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Effectiveness of M6A1 Detector Paper for Small Airborne Drops of Chemical Warfare Agents

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M6A1 detector paper is a standard military item which undergoes a rapid and permanent color change from olive-green to red on contact with droplets of liquid chemical warfare agents. The paper has been studied to determine the smallest size and number of spots which can be detected visually at several intensities of illumination. At 11 foot-candles or more (about equal to daylight at 5 to 10 minutes after sunset on a clear day), nine out of eleven laboratory personnel were able to detect a single 290-micron spot per square inch of paper. This is equivalent to a spherical droplet of 65 microns diameter, weighing about 0.14 microgram. Extrapolated to the projected area of a man, even unprotected, this quantity is negligible toxicitywise. Thus, M6A1 paper is a satisfactory detection of minimal CW attacks. Furthermore, at least at the higher illuminations used in this study, there is no need for improvement in the speed or certainty of attack detection. However, the margin of safety provided by an M6A1 paper response decreases rapidly as the intensity of CW attack increases, since even instantaneous detection is too late in a heavy attack unless prior protective action has been taken.

INTRODUCTION

M6A1 detector paper is a heavy paper or card stock that is coated with an olive-green paint containing particles of a solvent-extractable red dye (1). Any solvent capable of rapidly softening dried linseed-oil paints will produce immediately on contact with the paper a red spot on the general green background.* M6A1 paper was designed to detect large drops or splashes of liquid chemical warfare agents of the vesicant group.

Although M6A1 paper was standardized by the U.S. Forces early in World War II,† some currently important characteristics and limitations of the paper have not previously been determined. The need for more information concerning the performance of the paper as a component of the shipboard BW/CW (biological and chemical warfare) defense system, especially under the conditions to which modern chemical warfare agents are best adapted, resulted in this investigation. The primary objectives of the study were (a) to determine the minimum size and number of drops of airborne liquid which would produce red spots on the paper visible to a person

with normal vision under varying conditions of light and distance, and (b) to evaluate this size and number of drops in terms of the hazard to topside shipboard personnel when the drop liquid is a toxic chemical warfare agent.

Diethyl phthalate was the liquid chosen for use throughout the study as a simulant chemical warfare agent. Not only does it act instantaneously on M6A1 paper, but its viscosity, surface tension and vapor pressure render it a reasonably satisfactory substitute for the general class of liquid chemical warfare agents in situations where a toxic agent is undesirable.

THE SPREADING FACTOR OF DIETHYL PHTHALATE ON M6A1 DETECTOR PAPER

The ratio of the diameter of the circular area produced on a solid surface by a drop of a given liquid to the diameter of the airborne spherical drop of the liquid is defined as the spreading factor of the liquid on the solid. This factor was found to be surprisingly constant for diethyl phthalate on M6A1 paper over the drop diameter range 22 to 130 microns.*

Since the spreading factor is characteristic of a given liquid and substrate in a given temperature range, it may be desirable to redetermine the factor as these conditions are varied. However, the

NRL Problem C08-22; Project SF-011-08-01, Task 3332. This is an interim report; work on the problem is continuing.

*Of the non-chemical-warfare liquids present in quantity aboard ship, only Cellulube 220 — a hydraulic elevator fluid — has a significant effect on M6A1 paper; in this case the color is a pale brownish-red and is slow to appear.

†Strictly speaking, M6 paper was the World War II item, and is now obsolete. The two papers differ in size only; M6 was 5 in. x 5 in.; M6A1 is 2.5 in. x 3.5 in.

*A micron, commonly abbreviated μ , is 0.001 mm or 0.00004 inch.

range in spreading factor for various chemical warfare liquids and simulants on surfaces of interest is not extreme and frequently falls between 4 and 6 when measured by a conventional method, as was done in this study. Such methods involve laying the drops down on the M6A1 paper or other substrate at essentially zero velocity. High-speed impaction of the drops on the paper, as would be common in its use at sea, could well result in abnormally large spreading factors for the larger drop sizes.

PROCEDURES FOR PRODUCING DROPS

Several procedures of drop generation were investigated to find a simple method for generating single liquid drops of various sizes. Many methods of aerosol generation such as atomizers (2) and rotating disks (3-7) were regarded as unsatisfactory because of lack of control of the number or size of the drops produced. The several elegant procedures (8-12) for producing single droplets by compressed-air stripping of liquid from a stylus or hollow needle were also discarded because the equipment was considered too complex for construction in the time available. It was noted, however, that Asset (9) and Abberton (11) provide useful reviews of the literature in this field. The vibrating-reed technique (13) appeared not well suited to the production of single droplets, except in the manually operated modification described by Wolf (14). This simple device, although capable of forming single aqueous droplets over a wide range of sizes with high precision (15), was believed to require some redesign in order to perform equally well with organic liquids. Of the various methods considered for use, three rather simple methods were selected.

Drops Produced With a Syringe and Needle; Drop Size Given by Direct Measurement of the Pendant Drop Diameter

In the first method selected, a known volume of diethyl phthalate was expelled from a 1-microliter syringe,* graduated in 0.01 microliters, and the point of the needle was then touched to

*Microliter Syringe No. 7001N, The Hamilton Co., Whittier, Calif. This syringe is fitted with a 25-gage needle of 500 μ O.D.

the detector paper. From the volume of liquid used, the diameter of an equivalent spherical drop was determined using the expression $d = (6V/\pi)^{1/3}$.

This method was satisfactory for producing drops of about 275 μ or larger, but has several disadvantages. The drop forced to the end of the needle is not a precise sphere for small volumes. One might expect a different spot diameter from a drop that is touched to the paper and one that falls freely on the paper, because capillary action between the paper and the end of the needle may result in removal of a volume of liquid slightly in excess of that indicated on the syringe.

Two diameters, 90 degrees apart, of the spots produced on the paper were measured with a microscope equipped with a calibrated reticle, and the average diameter used to calculate the spreading factor. A summary of the data is given in Table 1. The average spreading factor found by this method was 5.80 with an average deviation of 0.12, or 2.1 percent.

TABLE 1
Spreading Factor on M6A1 Paper
of Diethyl Phthalate Drops Produced
by Microsyringe Delivery

Volume (microliter)	No. of Spots	Average Spot Diameter (measured)	Average Airborne Diameter (calculated)	Spreading Factor
0.5	12	5653 μ	985 μ	5.84
0.2	21	4303 μ	726 μ	5.93
0.1	30	3452 μ	577 μ	5.99
0.05	17	2581 μ	457 μ	5.65
0.02	18	1897 μ	337 μ	5.63
0.01	15	1546 μ	267 μ	5.79

Drops Produced With Teflon Capillaries; Drop Size Given by Direct Measurement of the Pendant Drop Diameter

Pieces of Teflon tubing of 500 to 700 μ inside diameter * were drawn at the tip to inside diameters of 20 to 100 μ in a microflame. Each piece of

*Teflon 100 FEP Electrical Spaghetti Tubing AWG #24, 0.020 in. to 0.027 in. I.D., 0.008-in. wall, Carmer Industries Inc., Kenilworth, N.J.

drawn Teflon was fitted onto a 3-inch piece of 7-mm glass tubing that had been drawn down at the tip to an outside diameter of 500 μ . The glass tubing served as a reservoir for the diethyl phthalate. Some diethyl phthalate was pipetted into the glass reservoir and about 2 feet of rubber tubing was connected to the reservoir. A slight pressure was applied to a squeeze bulb connected to the rubber tubing, and a drop of diethyl phthalate was forced out of the Teflon tip. In many instances, the drop moved up the outside wall of the Teflon tip and was removed by blotting it with filter paper. When a drop was expelled which remained on the end of the tip, it was measured with a microscope and then deposited on a piece of M6A1 detector paper which was carefully raised by a micrometer stage into contact with the suspended drop. The spot produced on the paper was measured with a microscope as described above.

