmed by further evaluations, appear to have provided a new incapacitating agent with the advantages of CS but with much more prolonged effects and with unique capabilities for tailoring by formulation and capsular design to meet a wide variety of specific tactical requirements.

Recommendations for Future Research

A wide variety of potential applications of microencapsulation in CW systems has been suggested and should be explored further to provide operational materials.

It is recommended that major emphasis be directed to further development and evaluation of prolonged-effect capsular CS because of its major tactical significance. A comprehensive study is suggested to thoroughly explore the effects of capsular parameters (wall materials, wall thickness, wall modifications including composite walls), drying methods, formulation variables designed to achieve specific activity and

disseminability goals, and finally, dissemination methods, including hot-gas dissemination. The goal of these studies would be optimum operational materials and dissemination methods. An essential part of the study would be a closely associated biological assay with complete control of variables such as particle size, distribution, and dosage. Initially the biological assays should be closely integrated with the capsular optimization research and should later be extended to field trials. Concurrently an analysis should be made of tactical mission requirements as a basis for design of specific formulations and dissemination systems. The overall goal should be to provide operational systems capabilities designed to meet specific tactical requirements.

CONTRIBUTORS

SRI contributors to this study include G. F. Sirine, Physical Chemist; W. H. Breen, Chemical Engineer; W. W. Gibson, Chemist; and S. B. Radding, Chemist. NCR contributors include D. D. Emrick, Senior Research Chemist; R. G. Bayless, Research Chemist; and H. F. Huber, Section Head (presently Director of Research, W. R. Grace International, Heidelberg Laboratory, Germany).

REFERENCES

1. Special Technical Report No. 17. See Appendix A.

2. Yves Alarie, Hazelton Laboratories, Inc., letter report August 14, 1967, to W. E. Sultan, Chemical Research Laboratory, Edgewood Arsenal.

3. Private communication from Mr. Donald E. Buck.

4. Special Technical Report No. 2. See Appendix A.

5. Special Technical Report No. 22. See Appendix A.

6. Special Technical Report No. 4. See Appendix A.

FORMATION OF FORCED CLOUDS

W. E. Ranz, Department of Chemical Engineering,
University of Minnesota, Minneapolis, Minnesota[*]

Controlled dissemination of aerosol-sized particles of solid and
liquid agents requires that the atmosphere of the target area be turned
into a forced cloud. In addition to producing a dispersion of micron-
sized particles, the disseminating device must be the means by which enor-
mous volumes of air become involved in the disseminating process. Indeed,
it is this need for dilution to very low concentrations in very large vol-
umes which puts severe limits on effective use of minute amounts of high-
potency compounds.

Because of small settling velocities (less than 1 cm/sec) and short
stopping distances (less than 10 cm), dissemination of aerosol particles
smaller than about 20 microns must be accomplished by disseminating a
dense aerosol cloud in which the particles are initially suspended. The
distribution of particles over large distances requires further develop-
ment of a cloud whose air mass exceeds the mass of suspended particles
by a factor larger than 10.[3] All air in a forced cloud formed in a few
seconds by a disseminating device is there because energy released by the
device has been used to put it there. Air has to become involved during
formation of the cloud, and energy from the device has to be dissipated
in the mixing process. How air is incorporated, how energy is utilized,
and how clouds can be designed with the desired amount of air were
reported in a special technical report.[1]

For a quantitative description of the final stages of controlled
dissemination, it was found necessary to define a _forced cloud_ as a region

---

[*] Professor Ranz served as a general consultant on the program while on
the staff of Stanford University's Department of Chemical Engineering
during the academic year 1966-67.

where cloud-forming streams of agent, gas, and entrained air move at velocities larger than some local wind velocity v', say 10^2 cm/sec. This criterion is based on the idea that dissemination is not controlled otherwise. All disseminating methods--except the possibility of electric charging of particles--become mechanically similar in the final stages of forced-cloud development. This is so because all have become momentum exchange processes where a spray or cloud jet of higher velocity and particle concentration is entraining air. As momentum is transferred and kinetic energy dissipated, these cloud-forming streams dilute with air, slow down, and fill the forced-cloud volume.

