

UNCLASSIFIED

Liquid Vesicant Detector Paint M5
 Liquid Vesicant Detector Paper M6
 Liquid Vesicant Detector Crayon M7
 HS Vapor Detector Kit M4

Paint, Liquid Vesicant Detector, M5. This paint was a modification of a British detector paint (130). It was recommended for standardization as Chemical Agent Detector M1 (131). This paint consisted essentially of a paint vehicle, inert pigments, and a dye pigment known as B-1 (p-nitro-phenylazo- β -naphthylamine). The value of this paint as an indicator for H and other liquid persistent agents lay solely in the fact that the dye pigment was soluble in such agents and produced a brilliant red color.

The British paint contained (132):

<u>Ingredient</u>	<u>Parts by weight</u>
Zinc oxide.....	13
Lithopone (30%).....	12
Cadmium lithopone.....	17
Burnt sienna)	
(or burnt turkey umber).....	8
Ochre of F.L.S.)	
Ultramarine blue.....	5
Gold size (type Q).....	35
White spirit.....	8
B-1.....	2

B-1 was a blue dyestuff that dissolved to form a brilliant red solution (133). When mixed with yellows, B-1 formed green; with yellows and brown, khakis and browns. In all the mixtures, however, solution of the B-1 resulted in formation of a red color.

Difficulty was encountered in attempting to duplicate the British formula in this country (134). Therefore, the proportions were varied; and after a series of paints had been prepared, the following was decided as the best on the basis of sensitivity of liquid vesicants, comparative cost, and anticipated stability. This paint consisted of:

130. TDMR 273. 17 May 1940.

131. CWTC Item 296. 12 May 1940.

132. TDMR 273.

133. "Para-Nitrophenyl-azo-Beta-Naphthylamine" Military Intelligence Division (Canada) Specification CS/791, 22 May 1940.

134. TDMR 273.

UNCLASSIFIED

<u>Ingredient</u>	<u>Percent by weight</u>
Cadmium lithopone.....	55
Gold size.....	35
White spirit.....	8
B-1.....	2

Weathering tests showed that this paint had a useful life of not greater than one week when exposed to full sunlight (135). It was believed that the vehicle was responsible, and future work was planned to develop a vehicle that would not dissolve B-1 and would be more resistant to climatic conditions.

The gold size type of vehicle, in common with vehicles containing drying oils, went through a progressive hardening action that was greatly accelerated when exposed to sunlight. This hardening action finally reached a point where the film became impermeable to H, and so its ability to detect H was destroyed. On further aging, the film became brittle and porous and was again permeable to H. When this condition was reached, however, the paint film readily disintegrated.

A further action of sunlight was the destruction of the sensitive agent, B-1. Light alone caused some destruction of this agent in its blue pigment form, but this was not rapid enough to be of any serious consequence.

The action of heat was marked. Due to the increased solubility of the B-1 in the paint film at elevated temperatures, it caused a change in color from greens to drabs or even to tans.

The combined action of heat and light, as in the case of sunlight, first caused a rapid change from green to reddish shades of green, and was followed by the destruction of the red color which was more light sensitive. The rate at which this destructive action took place was proportional to the solvent action of the paint film on the B-1. The solvency was greater in a high-oil-content than in a low-oil-content varnish. The various oils and resins had different solvency effects at elevated temperatures.

The problem resolved itself into a two-phase program: finding a paint that wouldn't dry to a hard, impervious coat; and finding a paint in which the B-1 pigment would not be too soluble.

A suitable varnish for detector paints was developed (136) from ester gum and bodied linseed oil. The proportion of oil in the varnish was kept low - 10 gallons to each 100 parts of the ester gum. The thinner used was

135. "Chemical Agent Detector, Gas Detector Paints, Weathering Tests,"
TDMR 281, 24 Apr 1941.

136. TDMR 314, p. 18.

UNCLASSIFIED

UNCLASSIFIED

a pure petroleum product of low-solvent number; the drier, manganese naphthionate, one liquid ounce (6.0 percent Mn as metal) to each gallon of varnish.