The data obtained by this method are given in Table 2. The average spreading factor found by this method was 5.69 with an average deviation of 0.34, or 6.0 percent.

Even though Teflon FEP is somewhat difficult to draw into capillaries, it was chosen because it is not readily wetted by diethyl phthalate as are most other thermoplastic materials. If the Teflon tubing is wetted by the liquid, the spreading factor found will be too small. There may be some capillary action between Teflon tip and paper due to the method used to deposit the drop, as with the syringe deposition, but no such action was detected with the microscope. This method was acceptable for producing single drops 30 μ or larger. However, because of the vibration of the tip, the

difficulty in maintaining a constant pressure on the rubber bulb, and the occasional tendency for the liquid to move up the outside wall of the Teflon tubing, it was difficult to get consecutive drops of the same size.

Drops Produced by Electrical Dispersion; Drop Size Given Gravimetrically or by the Liquid Lens Technique

The third and the most frequently used method for generating uniform drops was the electrical dispersion method (16-22). In this method, drops are forced from a capillary by electrostatic pressure when the liquid is subjected to an emf from 0 to 20 kv. In most of the studies the voltage was varied between 3 to 10 kv and was never over 20 kv. The apparatus used (Fig. 1) consisted of a 0 to 30 kv dc power supply,* a piece of 8-mm glass tubing approximately 2 inches long which served as a reservoir tube, several 2 to 3 inch glass capillary tubes which were drawn to tips with inside diameters of 50 to 300 μ , a grounded collector plate that could be mechanically adjusted to various heights, and a microscope illuminator. The capillary tube was joined to the 8-mm reservoir tube by means of a very small Tygon sleeve. The reservoir was filled with diethyl phthalate, the wire lead from the high voltage source was inserted into the liquid in the reservoir, and the collector plate was set at a distance varying from 1/4 to 1 inch directly below the capillary tip. The high voltage source then supplied

TABLE 2
Spreading Factor on M6A1 Paper of Diethyl
Phthalate Drops Produced by Delivery from
Teflon Capillaries

Spot Diameter	Drop Diameter	Spreading Factor
5161 μ	855 μ	6.04
5044 μ	941 μ	5.46
4782 μ	941 μ	5.08
4585 μ	769 μ	5.96
3537 μ	598 μ	5.92

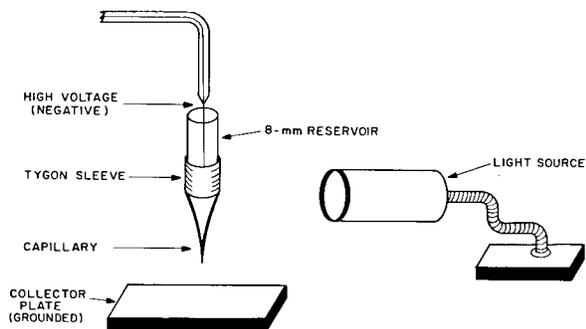


Fig. 1 - Apparatus to generate drops by electrical dispersion

*Beta Electronics Co., New York, N.Y.

a negative charge to the liquid in the reservoir. A piece of M6A1 detector paper was placed on the collector plate and the power supply turned on. In general, as the voltage was increased, the liquid was dispersed from the tip, first in the form of individual drops, then as fine threads, and finally as a spray or cloud. If the voltage was increased beyond this point, there was a reversal from a cloud back to a stream of drops. These drops and sprays were readily visible in a Tyndall beam. A voltage range was selected which would yield small individual drops at a visually countable rate (not greater than 140 drops per minute) from the capillary used.

Several factors were found to influence the voltage required to produce individual drops at a rate which could be easily counted. The inside diameter of the capillary tube was the most important single factor. About 3 kv was sufficient to produce large drops from a capillary of from 100 to 200 μ inside diameter, whereas 10 to 15 kv was needed to produce drops from the capillaries with inside diameters of from 20 to 60 μ . The outside diameter of the capillary appeared also to have an effect on drop size. In addition, the geometry of the tip affects the size of drop discharged, since the liquid leaves the point of highest electrical stress. Therefore a tip with a flat or symmetrically rounded surface appears to be most desirable for producing uniform droplets. The distance between the end of the high voltage wire and the end of the capillary directly influences the voltage required for drop formation, since a greater distance means a smaller voltage gradient in the liquid conductor. Similarly, the distance between the collecting plate and the end of the capillary is a major consideration, for if this distance is decreased, the voltage gradient in the air is increased and the voltage required to cause a drop to fall is decreased. The electrical conductivity of the collecting plate is an important factor, because the better the conductor beneath the capillary, the less the voltage required. When a nonconductor such as glass was used as a collecting plate and was well insulated, the dropping rate decreased and eventually stopped due to a buildup of charge on the collecting plate. This effect has been observed previously (17). The major factor involved in the dispersion of liquids from small capillaries is electrostatic pressure within the liquid, and since this pressure is dependent upon the dielectric constant of the liquid, liquids with

higher dielectric constants are easier to atomize electrically.

The capillaries used in this study were drawn to a sharp taper, from Pyrex capillary tubing of about 350 μ thus giving a capillary with a sturdy glass wall. The majority of the capillaries had inside diameters between 25 and 100 μ . A capillary normally will produce a drop approximately 1/3 the inside diameter of the tip of the capillary; however, by varying the voltage and the distance of the collector plate, it is possible to obtain a range of various size drops both greater than and less than 1/3 the inside diameter of the tip.

To determine the size of the drops dispersed from the capillary, two methods were used. In the first method, the size of the airborne drops was determined by collecting a large known number of these drops on a thin microscope cover glass which rested in the center of a square of M6A1 detector paper. The microscope cover glass had been previously weighed on a microbalance. The drops were collected alternately on the paper and the cover glass (25 to 50 drops on one and then on the other). Assuming that the drops are spherical and uniform, one can calculate the volume of each drop from the total weight of a known number of drops and thus arrive at the airborne diameter. Since the same size drops were falling on the paper and on the cover glass, the spreading factor was readily obtained from the ratio of the spot diameter on the paper to the calculated airborne diameter. A summary of the data obtained is given in Table 3.