The volume of forced cloud formed is approximately $m_o(2(\widehat{KE}))^{1/2}/\rho_g v'$ and is controlled only by that portion of the forced-cloud mass which originated in the disseminating device (m_o) and by the specific kinetic energy $(\widehat{KE})$ or initial velocity $(U_o = (2(\widehat{KE}))^{1/2})$ imparted to that partial mass by the disseminating device. m_o includes only the liquid agent in the case of pressurized sprays, and only the liquid or solid agent in the case of ultrasonic aerosol production; m_o includes pumped air, compressed gases or propellant, as well as liquid or solid agent in the case of air or gas atomization processes; m_o includes explosive and agent in the case of explosive aerosol production processes, and propellant (as well as agent) in the case of thermal and pyrotechnic aerosol production processes. U_o or $\widehat{KE}$ is a distributed quantity in actual systems, varying not only over initial flow cross-sections but also between phases at the start of the final stage of the disseminating process. U_o is the orifice velocity in the case of pressurized sprays, and the ejection velocity in the case of ultrasonic aerosol production. U_o is the orifice velocity in the case of air or gas atomization if the agent has been accelerated to near gas velocities in the orifice region. In the case of explosions U_o can be taken as the maximum velocity of the fill shell. In the case of thermal or pyrotechnic aerosol production processes, U_o is the orifice velocity.

The particulate density of a forced cloud is approximately $\alpha \rho_g v'/(2(\widehat{KE}))^{1/2}$ where α is the fraction of m_o which becomes particulate material and where ρ_g is air density. This follows directly from the definition of forced cloud volume and the assumption of a cloud density not much

130

different from that of air. Thus, because the later stages of the process are fluid-mechanical and similar, the volume and particulate density of forced clouds formed by mechanical, chemical, or thermal energy are not dependent on the type of device or on the method of dissemination.

Taking the practical maximum of U_o to be sonic velocity (3×10^2 m/sec), with $\rho_g = 1$ kgm/m^3 and $v' = 1$ m/sec, the maximum forced-cloud volume is found to be on the order of 300 cubic meters per kilogram released by the disseminating device. If it had a spherical shape, this cloud would be only six to seven meters in diameter. On the same evaluation basis the minimum particulate density of the forced cloud would be about three one-thousandths kilogram per cubic meter if m_o were all particulate material.

A thought-experiment approach was used in the special technical report[1] to derive design equations for various ways of forming forced clouds. Topics included in the report are:

Projection Models of Cloud Formation

Single particle mechanics
Particle-projection model of cloud formation
Disintegration-projection model of cloud formation
Spray model of cloud formation
Expansion of electrified clouds; electrical projections

Gas Jet Models of Cloud Formation

Continuous free jet
Short cloud jets, puff jets, and vortex rings
Strategic role of forced cloud geometry; porous clouds;
   clouds formed by jets from moving sources

Subordinate processes of turbulent breakup and coalescence are treated in an appendix to the report.

While some dissemination methods are analyzed in detail in the report, a considerable generalization appears possible. This generalization is summarized in Table I, where symbols have the following meanings:

ρ_p = density of particulate material

ρ_g = air density

ρ_{go} = density of cloud-forming stream at the flow cross section which has highest velocity U_o and equivalent diameter D_o

Table I

SUMMARY OF ELEMENTARY DESIGN EQUATIONS FOR FORCED CLOUDS FORMED BY VARIOUS DISSEMINATING PROCESSES

(A forced cloud is defined as a region of air dilution where cloud forming streams move at velocities larger than some local wind velocity, say, 10^2 cm/sec)