The following detector paint formula was developed:

<u>Ingredient</u>	<u>Parts by weight</u>
Cadmium lithopone.....	57
Varnish.....	32
B-1.....	2
Mineral spirits.....	9
Drier.....	1 oz. to each gallon

The above paint became known as Type I (137). Another was designated Type II. Its formulation was:

<u>Ingredient</u>	<u>Parts by weight</u>
Hansa Yellow G.....	11
Lithopone.....	33
Varnish.....	44
Mineral spirits.....	10
B-1.....	2
Drier.....	1 oz. to each gallon

These two new paints became standardized as Liquid Vesicant Detector Paint M5, and Chemical Agent Detector M1 was destandardized (138).

A Type III paint was later developed (139). It was optional to manufacturers to choose the type they wished to make. The formulation of this Type III was:

<u>Ingredient</u>	<u>Parts by weight</u>
Chrome yellow.....	28
Magnesium silicate.....	19
Varnish.....	40
Mineral spirits.....	11
B-1.....	2
Drier.....	1 oz. to each gallon

137. "Paint, Liquid Vesicant Detector, M5," Chemical Warfare Service Specification (hereinafter CWS Spec.) No. 197-54-192, 2 Apr 1942.

138. CWTC Item 456; CWTC Item 483.

139. CWS Spec. No. 197-54-192.

36
UNCLASSIFIED

UNCLASSIFIED

~~CONFIDENTIAL~~

The use of these paints was simple. They were stirred up like normal paints, and if any thinning was needed, mineral spirits were used. Painting was in the normal manner, spray gun or brush, and any surface could be painted. Contact of liquid droplets of chemical agents with the paint produced red spots. There were a few interferences in the form of organic solvents such as acetone, nitrobenzene, methyl salicylate, and acetylene tetrachloride, a constituent of DANG. Most gasolines and lubricating oils did not interfere, but those containing aromatics did show some reddening on standing.

The paint was olive-drab in color. It was touch dry within two hours, but a considerably longer time was required for complete dryness. For this reason, it was advisable to carry out painting in the late afternoon or evening to permit overnight drying. The paint lost much of its sensitivity if exposed to the heat of the sun while wet.

The length of life of the paint under continuous exposure to severe conditions of heat and sun could safely be considered as two to three weeks. Under milder conditions, the life was much longer, extending under temperate conditions to months. When the color of the paint turned to yellow, it indicated that the usefulness of the paint had been destroyed by light. In general, conditions which caused the deterioration of ordinary paint, also affected the detector paint. Conditions of extreme heat, above 150°F, caused the paint to turn reddish brown because of solution of the B-1 in the paint film. In this case, it was advisable to repaint the surface because of possible confusion. The paint was service tested, and the conclusion was drawn that (140):

1. It complied with the military characteristics set up by CWTC Item No. 296.
2. It had a sensitive life of at least one month when exposed to severe summer conditions such as prevail at Edgewood Arsenal, Maryland, in the month of August.
3. At least five successive layers of detector paint could be applied without excessive peeling.
4. Color change produced in the paint was a reliable indication of the type of vesicant used.
5. When in contact with DANG or M4 ointment, the paint underwent a color change similar to that caused by contact with liquid H.

140. "Paint, Liquid Vesicant Detector, No. 5," CWB Project No. 339,
22 Oct 1943.

UNCLASSIFIED

UNCLASSIFIED~~CONFIDENTIAL~~

6. Paint applied to the surfaces of a vehicle was not seriously affected by the wear incident to the operation of the vehicle over all types of terrain.
7. Detector paint was satisfactory for use on leggings and helmets.

The paint was tested under conditions of extreme cold, with the following results (141):

1. Paint mixed easily at temperatures down to minus 25°F.
2. Paint was applied easily at temperatures down to 0°F.
3. Paint dried on a metal surface:
 - a. In 20 hr. at 15°F.
 - b. In 30 hr. at minus 5°F.
4. Liquid H placed on a painted metal panel at a temperature of:
 - a. 34°F. caused a color change in less than one minute.
 - b. Minus 5°F. in two minutes.
5. Exposure of painted panels to alternate warmth (65°F.) and extreme cold (0 to minus 25°F.) for a period of 15 days did not noticeably crack or peel the paint.