TABLE 3
Spreading Factor on M6A1 Paper of Diethyl
Phthalate Droplets Produced by
Electrical Dispersion; Gravimetric
Measurement of Size

Number of Drops	Spot Diameter	Airborne Diameter	Spreading Factor
400	882 μ	179 μ	4.93*
1040	947 μ	160 μ	5.92
140	1076 μ	173 μ	6.22
200	938 μ	156 μ	6.01
150	908 μ	162 μ	5.60
150	834 μ	167 μ	5.00*

*A definite decrease in the rate collected on the glass was observed. These data were not used in computing the average.

One objection to this method is that the microscope cover glass and the detector paper do not have the same electrical conductivities. Thus the rate of production and the diameter of the drops may not be constant. By rapidly passing from the cover glass to the paper, this situation is improved; however, the difficulty is not eliminated. Upon collecting a large number of drops on glass only, it was observed that there was a decrease in the dropping rate from the original rate. The rate was also altered if minute particles lodged in the tip of the capillary. By using a sealed capillary tube and an exceptionally clean environment the number of particles that can clog the capillary could presumably be minimized, although this technique was not explored. The diethyl phthalate was, however, filtered twice through a sintered glass filter to avoid small particles in the liquid that might cause clogging.

The second method for determining the diameter of an airborne drop and the one which seemed to be the most reliable is the liquid lens method (23). A thin microscope cover glass was cleaned free of grease by washing in a detergent solution (Aerosol OT) and then polished with lens paper. The cover glass was placed in the center of the detector paper, and after the dropping rate appeared constant the edge of the cover glass was rapidly passed under the tip of the capillary. This was done until there were several drops on the cover glass and the paper. The red spots on the paper were measured with a microscope. The size of the original spherical drop in air was obtained from the diameter of the liquid lens formed by a drop of diethyl phthalate on the glass and from the focal length of the lens according to the method described by May (23) (see Appendix A). It was assumed that the drops falling on the paper and on the glass were of the same size. This assumption is reasonable since only a few drops were collected and these were collected rapidly near the edge of the cover glass. An electrically conducting microscope cover glass was prepared with a stannic oxide surface* that gave a resistance of 10,000 to 30,000 ohms; however, the rate of fall onto this surface was much greater than that onto the detector paper.

The data obtained using the electrical discharge method in conjunction with the liquid lens method

*Produced by treatment with a stannic chloride/methanol solution followed by baking at the annealing temperature of the glass.

TABLE 4
Spreading Factor on M6A1 Paper of Diethyl Phthalate Droplets Produced by Electrical Dispersion; Liquid Lens Measurement of Size

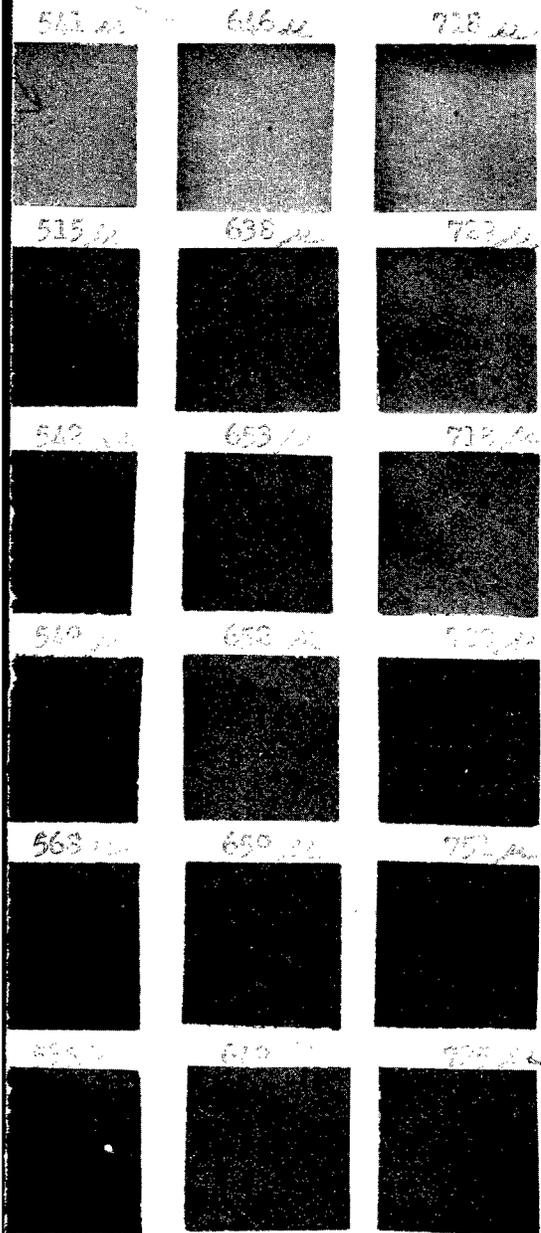
Number of Drops	Spot Diameter	Airborne Diameter	Spreading Factor
≥3	1573 μ	281 μ	5.60
≥3	1364 μ	220 μ	6.20
≥3	934 μ	164 μ	5.69
≥3	732 μ	118 μ	6.20

are summarized in Table 4. The average spreading factor obtained by this method was 5.92, with an average deviation of 0.28, or 4.7 percent. The average spreading factor for the four different methods used is 5.84.

VISIBILITY OF SPOTS ON M6A1 DETECTOR PAPER

With a knowledge of the spreading factor, the diameter of an airborne spherical drop can be obtained from the diameter of the red spot it produces on M6A1 detector paper. In order to determine the size of the red spot or spots that can be seen under different illuminations, a series of 48 one-inch squares of detector paper was prepared upon which were placed 1, 5, 10, 20, 40, and 80 drops of various sizes to give circular spots 130 to 751 μ in diameter on the paper. These drops were distributed as uniformly as possible, and there was no merging of spots to form a spot larger than that which would be caused by a single drop. The majority of the squares of paper requiring only one drop were prepared using the Teflon capillary method. For a few of the squares of detector paper requiring only one drop and for all the other squares prepared, the electrical dispersion method was used. Several capillaries were prepared for use in the electrical dispersion method to cover the range of drop sizes necessary for these squares. After each square was prepared, it was examined under a microscope to make sure the drops were of uniform diameter, of the right size, and in the right number. After all the squares were made they were mounted on 8.5 by 11 inch white cardboard as shown in Fig. 2. The squares were arranged in rows of 1, 5, 10, 20, 40, and 80 drops per square, and in columns in which the diameter of the red spot increased from 130 to 751 μ (22 to 130 μ drops in air).