Type of dissemination:	Pressurized liquid sprays; aerosol dispersion from ultrasonic generator	Air or gas atomization and dispersion; thermal and pyrotechnic aerosol production processes	Explosive aerosol production processes
Maximum time during which m_0 should be released at velocity U_0 to form a forced cloud:	$\left(\dfrac{c_p}{c_g}\right)^{1/2}\dfrac{D_0}{2.5\tan\theta\,V'^2}$	$\left(\dfrac{c_g0}{c_g}\right)^{1/2}\dfrac{D_0}{2.5\tan\theta\,V'^2}$	Nearly impulsive energy input, minimum time conditions
Approximate forced cloud volume:	$\dfrac{m_0 U_0}{\rho_g V'^2}$	$\dfrac{m_0 U_0}{\rho_g V'^2}$	$\dfrac{m_0 U_0}{\rho_g V'^2}$
Average particulate density in forced cloud:	$\dfrac{\rho_g V'^2}{U_0}$	$\dfrac{\alpha z V_g^2}{U_0}$	$\dfrac{\alpha \rho_g V'^2}{U_0}$
Approximate form and composition of forced cloud:	Spherical vortex at distance $\left(\dfrac{c_p}{c_g}\right)^{1/2}\dfrac{D_0}{.5\tan\theta\,V'}$ in front of orifice or generating surface	Spherical vortex at distance $\left(\dfrac{\rho_g0}{c_g}\right)^{1/2}\dfrac{D_0}{.5\tan\theta\,V'}$ in front of orifice	Pincushion of cloud spike jets. About half of the apparent volume is composed of forced clouds.
Nature of control quantities:	m_0 is mass of liquid or solid agent dispersed. In pressurized sprays, U_0 is controlled by liquid supply pressure; spray half-angle θ is controlled by vortex generators upstream of orifice of diameter D_0. In ultrasonic generation, U_0 is controlled by amplitude and frequency of generator surface, which has equivalent diameter D_0, and $\tan\theta$ is controlled by the shape of this surface.	c_g0 is density of jet stream at flow cross section which has highest velocity. U_0 and equivalent diameter D_0. m_0 is all mass released by the device. α is fraction of m_0 which forms particles. U_0 is controlled by air or gas pressure in atomization and by chemical energy release of propellant in pyrotechnic processes. $\tan\theta$ is controlled by upstream vorticity generation, by nozzle shape, and by time of injection, having values varying from 0.5 for turbulent puffs, to 0.1l for free continuous jets, to 4×10^{-3} for vortex rings.	U_0 is initial fill velocity and is controlled by the energy of the explosive and the fill-to-explosive mass ratio. m_0 includes explosive and agent. α is fraction of m_0 which forms particles.
Comment:	For continuous dispersal of more mass than m_0 in the maximum time specified, a naturally disseminating cloud issues from a cone-shaped forced cloud. In such cases, the forced cloud volume can be increased by moving the source.	For continuous dispersal of more mass than m_0 in the maximum time specified, a naturally disseminating cloud issues from a cone-shaped forced cloud. In such cases, the forced cloud volume can be increased by moving the source.	Since explosions will have a forced-cloud porosity of about 50%, their apparent forced cloud volume will be twice that of the volume listed above. Some energy may be lost to air shock wave.

132

θ = half-angle of cloud jet

v' = local wind velocity

m_o = total mass of cloud-forming materials released by the disseminating device

α = fraction of m_o which becomes particulate material

Except for the possibility of electric charging of particles and the electrical force projection of particles into dilute clouds, the only way of overcoming inherent restrictions on forced-cloud volume and geometrical coverage is to form a "porous" cloud of miniaturized air-mixing elements. For efficient use of energy, the size of each forced-cloud element should approach a scale equal to the small distances which can be reached by the projection of individual particles. If a maximum starting Reynolds number of 10^2 is applied as a practical limit (initial sonic velocity gives approximately the same result), this projection distance is less than $5\rho_p D_p / \rho_g$, where D_p is the desired particle size and ρ_p is particle density. Under this criterion also, the minimum $\widehat{KE}$ for forming an aerosol cloud of uniform density is found to be approximately $3 \times 10^3 \mu_g^2 / \rho_g^2 D_p^2$. Thus, exploded units of forced cloud in a porous cloud should have small radii of about one-tenth meter.