Paper, Liquid Vesicant Detector, M6. The detector paper was a modification of the Liquid Vesicant Detector Paint M5 in that it represented a prepared use of the paint. It was standardized with the paint (142).

Light Bristol board was roller-coated with the paint, cut up, and bound in small booklets for issue (143).

The use and limitations were similar to those of the paint, except that none of the problems in the application and drying of paints were present.

Sheets of detector paper were detached from the booklets and placed, olive-drab-color side up, on a surface fully exposed to the fall of liquid agents. Drops of liquid agent produced red spots on touching the paper.

141. "Test of CWS Materiel in Extreme Cold," CWB Project No. 426, Appendix AA, 23 Feb 1944.

142. CWTC Item 456; CWTC Item 483.

143. "Paper, Liquid Vesicant Detector, M6," CWS Spec. No. 197-54-231, 5 Dec 1942.

~~CONFIDENTIAL~~
UNCLASSIFIED

CHAPTER VI

Description of Standard ItemsKit, H Vapor Detector, M4 (Limited Standard)

Military Requirement. A kit to detect and identify mustard and nitrogen mustard vapors.

Description. The carrier is a small wooden box, 7-3/4 x 4-1/2 x 3-1/2 inches, with a carrying handle. The contents consist of: (1) a one-ounce jar containing thirty-six detector tubes; (2) a one-ounce jar containing developing solution; (3) a one-ounce jar containing test reagent; (4) a medicine dropper and holder; (5) a box of safety matches; (6) a set of instructions (CWS Instructions No. 23); and (7) a rubber sampling bulb (see fig. 27). When filled it weighs 2 pounds.

Operation. One man, usually a gas NCO, operates the gas detector. A tube from bottle A is placed in the hole of the rubber bulb, red dot forward. The bulb is squeezed and released several times to draw a sample of air through the tube. The tube is heated by means of a flame until the red dot turns yellow. On cooling, a few drops of solution from bottle B are added by means of the medicine dropper. A blue color indicates the presence of mustard or nitrogen mustard.

Packaging. Each kit is packed in an individual, regular slotted-style, double-faced, corrugated fiberboard box.

Packing. Ten kits, in their individual cartons, are packed in either a cleated plywood box or a nailed wood box equipped with a water proof paper liner. The box has inside dimensions of 27 x 8-1/8 x 8-3/4 inches.

Paint, Liquid Vesicant Detector, M5 (Standard)

Military Requirement. A paint to be applied to surfaces to indicate the subsequent presence of liquid vesicant.

Description. The paint is an olive drab paint that dries in about 5 hours.

Operation. The paint is handled much like an ordinary paint. It is stirred up and applied with a brush. Contact of liquid vesicant with the paint produces a red spot.

Packaging.

1. 4-oz., round, friction-top metal cans.
2. 32-oz., round, friction-top metal cans.

molten iron at very high temperature according to the following equation:



The magnetic oxide of iron (Fe_3O_4) may also be used in the thermit mixture. It reacts as follows:



Various binders have been used to prevent the components of the thermit from segregating. When sulfur is used as a binder the special thermit produced is called *Daisite*. All thermites require a means of ignition at a high temperature.

d. White phosphorus in explosive shell or air bombs is an effective incendiary against grass, woods, and buildings of light wood construction. Combustible oils mixed with a soap or jelly producing substance have been used as solid oils for incendiaries. Small pieces of metallic sodium are frequently added to the solid oil to prevent the fire from being easily put out by water, since the sodium reacts with the water to rekindle the oil fire.

e. Incendiary munitions are marked with one (1) purple band, the symbol of the agent, and the word "Incendiary."