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square, with the drop diameters in air (130 to 751 μ)

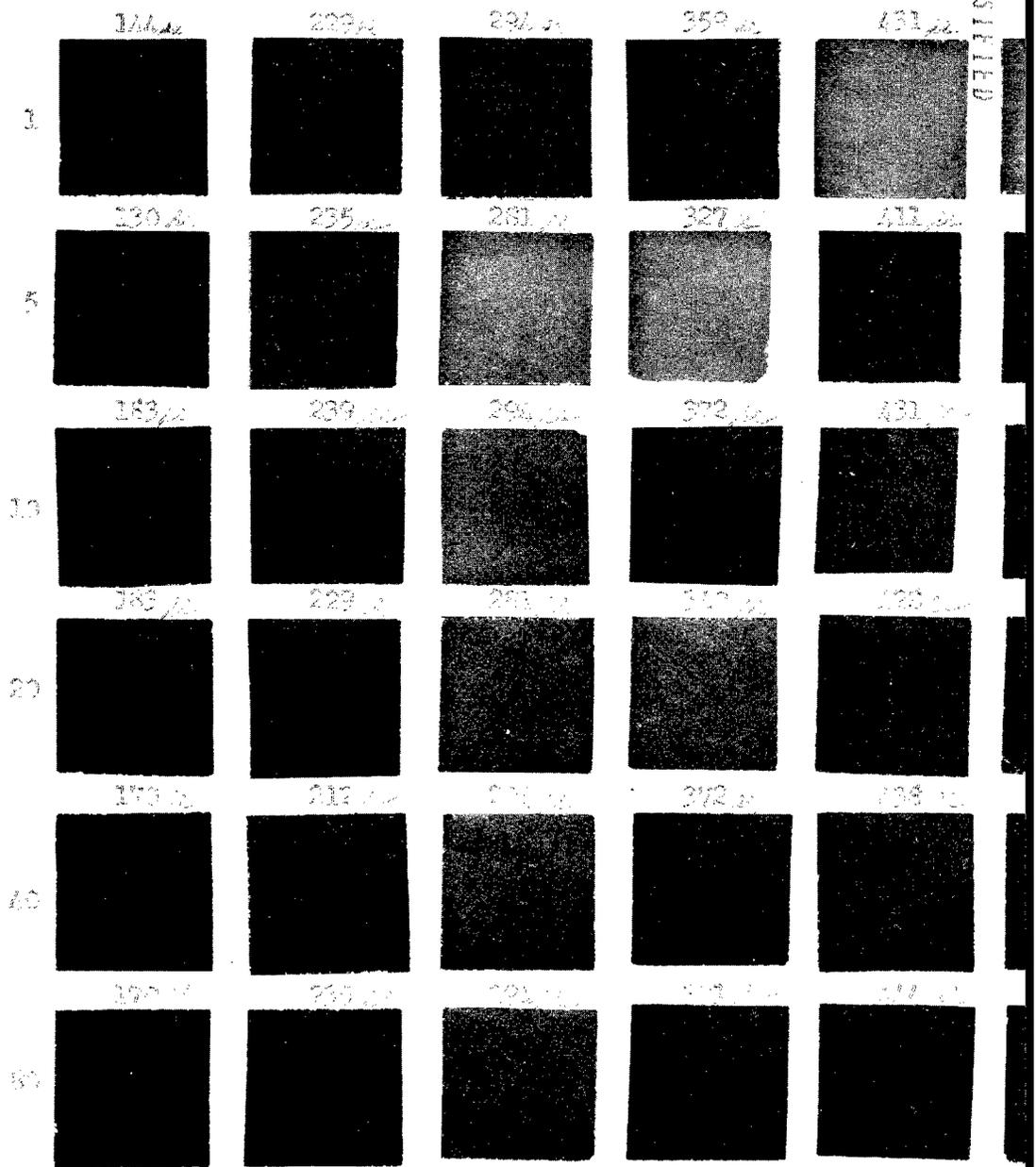


Fig. 2 - One-inch squares of detector paper arranged in rows of 1, 5, 10, 20, 40, and 80 drops per increasing from 22 to 130μ from left to right (spot diameters increasing from

The original mounted squares of detector paper were examined by 11 people under incandescent tungsten illuminations of 1.4, 11, 17, and 47 foot-candles (fc) at distances of 1, 2, and 4 feet to determine whether the red spots were visible. The illumination was measured as incident light with a light meter* oriented with the sensitive surface parallel to the surfaces observed. Several readings were made over the entire surface of the cardboard to be certain that the same amount of light was falling on all the squares.

For the 1.4, 11, and 17 fc illuminations, overhead frosted light bulbs were used, and for the 47-fc illumination, one overhead bulb and one flood lamp with the optical axis approximately perpendicular to the detector paper were used. Tables 5 and 6 indicate familiar intensities to which the illuminations used can be related.

Of the 11 people used for this study, five wore glasses all the time, four wore glasses for close work, and two did not wear glasses. Of the people who wore glasses all the time, four wore bifocals. All of the observers were laboratory personnel accustomed to careful work; none were color blind. The observations were made in an isolated room which offered a minimum of distractions. The observers were told that the squares

TABLE 5
Typical Levels of Indoor Illumination,
Good Current Practice

Illumination (fc)	Location or Task
5	Simple seeing tasks in offices; hallways and corridors in schools and offices.
10	Stairways and washrooms in schools and offices; general lighting in homes.
20	Writing and casual reading in homes; school gymnasiums.
30	General office work; school classrooms, libraries, shops, laboratories.
50	Bookkeeping, drafting, transcribing.
100	Close laboratory work; fine bench and machine work in shops.

*Metravo Universal AC and DC Test Meter and Lightmeter, Lux Scientific Instrument Co., New York, N.Y.

TABLE 6
Low Levels of Natural Outdoor Illumination;
Winter; Latitude of Washington, D.C.;
Clear Sky

Time Relative to Sunset (minutes)	Illumination in Direction of Sunset (fc)	Illumination 180° from Direction of Sunset
-10	90-135	-
- 5	50-61	20-24
0	32-40	12-15
+ 5	19-25	8-10
+10	10-13	3.5-4.5
+15	5-7	1.4-2
+20	1.5-2.8	0.4-0.8

were arranged in rows and columns, and that they should observe one row at a time, starting at the top row and scanning from left to right. They were instructed to report any square with one or more red spots.† A short time was allowed for the eyes to become accustomed to the changes in the illumination. A summary of the size of spots seen by these 11 people at different distances and under different conditions is given in Fig. 3. The data show the number of persons able to see one or more spots per square under the indicated conditions of distance and illumination.

The data are also plotted in Fig. 4, which shows the effect of the illumination, the size of the spot, the number of spots, and the distance of the observer from the squares. The curves indicate the approximate size of spot or spots that were visible to 9 out of the 11 observers.

For each degree of illumination, the lateral displacement of the curves shows the effect of distance on the visibility, while the slope of each curve shows the effect of the size and number of spots on the visibility.

In Table 7, the data of Fig. 3 are normalized in terms of the angular size of the spot or spots just visible to 9 out of the 11 observers. This was done in an effort to eliminate the variable of the observers' distance from the spots on the paper.

†The following statement was used to instruct all observers: "You will stand at distances of 1, 2, and 4 feet under different illumination. The rows are lettered A through F, and the columns are numbered 1 through 8. Read from left to right in each row until you can distinguish one or more red spots on the green background. Report only those spots which are visible without undue strain."