Porous-cloud attributes can also be achieved by a moving cloud generator forming a forced cloud continuously. If the device moves at velocity V, the maximum length of forced cloud which can be formed at a uniform rate is approximately

$$3 \left(\frac{\rho_g}{\rho_{go}} \right)^{1/2} \left(\frac{D_o U_o V}{v'^2} \right)$$

Here, ρ_{go} is the density of the cloud-forming stream at the flow cross-section which has highest velocity U_o and equivalent diameter D_o. The diameter of this maximum length cloud is

$$\left(\frac{\rho_{go} U_o^2}{\rho_g v' V} \right)^{1/2} D_o$$

133

The m_o needed to form this maximum length cloud at a uniform rate, in the time the source moves the maximum length at velocity V, is approximately

$$3\left(\frac{\rho_{go}}{\rho_g}\right)^{1/2}\left(\frac{U_o}{v'}\right)^2 \rho_{go}D_o^3$$

If one uses an $m_o < m_{o,max}$ with the same $\widehat{KE}$, the forced-cloud length will be shorter than the maximum length. If $m_o > m_{o,max}$, then a forced cloud of the maximum length will be trailed by a natural cloud of unknown characteristics.

REFERENCES

1. Special Technical Report No. 7. See Appendix A.

134

Appendix A

LIST OF PROJECT SPECIAL TECHNICAL REPORTS
CONTRACT DA-18-035-AMC-122(A)

Appendix A

LIST OF PROJECT SPECIAL TECHNICAL REPORTS
CONTRACT DA-18-035-AMC-122(A)

Special technical reports were published on completion of investigations in the various areas of research described in the text of this report. Report number, title, author(s), date of publication, and Defense Documentation Center Accession Number (where available at time of publication) of each report are given below.

1. Special Technical Report No. 1, Bibliography on Electrostatic Phenomena in Aerosol Dissemination, D. E. Blake and C. E. Lapple, August, 1965. AD 468-320L.

2. Special Technical Report No. 2, Aerosol Dissemination Processes--A Critical Review. Vol. I, (Unclassified), I. G. Poppoff, October 31, 1965. AD 477-677L.

    This volume contains complete reviews of mechanics of explosive dissemination; shock, detonation, and reaction processes; droplet ignition processes; condensation processes; ultrasonic aerosol production processes; pneumatic dissemination of dry powders; natural generation of aerosols; electrostatic phenomena in disseminations; and microencapsulation. Abstracts are given of thermal and pyrotechnic dissemination processes; pyrolytic and oxidative degradation processes; and hydrolytic degradation processes.

    Aerosol Dissemination Processes--A Critical Review, Vol. II (Confidential), L. A. Dickinson, E. L. Capener, J.E. Baldwin, T. Mill, and R. C. Robbins, March 30, 1966. AD 370-921L.

    This volume contains complete reviews of thermal and pyrotechnic dissemination processes; pyrolytic and oxidative degradation processes; and hydrolytic degradation processes.

3. Special Technical Report No. 3, Equations of State of Liquids and Calculations of Waste Heat, G. E. Duvall, November 6, 1966. AD 802-180.

4. Special Technical Report No. 4, Secondary Injection of C. W. Agents into a Supersonic Rocket Exhaust, J. E. Baldwin, December 14, 1966. AD 804-182.

5. Special Technical Report No. 5, <u>Explosive Dissemination from Spherical Devices</u>, G. R. Abrahamson, R. W. Gates, S. Hanagud, and G. M. Muller, December 9, 1966. AD 804-622L.

6. Special Technical Report No. 6, <u>Atomization--A Survey and Critique of the Literature</u>, C. E. Lapple, J. P. Henry, Jr., and D. E. Blake, April, 1967. AD

7. Special Technical Report No. 7, <u>Dissemination of Aerosol Particles by Forming Clouds</u>, W. E. Ranz, February 15, 1967. AD 807-624.

8. Special Technical Report No. 8, <u>Ignition and Combustion of Single Droplets</u>, B. J. Wood and W. A. Rosser, Jr., March, 1967. AD 808-879.

9. Special Technical Report No. 9, <u>Ultrasonic Dissemination of Aerosols</u>, C. W. Smith, C. M. Ablow, S. V. Hanagud, E. M. Spurlock, and D. R. Grine, July, 1967. AD 818-285.