158. **Other possible agents.**—a. Carbon monoxide is formed by every gun blast, bursting shell, and in every fire burning in a closed space, as well as by automobile exhausts and in countless other ways. Carbon monoxide has been suggested as a chemical agent since little protection against it is afforded by the ordinary gas mask. However, carbon monoxide is lighter than air and its concentration is rapidly reduced by diffusion, except in closed spaces. It has about the same toxicity as chlorine. It cannot be held as a liquid in the ordinary light cylinder or shell. The chance of anyone's successfully using carbon monoxide is thus very small but should be held in mind. Carbon monoxide is very insidious in its action, the victim gradually and painlessly passing into a coma before death occurs.

b. Hydrocyanic acid was used by the French in a solution with arsenic trichloride, called *Vincennite*. The material was practically useless. The French supplied the American army with many thousands of these shell. The Germans were said to have successfully mixed hydrocyanic acid with phosgene as a filling for Livens projectors. This has not been confirmed. As yet no method for the successful application of this agent in the field has been proposed. Its low vapor density compared to air renders its use in the field difficult.

as in the case of carbon monoxide. Hydrocyanic acid is about 10 times as toxic as chlorine or carbon monoxide.

c. Carbon monoxide and hydrocyanic acid affect the nerve and functions of the body. Carbon monoxide reacts with the red color matter of the blood and renders the blood incapable of taking oxygen and distributing it to the body. Hydrocyanic acid paralyzes the central nervous system and the heart, and prevents the oxygen by the body. A number of substances which act in a more or less similar manner to these two substances are known, but none of them seem to have the properties requisite in a chemical agent.

SECTION IV

SIMULATED AGENTS

	Paragraph
General.....	159
Simulated HS (molasses residuum).....	160
Simulated HS (asbestine suspension).....	161

159. **General.**—Since the war a number of substances having physical properties similar to mustard and generally containing a dye and an odoriferous constituent have been tried as a substitute for mustard in testing mustard dispersion apparatus and munitions and for training purposes. Almost all, however, had some disadvantageous feature, such as instability, corrosive action on metals, difficulty of removing stains produced by the material, relatively high cost, etc., and in the case of those containing aniline and nitrobenzene some toxicity. The two following mixtures are believed to be best suited, and have been adopted as standard.

160. **Simulated HS (molasses residuum).**—a. *Composition.*—This simulated agent is a 25 percent solution (by volume) in water of the thick sirupy residue obtained in the manufacture of ethyl alcohol from molasses by evaporating the solution of fermented molasses after the ethyl alcohol has been distilled off.

b. *Physical properties.*—(1) As obtained from industry the concentrated molasses residuum (marketed by one manufacturer under the registered trade name "Curbay binder") is a dark brown viscous liquid with a characteristic molasses odor and soluble in water to the extent of 90 percent. The specification covering this material requires that its specific gravity at 60° F. shall not be less than 1.20.

(2) The undiluted material is too viscous to use as such, but when it is diluted with 3 volumes of water it forms a dark brown liquid of thin sirupy consistency which, although having a lower specific gravity than either pure or crude mustard, has a viscosity and surface

tension sufficiently close to those of mustard to insure comparable flow characteristics.

(3) Its freezing point is lower than that of low-melting mustard, permitting use of the solution in moderately cold weather without danger of freezing.

(4) The solution has a distinctive molasses odor which, while not similar to that of mustard and not very intense, is readily recognizable. When the solution is sprayed from an airplane, the molasses odor can be detected on the contaminated area for about 45 minutes to 1 hour after the spraying.