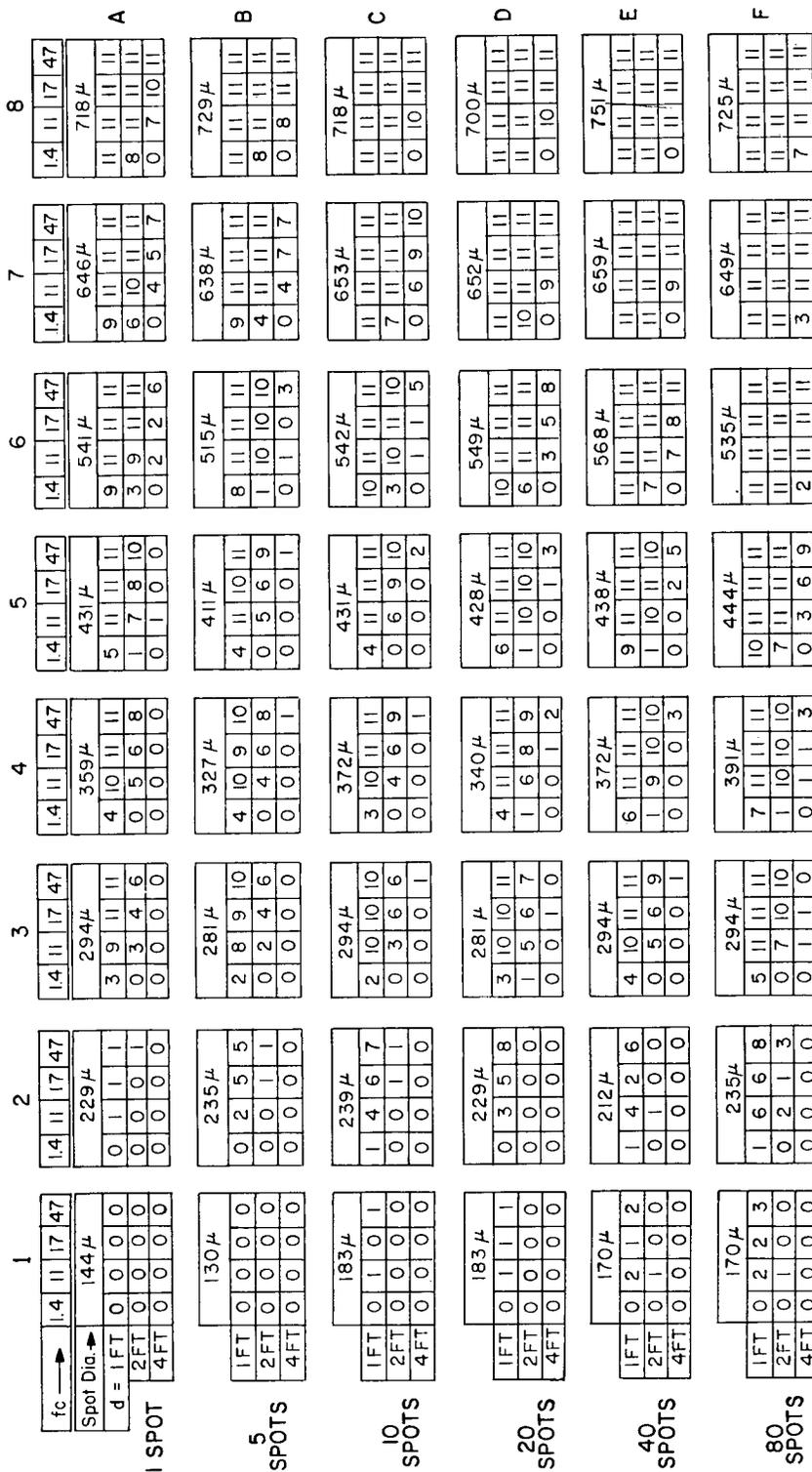


Fig. 3 - Number of observers out of 11 reporting distinguishable spots in the squares arrayed as shown in Fig. 2 when viewed at distances of 1, 2, and 4 feet and under illuminations of 1.4, 11, 17, and 45 fc

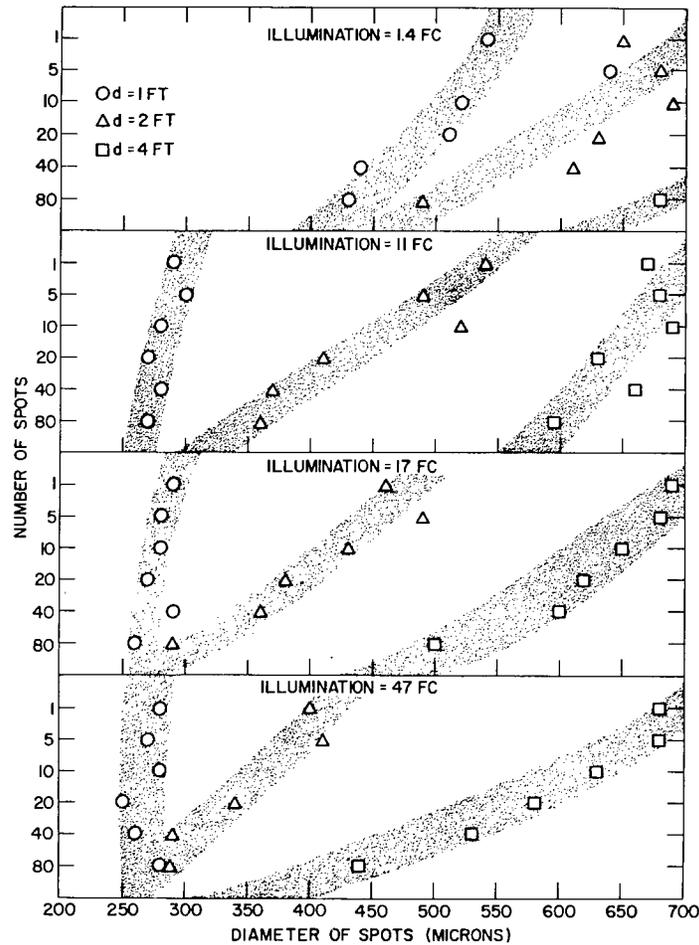


Fig. 4 - Number and size of spots visible to 9 out of the 11 observers for the various illuminations and viewing distances

From Fig. 4 and from Table 7, it can be readily seen that at a distance of 1 foot there is essentially no difference in the visibility of the drops under illuminations of 11, 17, and 47 fc. This indicates that little is gained in visibility at 1 foot by increasing the intensity beyond 11 fc. The difference in visibility of the spots with illumination under these three illuminations is noticeable at 2 feet and at 4 feet, but the variation is small. A pronounced difference in visibility is noticed between 1.4 fc and the more intense illuminations; this is shown by a lateral shift in the curves for 1.4 fc relative to the curves at higher illuminations. The slope of the curves indicates that a distance of 1 foot under illuminations of 11, 17, and 47 fc, the number of spots present has little effect on the visibility.