10. Special Technical Report No. 10, <u>Condensation Studies</u>, R. C. Robbins and C. Naar, April, 1967. AD

11. Special Technical Report No. 11, <u>Development of Aerosol Charge Analyzer</u>, C. E. Lapple, D. E. Blake, and G. L. Pressman, April, 1967. AD 813-407.

12. Special Technical Report No. 12, <u>Detonation, Shock, and Chemical Reaction Processes in Explosive Dissemination: Boundary Stability and Cavitations</u>, L. B. Seely, and J. G. Berke, June, 1967. AD

13. Special Technical Report No. 13, <u>Detonation Calculations</u>, J. Roth, August, 1967. AD

14. Special Technical Report No. 14, <u>Temperature of Shocked Liquids</u>, M. Cowperthwaite and J. H. Blackburn, July, 1967. AD

15. Special Technical Report No. 15, <u>Light Emission from Explosively Disseminated Clouds of Agent Simulant</u>, G. L. Stevens and L. B. Seely, June, 1967. AD

16. Special Technical Report No. 16, <u>Pyrotechnic Dissemination Research Studies</u>, J. E. Baldwin and C. E. Wooldridge, June, 1967. AD

17. Special Technical Report No. 17, <u>Microencapsulation</u>, W. H. Breen, R. W. Gibson, S. B. Radding, G. F. Sirine, and A. G. Brown, June, 1967. AD

18. Special Technical Report No. 18, <u>Mechanics of Explosive Dissemination</u>, G. R. Abrahamson, R. W. Gates, S. Hanagud, G. M. Muller, and K. Schreiner, November 1967. AD

19. Special Technical Report No. 19, <u>Pneumatic Dissemination of Dry Powders</u>, P. L. Magill and D. Pon, July 1967. AD

20. Special Technical Report No. 20, <u>Thermal Stability of a Reactive Spherical Shell</u> (Supplement to Special Technical Report No. 8), W. A. Rosser, Jr. and Y. Rajapakse, June 1967. AD

21. Special Technical Report No. 21, <u>Waste Heat in Liquid Spherical Bursters</u>, (Supplement to Special Technical Report No. 3), G. E. Duvall, November 1967. AD

22. Special Technical Report No. 22, <u>Encapsulation of Small Particles (1-10 Microns) Diameter</u> (Supplement to Special Technical Report No. 17), D. D. Emrich, September 1967. AD

Appendix B

LIST OF PROJECT QUARTERLY REPORTS
CONTRACT DA-18-035-AMC-122(A)

12. Twelfth Quarterly Progress Report, W. C. Thuman, January 1 to
     March 31, 1967. AD 813-779L.

13. Thirteenth Quarterly Progress Report, W. C. Thuman, April 1 to
     June 30, 1967. AD _____

144

Appendix B

LIST OF PROJECT QUARTERLY REPORTS
CONTRACT DA-18-035-AMC-122(A)

All quarterly reports were titled <u>Research Studies on the Dissemination of Solid and Liquid Agents</u>. The period covered, author, and Defense Documentation Center Document Accession Number (where available at time of publication) of each report are given below.

1. <u>First Quarterly Progress Report</u>, I. G. Poppoff, April 1 to June 30, 1964. AD 603-644.

2. <u>Second Quarterly Progress Report</u>, I. G. Poppoff, July 1 to September 30, 1964. AD 451-067.

3. <u>Third Quarterly Progress Report</u>, I. G. Poppoff, October 1 to December 31, 1964. AD 458-017L.

4. <u>Fourth Quarterly Progress Report</u>, I. G. Poppoff, January 1 to March 31, 1965. AD 467-487L.

5. <u>Fifth Quarterly Progress Report</u>, I. G. Poppoff, April 1 to June 30, 1965. AD 468-319L.

6. <u>Sixth Quarterly Progress Report</u>, I. G. Poppoff, July 1 to September 30, 1965. AD 474-130L.

7. <u>Seventh Quarterly Progress Report</u>, I. G. Poppoff, October 1 to December 31, 1965. AD 477-674L.