(5) The solution has sufficient color to produce easily defined patterns. The patterns obtained by dispersion from airplane chemical spray tanks, chemical land mines, and thin-case bombs are similar to those given by mustard although the individual drops do not spread over as wide an area as do mustard drops. The brown droplets of all sizes are easily visible on either dry or green vegetation and the larger droplets are readily detectable on dry soil. The droplets dry completely in about half an hour. They are easily removed from painted and lacquered surfaces by cold running water and leave no stain. The spots produced on service fabrics are also readily removed by standard quartermaster laundry procedure except in the case of webbing, which requires a second soap wash. Ordinary dry-cleaning procedure will not remove the spots from woolen overcoat material, but dry cleaning followed by "spotting" with warm water will remove the stains.

c. Chemical properties.—(1) The specification covering the concentrated molasses residuum requires that it shall not lose more than 60 percent in weight when mixed with pure quartz sand and dried at 100° C., that its ash content shall not exceed 25 percent, and that its acidity, calculated as SO_3 , shall not exceed 3.5 percent.

(2) The material has a tendency to undergo secondary fermentations on storage but it has been found that after addition of 1.6 percent cresol the concentrated residuum will meet the stabilization requirement of the specification.

(3) The 25 percent aqueous solution of molasses residuum is somewhat acid (pH about 4.5) but no rusting or other evidence of corrosion has been observed as the result of using this solution in airplane chemical spray tanks, chemical land mines, and thin-case bombs. The solution is harmless, by contact, to man and animals but, because of the cresol used as stabilizing agent, it should not be swallowed.

(4) With 0.4 percent cresol, the solution is stable in storage for at least 6 months.

d. Properties.—The detailed properties of molasses residuum solution follow:

Chemical name.....	Solution in 3 volumes of water of the residuum obtained in the manufacture of ethyl alcohol from molasses.
CW symbol.....	MR.
Persistence (odor).....	45 minutes to 1 hour when sprayed from an airplane.
Tactical classification.....	Simulated gas.
Physiological classification.....	None.
Odor in air.....	Like molasses.
Freezing point.....	-3° C. (25° F.).
Boiling point.....	About 101° C. (214° F.).
Vapor pressure.....	Approximately the same as water.
Density at 20° C. (68° F.).....	1.09.
Surface tension at 20° C. (68° F.).....	41 dynes/cm.
Viscosity at 20° C. (68° F.) (c. g. s. units).....	0.0252 poise.
Viscosity at 20° C. (68° F.) (water = 1).....	2.5.
Solvents for.....	None needed.
Action on metals.....	None.
Stability on storage.....	Stable at least 6 months when stored in cool shaded locations with phenol added to prevent fermentation.
Action with water.....	None.
Hydrolysis product.....	Does not hydrolyze.
Physiological action.....	None.
First aid.....	None needed.
Method of neutralizing.....	Do.
Munitions suitable for use.....	Airplane spray and bombs, artillery and chemical mortar shell, land mines.
Marking on munitions.....	2 green bands—MR.
Protection required.....	None.

e. Historical sketch.—The use of molasses residuum solution was first suggested in March 1937. It has been used successfully in engineering tests of airplane chemical spray tanks, thin-case bombs, and chemical land mines, and has also been tested by the Army Air Forces, Infantry, Chemical Warfare School, and Chemical Warfare Board.

161. Simulated HS (asbestine suspension).—a. Composition.—This simulated HS is a suspension of finely ground fibrous magnesium silicate in water (to which butyric acid may be added to impart an odor) in the proportion of 1 pound of the silicate to 2.5 gallons of water (and 0.4 lb. butyric acid, if desired). It is suitable for use by the Army Air Forces as a simulated HS for spraying from aircraft for training purposes as provided for in TM 1-250 and 1-270.

~~CONFIDENTIAL~~
~~CANCELLED~~
~~CONFIDENTIAL~~

Kit M9 was tested in extreme cold. The kits gave a positive test on H-contaminated surfaces at temperatures as low as minus 25°F. Contaminated surfaces after decontamination with DANC gave negative tests. Kits gave a positive test for CG at minus 10°F. when tested in a CG cloud produced by a vial from a field identification set. The red top bottle (nitrogen mustard indicator) froze, but did not break, at plus 28°F. The blue top bottle (mustard indicator) froze, but did not break, at minus 50°F. The frozen solutions were satisfactory after being thawed. At temperatures below 0°F, the heating element of the H tube was slow to react with the solution in the aluminum top bottle, but it provided sufficient heat for the test. The pump did not function properly at cold temperatures due to failure of the piston to seal. The solutions were kept from freezing in extreme cold by carrying the kit under the outer clothing (205).