Table 7 was constructed in an attempt to eliminate the factor of distance in considering visibility,

the assumption being that in principle the angle subtended by spots just visible would remain constant. However, the assumption proved not to be true in this experiment, as is clearly shown by comparing the angular sizes of the spots just visible at 1, 2, and 4 feet. Two factors are postulated to reduce the visibility of the spots per unit angular size at the shorter distances. The principal reason for the lower visibility of the spots per unit angular size, at the shorter distances is believed to be the characteristic farsightedness of advancing age, presbyopia. A second factor is that the observers who wore reading glasses at the shorter distances and none at the longer distances would experience a total light loss of 9 or 10 percent (4.5 to 5 percent at each glass-air surface). This effect would be substantial, however, only under marginal illumination. Other factors

TABLE 7
 Smallest Spots on M6A1 Paper Detected by 9 out of the 11 Observers;
 Spot Size, Illumination, and Observers' Distance d Varied

Illumination (fc)	No. of Spots	d = 1 ft		d = 2 ft		d = 4 ft	
		Smallest Size Seen (μ)	Angular Size (Min. of Arc)	Smallest Size Seen (μ)	Angular Size (Min. of Arc)	Smallest Size Seen (μ)	Angular Size (Min. of Arc)
1.4	1	540	6.1	650	3.7	—	—
	5	640	7.2	680	3.8	—	—
	10	520	5.9	690	3.9	—	—
	20	510	5.8	630	3.6	—	—
	40	440	5.0	610	3.4	—	—
	80	430	4.9	490	2.8	680	1.9
11	1	290	3.3	540	3.0	670	1.9
	5	300	3.4	490	2.8	680	1.9
	10	280	3.2	520	2.9	690	1.9
	20	270	3.1	410	2.3	630	1.8
	40	280	3.2	370	2.1	660	1.9
	80	270	3.1	360	2.1	520	1.5
17	1	290	3.3	460	2.6	690	1.9
	5	280	3.2	490	2.8	680	1.9
	10	280	3.2	430	2.4	650	1.8
	20	270	3.1	380	2.2	620	1.8
	40	290	3.3	360	2.0	600	1.7
	80	260	2.9	290	1.6	500	1.4
47	1	280	3.2	400	2.3	680	1.9
	5	270	3.1	410	2.3	680	1.9
	10	280	3.2	370	2.1	630	1.8
	20	250	2.8	340	1.9	580	1.7
	40	260	2.9	290	1.6	530	1.5
	80	280	3.2	290	1.6	440	1.2

may also have been influential in producing the anomaly, such as more complete accommodation of the observers' eyes to distance at the greater distances. This effect seems plausible in that all observations started at 1 foot and progressed to the larger distances; during the observations accommodation could progress.

HAZARD CORRESPONDING TO VISIBLE SPOTS

It is desirable to translate the data of Table 7 into estimates of corresponding hazard to ship-board personnel when the liquid which produces the spots on M6A1 paper is in fact a highly toxic

chemical warfare agent. It will be assumed that the toxic liquid has a spreading factor of 4.5, a figure comparable with unpublished average data. Thus, the single 290- μ spot, which was detected by 9 out of 11 laboratory personnel at a distance of 1 foot under an illumination of 11 fc or more, is equivalent to an airborne sphere of 65 μ diameter (i.e., 290/4.5). This is a volume of 0.14×10^{-6} ml and, assuming a specific gravity of unity, is a weight of 0.14 microgram.

The extent of deposition of windborne droplets per unit area on a relatively large object such as a man is generally less than on the 1- or 2-inch-diameter cylinder commonly used as the support for M6A1 paper in the Navy. If a man is regarded as a 10-inch-diameter cylinder, the collection efficiency of the man, as well as of the 1-inch cylinder can be calculated (24-27). Table 8 presents such data.

It is recognized that both the clothed and unclothed surfaces of the human body are better collectors, in general, than the surface of a 10-inch smooth cylinder. This effect is due to the folds, creases, protuberances, and hair or nap of both the body surface and clothing, which all act as portions of much smaller cylinders. Thus the actual collection efficiency of the man will be between that for the 1-inch and the 10-inch cylinders. The error in an assumption that the man's collection efficiency is 1/2 that of the 1-inch cylinder of detector paper for 65-micron particles probably will not be large. It will further be assumed that the man-cylinder is 6 feet tall and therefore presents to the wind a surface of 5 square feet, or 720 square inches. Consequently, when one 65- μ particle is detected on a square inch of the paper, the average man exposed to the same wind and the same concentration of airborne particles will be contaminated with $720 \times 1/2 = 360$ particles. This is a weight of 360×0.14 microgram or 50 micrograms.

The physiological and military significance of a 50-microgram deposit (0.05 mg) of toxic chemical warfare (CW) agent on a man and/or his clothing depends on at least four factors:

1. The extent to which the body is covered with clothing or other protective equipment, such as the protective (gas) mask.

2. The protective value of the clothing and accessories. This is often expressed as a "protective factor," which is the ratio of the LD50 (average lethal dose) of a particular agent depos-

TABLE 8
Approximate Collection Efficiency* of Smooth Uniform Cylinders For Airborne Particles of Unit Specific Gravity at Various Wind Speeds

Particle Diameter (μ)	Wind Speed (knots)	Collection Efficiency (%)	
		1-Inch-Dia. Cylinder	10-Inch-Dia. Cylinder
50	1	0	0
50	10	50	0
50	30	75	20
65	1	10	0
65	10	70	10
65	30	90	35
80	1	15	0
80	10	75	15
80	30	100	50
100	1	30	0
100	10	80	30
100	30	100	60
150	1	50	0
150	10	100	50
150	30	100	75
250	1	75	15
250	10	100	75
250	30	100	100

* These figures do not take into account the settling velocity of the particles, which are 2/3 mph for 100 micron drops, 1-1/3 mph for 150 micron drops, and 4 mph for 250 micron drops. The effect of these terminal velocities on the collection efficiency of the cylinder is somewhat complex but is probably to increase slightly the lower efficiencies at the lower wind speeds.

ited on the clothing to the LD50 when the agent is deposited directly on the skin.

3. The intrinsic percutaneous toxicity of the agent itself. This varies with the part of the body exposed, and is much higher for a droplet in the eye, for example, than for a droplet on the hand.

4. The effective time of exposure, that is, the time the deposit remains on the skin or clothing before cleansing of the skin or removal of the clothing occurs.

The magnitude of factor 1 is inherently unpredictable. It can be pointed out, however, that unless correct and adequate chemical warfare protection is in effect, topside shipboard personnel

in all but the coldest climates will expose some part of their bodies to direct CW contamination.

Factor 2, the protective value of body covering, has not been well evaluated for typical shipboard clothing. It is known that woolen uniform fabrics afford relatively good protection, and that cotton fabrics, especially thin materials such as chambray and denim, are relatively poor. Two layers of any fabric give a protective factor considerably higher than double the factor for one layer. A comparatively impermeable garment, such as rain clothing, provides good protection as long as the closures at the face, wrists, and ankles are tightly closed, and until gross penetration of the fabric itself occurs. It can be estimated that the protective factor of a single layer of well-worn chambray, pulled tightly against the skin, is 5 or less, perhaps as small as 2 for large drops of liquid. The protective factor for most permeable fabrics is less for large drops and more for small ones. In addition, the protective factor for any woven fabric or garment will be less for large fast-moving liquid drops than for the same drops moving at slower speeds. This effect is important at sea because of the characteristically high relative winds on ships underway.