8. <u>Eighth Quarterly Progress Report</u>, I. G. Poppoff, January 1 to March 31, 1966. AD 482-346L.

9. <u>Ninth Quarterly Progress Report</u>, I. G. Poppoff, April 1 to June 30, 1966. AD 487-974L.

10. <u>Tenth Quarterly Progress Report</u>, I. G. Poppoff, July 1 to September 30, 1966. AD 802-069L.

11. <u>Eleventh Quarterly Progress Report</u>, I. G. Poppoff, October 1 to December 31, 1966. AD 807-700L.

DISTRIBUTION LIST

Copies	Organization
1-20	Defense Documentation Center ATTN: TISIR Cameron Station, Building 5 5010 Duke Street Alexandria, Virginia 22314
21-40	Commanding Officer Edgewood Arsenal ATTN: Mr. Donald E. Buck Research Laboratories Edgewood Arsenal, Maryland 21010

Internal Distribution List

21	Central Files, Research Laboratories
22-26	Technical Library
27-32	Contract Project Officer (Donald E. Buck)
33	USA Biological Laboratories, Fort Detrick, Md.
34	Commander, U.S. Naval Ordnance Test Station, China Lake, California 93555
35	D/Armament Development, Eglin AFB, Florida 32542
36-37	D/Wpn Dev & Engr Labs, Edgewood Arsenal
38	Chemical Research Laboratory
39	Dissemination Research Department, Phys Rsch Lab
40	CG, MUCOM, ATTN: AMS J-RE-R, Dover, New Jersey 07801

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
STANFORD RESEARCH INSTITUTE	UNCLASSIFIED
Menlo Park, California 94025	2b. GROUP
	N/A

3. REPORT TITLE

RESEARCH STUDIES ON THE DISSEMINATION OF SOLID AND LIQUID AGENTS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report - April 1964-December 1967

5. AUTHOR(S) (First name, middle initial, last name)

I. G. Poppoff and W. C. Thuman, contributing editors

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
December 1967	148	41

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA-18-035-AMC-122(A)	
b. PROJECT NO.	FR, PAU-4900
Task 1B522301A08101	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	N/A

10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
Dissemination investigation of liquid and solid agents	Edgewood Arsenal Research Laboratories Edgewood Arsenal, Maryland 21010

13. ABSTRACT

The objective of the program was to provide basic information necessary for an over-all improvement of chemical agent dissemination techniques. Studies were made of explosive generations of aerosols (mechanics of explosive processes; detonation, shock, and reaction processes; ignition processes; comminution processes); thermal and pyrotechnic generation of aerosols (thermal and pyrotechnic processes; pyrolytic and oxidative degradation processes; condensation processes); ultrasonic, pneumatic, and atomization processes; electrostatic phenomena associated with aerosol production; the application of microencapsulation to aerosol generation and enhancement; and natural aerosol generation.

A critical summary of the program and recommendations for future work is first presented. This is followed by a discussion of accomplishments and recommendations for future research in each of the study areas listed above, with reference to program reports (22 Special Technical Reports and 13 Quarterly Progress Reports) for details.

DD FORM 1473 (PAGE 1)
1 NOV 65

S/N 0101-807-6801

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Chemical agent						
Electrostatic phenomena						
Agent						
Dissemination						
Aerosol						
Explosive aerosol generation						
Detonation						
Shock						
Droplet ignition						
Thermal generation						
Pyrotechnic generation						
Pyrolytic degradation						
Oxidation						
Condensation						
Ultrasonic generation						
Pneumatic generation						
Natural aerosols						
Microencapsulation						
Hydrolysis						
Waste heat						
Equations of state						
Specific entropy						
Liquid fills						
Energy absorption						
Atomization						
Boundary instability						
Flashing						
Agent degradation						
Encapsulation						
Sustained release						
Powders						
Pretreatment						

DD FORM 1473 (BACK)
1 NOV 65
(PAGE 2)

148

UNCLASSIFIED
Security Classification

PAGES_____ ARE MISSING IN ORIGINAL DOCUMENT