The stability under tropical conditions of Chemical Agent Detector Kit M9 was markedly improved by packaging the detector tubes and solid reagents in lead. The stability of the mustards detector tubes was improved by including a small percentage of NaHCO₃ in the impregnating composition. The development of the arsenicals detector with sodium hydroxide solution makes this tube more sensitive to L, ED, and MD at high humidities. Of over 120 detectors evaluated for possible use in Chemical Agent Detector Kit M9, none was found to be superior to the tubes in Kit M9 in the following qualities: stability, sensitivity, specificity, and ease of use (206).

Among the 132 detectors which were investigated, only 2 could be recommended for use in Chemical Agent Detector Kit M9. These were a direct test arsenicals detector and an AC detector. Two other detectors which were of possible value for Chemical Agent Detector Kit M9 were a water developed mustards detector and CG-CX detector (207).

Kit, Chemical Agent Analyser, M10. This kit was a portable unit containing color tests and equipment for the detection and identification of CW agents. It contained tubes, papers, and reagents. As issued, the reagent bottles contained dry reagents and required the addition of solvents. The kit contained replacement material and was self sufficient to a considerable extent for extra solvents. It was designed primarily for use in conjunction with CWS Mobile Laboratory M3 which would usually serve

205. CWS Project No. 425, Appendix CC.

206. "Improvement of Kit, Chemical Agent Detector, M9," MIT MR No. 131, p. 1, 1 Jul 1944.

207. "Detector Tubes for Kit, Chemical Agent Detector, M9," MIT MR No. 145, p. 1, 28 Jul 1945.

~~CONFIDENTIAL~~
~~CANCELLED~~
~~CONFIDENTIAL~~

~~CONFIDENTIAL~~
~~CANCELLED~~

as the source of additional quantities of chemicals.

The container (see fig. 14) was a sheet steel box 19 x 8 x 7 inches painted olive drab interior and exterior, and carried by a leather handle. The interior was divided into two sections. A shelf contained sixteen bottles of solutions, three test papers, three heaters, and one rubber sampling bulb (see fig. 15). The bottom section (see fig. 16) contained sixteen bottles of reagents, seventy-five slotted wooden spatulas, a box of detector tubes (see fig. 17), a sampling pump, a tin can with funnel, and packages of detector papers (see fig. 18) (208).

The kit was designed for use by technical personnel who understand the chemistry and the properties of chemical warfare agents and are capable of improvising tests and interpreting results. It is more complete and flexible than other detector items. Agents covered include: H, HN, arsenical vesicants, CK, AC, DP, CG, PS, CN, and BEC. Tests for other agents can be added (209).

A field test of the kit was made, and it was found that agents used for the test were quickly and positively detected and identified. The kit was considered flexible since it included empty bottles available for filling with reagents as required (210).

Chemical Agent Analyser Kit E10 was standardized and designated Chemical Agent Analyser Kit M10 (211).

Kit, Smoke Identification, M11. This kit consisted essentially of a set of apparatus and reagents for the identification of smoke samples collected in special tubes. The kit contained sample tubes, but no pump. It was assumed that the pump from Detector Kit M9 would be available. Liquid reagents and solvents were required to prepare it for use. The item was designed primarily for use in conjunction with Mobile Laboratory M3 which supplied additional chemicals (212).

When field tests were conducted, it was found that all agents tried were positively identified, but careful color differentiation was necessary for proper recognition of negative results. Constant filling of the

208. "Kit, Chemical Analyser, E10," TDMR 1005, 29 Mar 1945; "Kit, Chemical Analyser, M10," CWS Instructions (Technical Command, Engineering Division, Edgewood Arsenal) No. 42, 20 Jul 1945.

209. TDMR 1005, Appendix, p. 1.

210. "Mobile Laboratory, M3," CWS Project 522, Report No. 2, 6 Mar 1945.