Factor 3, agent toxicity, is reasonably well-known. For the purposes of this report it can be taken to be somewhat greater than the intraocular lethal dose of 10 mg cited by Kondritzer (28), and 25 mg will be selected. One-tenth of this LD₅₀, or 2.5 mg, will be assumed to have marginal or harassing effects. Thus the 50-microgram deposit can be assumed to be of the order of 1/500 of a lethal dose on the skin, or 1/50 of a harassing dose.

Factor 4, time of exposure, is readily controllable, provided that the instant at which contamination occurs is known and that military duties permit cessation of the exposure and consequent countermeasures. The necessary contamination signal can be given by means of M6A1 paper plus an alert watch. In general, the modern low-volatility CW agents do not penetrate skin or clothing as rapidly as does mustard gas. Therefore, except for contamination of the eyes, a useful amount of time (29) is normally available in which to reduce the hazard of CW deposits by removal of contaminated clothing and/or cleansing of the skin. It must be noted, however, that in the case of eye contamination by any liquid CW agent, the time in which even partially effective decontamination can be performed is extremely short—a matter of

seconds. For example, Kondritzer, *et al.* (30) have shown that, of a drop of GB in the eye, one-third cannot be removed 5 seconds after contamination, one-half cannot be removed 15 seconds after contamination, and essentially none can be removed after 1 minute.

To aid further in evaluating the significance of the 0.05-mg deposit on a man, which is detectable as a single spot on the M6A1 paper, the protective value of various types of clothing must be considered. To do this, rough estimates are made in Table 9 of the protective factor (PF) afforded by various types of shipboard clothing. In addition, a new term, the integrated protective factor (IPF), is introduced to describe the overall, or average, protective factor afforded in situations where small fractions of the body area, such as hands, head, and neck, are entirely bare.

It must be emphasized that neither the PF figures used nor the fraction-clothed figures have any exact significance. Rather, the purpose of presenting these data is to show the dramatic reduction in overall protection brought about by failure to utilize completely the inherent protection of the clothing available. In addition, the IPF concept may, in the future, be capable of more refined utilization as experimental values of the PF's of standard shipboard uniforms become available. It must be pointed out that the IPF's given in Table 9 assume that all parts of the body are equally vulnerable to a liquid chemical warfare agent. This assumption is made because the present purpose is largely to introduce the IPF concept and to demonstrate the decrease in the practical value of M6A1 detector paper when exposed personnel are incompletely protected. Recent data by Sim (31) point out, however, that there are in fact striking differences in the toxicity and speed of action of VX when applied to different parts of the human body. It is the head, face, and neck which are by far the most sensitive to VX penetration; it may be estimated that the overall sensitivity of the head (not including the eyes or immediately adjacent tissues) is perhaps 20 times as sensitive as the back, and 5 to 10 times as sensitive as the forearm. It is, therefore, clear that the practical sensitivity of M6A1 paper, as well as the entire BW/CW protective system of the ship, is degraded even more seriously by incomplete protection of the head areas of topside personnel than is suggested by Table 9.

TABLE 9
Estimate of Fraction of External CW Deposit Absorbed by Men Variouslly Clothed

Clothing Type	PF: Protective Factor of Clothing	Fraction of Body Clothed	IPF: Integrated Protective Factor*
None	0	0	1
Tropical	5	1.0	5
	5	0.8	2.8
Temperate	10	1.0	10
	10	0.9	5.3
Cool Weather	20	1.0	20
	20	0.9	6.9
Cold Weather	100	1.0	100
	100	0.95	16.8
Impermeable	1000†	1.0	1000
	1000†	0.90	9.9
Impermeable	1000†	1.0	1000
	1000†	0.95	19.6

* IPF = PF / (fraction of body clothed + PF × fraction unclothed), obtained by taking the ratio of the LD50 for deposit on a partially clothed body to the bare-skin LD50.

† For limited periods.

LIMITATIONS ON THE VALUE OF THE M6A1 DETECTOR PAPER RESPONSE

At this point the data and estimates presented above will be reviewed. Although by no means exact in some instances, they clearly indicate that M6A1 detector paper has a maximum detection capability, under favorable circumstances, approximately equivalent to a 50-microgram deposit on a man or his clothing. Based on Kondrizer's estimate of 10 mg as the intraocular human LD50, the 50 micrograms is of the order of 1/500 of a bare-skin lethal dose. The protection afforded by any type of shipboard clothing is significant, and may be very high, provided that *all* parts of the body are fully covered. However, when the

potential protection of any type of clothing is incompletely utilized by leaving even a small fraction of the body uncovered, the overall protection may be heavily degraded, and this degradation is most serious for the clothing system having the greatest potential protection.

In the previous discussion of the performance of M6A1 detector paper, it has been stated that favorable conditions were assumed when citing 50 micrograms as the minimum detectable deposit per man. Two of these conditions which applied during the laboratory study were adequate illumination and attentive, well-motivated observers. The application of these conditions or restrictions to an operational situation is clear. Moreover, they are subject to some control. For

example, watchstanders charged with observing M6A1 detector paper cylinders can be trained and tested for performance, and provision can be made for night observation of the cylinders by removal to a lighted area.

A third favorable condition, which, by implication, applied throughout the laboratory study, is of major operational significance. Moreover, it is not subject to control as are illumination and observer motivation and training. Recognizing this factor, however, allows forearmng against it. Specifically, the condition referred to is that the 50-microgram deposit per man corresponds to an attack so light as to be highly improbable. When a single 65-micron airborne drop was found to be the minimum detectable quantity on a square inch of detector paper, it might be tacitly assumed that this quantity and no more indicated the strength of the CW attack. Such an attack poses little or no threat, even to a totally naked topside crew, and in fact makes the use of M6A1 paper entirely superfluous. An attack of this intensity must be assumed to be less likely than one capable of producing casualties.

Let us consider other, and more probable, intensities of attack, the response of M6A1 paper to such attack, and the overall demand placed on the BW/CW defense system of the ship. Two types of nerve-agent aerosol attack can be readily visualized. One is with a heavy concentration of approximately 65- μ droplets, such that a detector paper cylinder collects many droplets in a few seconds. The other attack uses larger drops, say 250 μ in diameter, but relatively few in number. (A real attack probably would in effect approximate a mixture of these, plus droplets of intermediate and smaller sizes. However, since the smaller sizes have little effect due to inability to impinge appreciably on a man, and since the two attacks postulated can be shown to have roughly equivalent effects, it is convenient to discuss the two model attacks only.)

In the first case, if one hundred 65- μ drops impinge on the paper almost simultaneously, or even within a period of perhaps half a minute, this becomes in effect the minimum detectable quantity, or, at least, the minimum quantity actually detected. The dose per topside man also is multiplied by 100 (and may continue to increase before useful countermeasures can be taken). One hundred times the original dosage of 50 micrograms is 5 mg, which is in the range

of one bare-skin LD50. With a high integrated protective factor and an effective BW/CW defense system, this dosage or a higher one need not have significant toxic effects on personnel. On the other hand, a weak training effort and/or meager preattack preparations are certain to result in a high casualty rate and a serious loss of the ship's fighting efficiency in this type of attack.