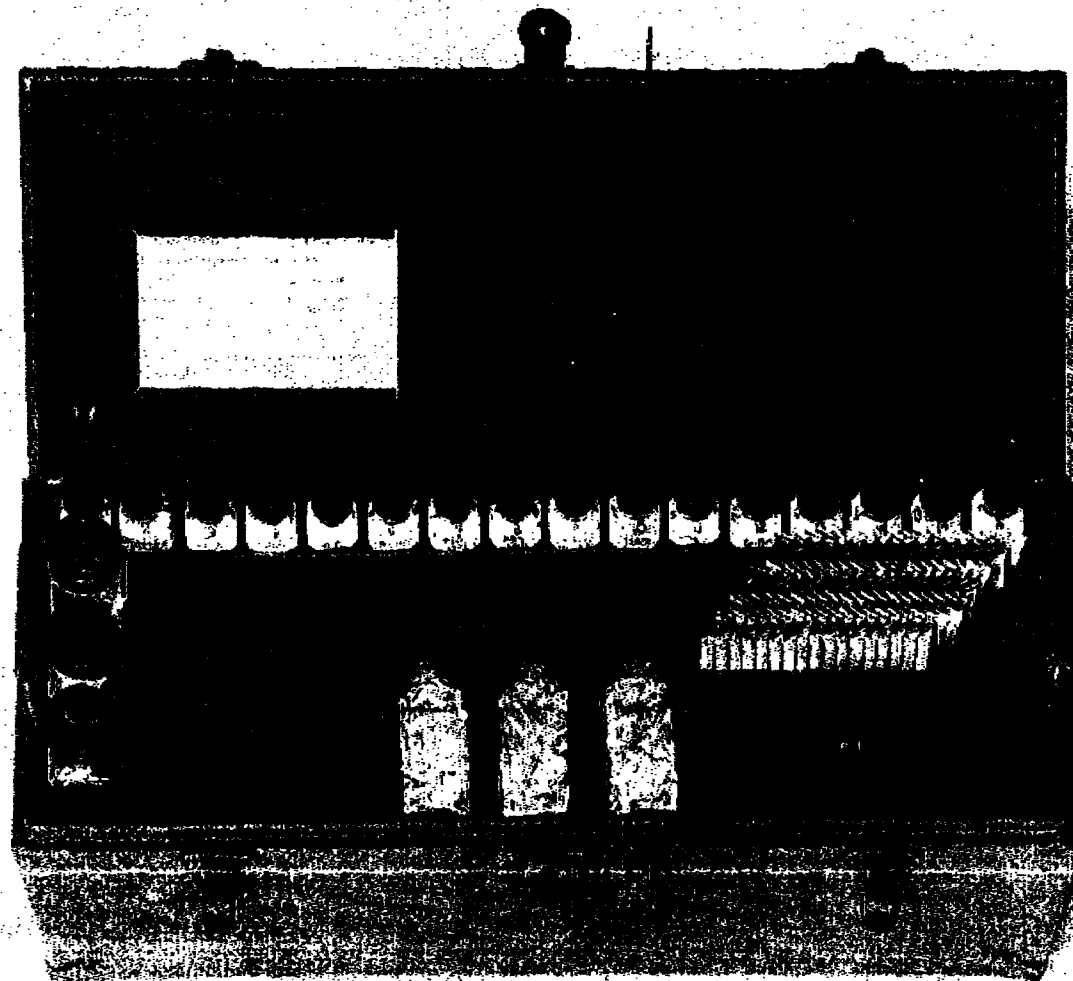
211. CWTG Item 1337.

212. CWS FILM 1-2-14A (Revised), Appendix, p. I.

~~CONFIDENTIAL~~
~~CANCELLED~~

79

Figure 14.--KIT, CHEMICAL AGENT ANALYSER, E10



DE LOCA
HAWAII
SERVICE



RESTRICTED 10650

Figure 15.--KIT, CHEMICAL AGENT ANALYSER, E10
(Open, Showing Top Tray With Contents)