The second case, that of the attack with 250- μ drops is essentially the same, in its effect, as that just described. The weight of a single 250- μ drop is 64 times that of the 65- μ drop originally assumed. Moreover, drops of this size are collected with the same efficiency by the 10-inch and 1-inch cylinders. (It will be recalled that a man's collection efficiency for 65- μ drops is assumed to be 1/2 of a 1-inch cylinder of detector paper.) Therefore the topside dose per man is $2 \times 64 \times 50$, or 6400 micrograms, or 6.5 mg, again in the range of one LD50. This dosage may also be increased as the drops accumulate on the man or his clothing before countermeasures are effective.

The situation outlined above, in which certain plausible types of chemical warfare attack can greatly reduce the usefulness of M6A1 detector paper, does not reflect deficiencies of the paper as such. Instead, the fault is the common fault of all "point-source" or local chemical warfare detectors and alarms when subjected to a concentrated attack. Under these conditions, even an instantaneous response time, whether of a fully automatic alarm or of a man-M6A1 combination, is much reduced in value because of the heavy dosage received by topside personnel before postattack defensive measures begin to operate. In concentrated attacks, therefore, M6A1 detector paper is still a necessary item in the BW/CW defense system in order that an attack may be promptly identified as such, but the controlling factors in the effectiveness of the defense are the taking of all available personnel-protective measures before the attack, plus the prompt and professional prosecution of postattack measures such as personnel decontamination, self-aid, and therapy.

SUMMARY AND CONCLUSIONS

The minimum liquid agent dosage per man detectable by M6A1 paper is about 50 micrograms as 65- μ droplets. This probably is less than

0.01 LD50 on the bare skin. The 50 micrograms becomes an even smaller fraction of an LD50 when deposited on clothing, although it has been shown that the protective value of clothing can be largely nullified if a man's body is not completely covered.

While M6A1 paper can detect instantaneously a man-dose of 50 micrograms, such a dose is probably small in that its military effect is negligible. The paper can detect more concentrated attacks no faster than instantaneously, and its usefulness therefore declines as the intensity of attack increases. This characteristic is common to all present or developmental CW detectors. In the heavy attack, therefore, the man-paper combination can still report or affirm the attack, but not in time to warn topside personnel to don protective clothing and masks. Accordingly these personnel protective items must be in place prior to heavy CW attacks. The various postattack countermeasures can then be triggered by an M6A1 signal to proceed on a smooth and suitably rapid schedule.

RECOMMENDATIONS

1. It is recommended that M6A1 detector paper, together with any other* available detector paper for chemical warfare agents, be evaluated aboard ship using typical enlisted watchstanders under various conditions of natural illumination.

2. To circumvent the dual problem of droplet detection at night and of possible inattention of watchstanders, it is recommended that an effort be made to develop a simple automatic photoelectric device to detect instantaneously the effect of liquid CW agents on a detector paper.

3. It is recommended that, for use in combination with item 2, a device be developed to allow the sampling of a much larger volume of air than is the case with the present 1-inch cylinder of M6A1 paper moving through the air at ship velocity.

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*Appendix B considers the potential improvement in visibility of spots on paper relative to the visibility experienced using M6A1 paper.

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APPENDIX A LIQUID LENS TECHNIQUE FOR DETERMINING DROP SIZES

The size of an airborne spherical drop can be obtained from the diameter of a liquid lens on a glass slide, plus the focal length of the liquid lens, according to a method outlined by May (Ref. 23 of the text). In this study the diameter of the liquid lens was measured with a binocular microscope fitted with a calibrated reticle. The focal length was obtained by focusing on the edge of the spherical drop on the glass, centering the drop in the microscopic field and then racking up the microscope with the micrometer drum until a distant illuminated object was brought into focus with the aid of the plane substage mirror. The focal length of the lens was equal to the vertical distance indicated by the micrometer drum. The theoretical relationship of the original spherical drop size to the diameter and the focal length of the lens has been shown by May, and it will suffice here to indicate the graphical solution that was used. In the graph reproduced (Fig. A1) from May's paper f' represents the focal length of the lens, A represents the radius of the periphery of the liquid lens, and μ represents the refractive index of the liquid (1.5 for diethyl phthalate). The ratio of $f'/2A$, which was found by microscopic measurements, gives a point on the

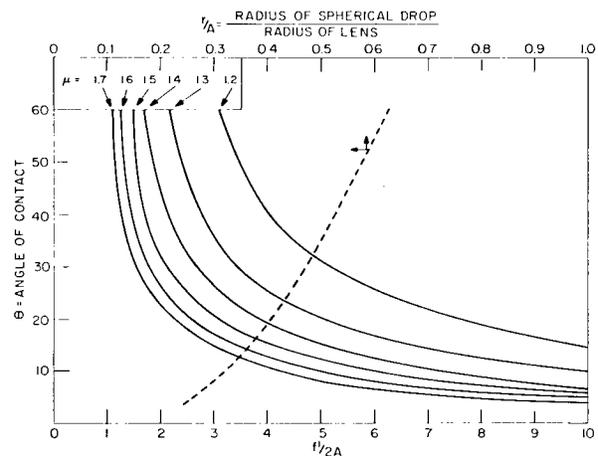


Fig. A1 - Theoretical relationship of the spherical drop radius r to the lens radius A and the focal length f' . To read the upper abscissa values, points on the curves must be translated horizontally to the dashed curve.

$\mu = 1.5$ curve. A horizontal line from this point intersects the dotted curve at a point which can be read off the upper abscissa r/A . By multiplying the observed lens diameter by the factor r/A the spherical airborne drop diameter is obtained.

**APPENDIX B
EXPERIMENTAL VS IDEAL VISIBILITY
OF SPOTS ON M6A1 PAPER**

It is of interest to estimate the extent to which the spots on M6A1 paper approach the ideal limit of visibility at the illuminations used. Two principal conditions are necessary to attain this limit: maximum brightness of background, and maximum contrast between background and object. These conditions are well represented by India ink spots on a good grade of white card stock under good illumination. Such spots are visible at an angular size of about 0.6 minute of arc under 47 fc illumination. The lower visibility of the M6A1 paper spots is undoubtedly due to deficiencies in both of the principal conditions named above. The relative background brightness of M6A1 paper compared to a white card stock is given by their relative reflectivities. This was measured to be 0.16 to 0.21 for fluorescent light, depending on the angles of viewing and illumination; that is, M6A1 paper has about 1/5 to 1/6 the

brightness of white card stock when both are illuminated to the same extent. The contrast of M6A1 paper spots relative to the paper itself is not easy to determine because both color and brightness are involved. However, the data provided by Luckiesh and Moss* permit the conclusion that a decrease in background brightness to 1/6 would increase the size of a just-visible spot to only about 0.8 minute of arc. Therefore, it may be assumed that the remaining departure of the experimental data from ideal figures is due to a deficiency in contrast. This factor is clearly the one most susceptible to improvement, inasmuch as the best visibility noted for single spots was 1.9 minutes of arc in this investigation.

*M. Luckiesh and F.K. Moss, "The Science of Seeing," New York: Van Nostrand, 1937