NRL Memorandum Report 1434

REACTIVITY OF VARIOUS DAMAGE CONTROL PROTECTIVE CLOTHING MATERIALS WITH CHLORINE TRIFLUORIDE

H. E. Moran, Jr. and J. C. Burnett

MECHANICS DIVISION

June 1963

U. S. NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

Chlorine trifluoride (CTF) has been proposed for use in an improved missile propellant system. Since this is a stronger oxidizer than any used heretofore, it was desirable to examine its effect on materials used, or proposed for use, in making protective clothing and other gear for damage control. Neoprene and Armalon (woven polytetrafluoroethylene laminated with a continuous sheet of polytetrafluoroethylenepropylene) showed promise as materials for the construction of protective coveralls. It was also shown that these materials must be kept free of local contamination with substances easily ignited by CTF, such as oil and grease, since, once ignited, the uncontaminated portion may continue to burn, even in dilute CTF vapor. The Armalon showed greater resistance to CTF over a wider range of concentration than the neoprene. Butyl rubber coated cloth and vinyl coated glass cloth were readily ignited by dilute CTF vapor, and they appear unsuitable for protective clothing. Hydrazoid propellant fuels were ignited by CTF vapor in concentrations as low as 1-1/2 percent by volume. Samples of the materials used in the construction of the Navy OBA (oxygen breathing apparatus) were found to be reactive with CTF, hence, the OBA must be worn inside a gas-tight protective coverall.

PROBLEM STATUS

This is an interim report. Work on the problem is continuing.

AUTHORIZATION

NRL Problems C05-19 and C08-28
Bureau Nos. SF 015-07-02-3350, RR 001-01-43,
RMMP-24-016/6521/F009-06-11

Reactivity of Various Damage Control
Protective Clothing Materials with
Chlorine Trifluoride

INTRODUCTION

Chlorine trifluoride (CTF) has been proposed for use as the oxidizer in an improved prepackaged missile propellant system. This is a low boiling point compound (53° F at atmospheric pressure). In practice, it will be contained in a sealed missile motor case where it will remain a liquid, exerting a moderate vapor pressure at ordinary temperatures; for example, about 7 psig at 70° F or 25 psig at 100° F. A handling mishap resulting in the rupture of the motor case would result in the expulsion of either liquid or gaseous CTF, both of which form hypergolic mixtures with most combustibles. In addition to the gross release of CTF, there is the possibility of small leaks, so called "pin hole" leaks. In either event, damage control personnel would require protective clothing resistant to both splashes of liquid CTF and to gaseous CTF in various concentrations. It should be noted that CTF is a much more vigorous oxidizer than fuming nitric acid or nitrogen tetroxide, so that protective clothing now approved for use with these materials is not necessarily adequate for protection against CTF. Neoprene has been recommended by the manufacturers of CTF for protective clothing, but this recommendation evidently did not contemplate the close quarters and confined space likely to be met in shipboard missile handling, and further examination of the suitability of this material is needed. "Armalon", a new fluorocarbon polymer has been recommended by its manufacturer (DuPont) for its resistance to CTF. Armalon, neoprene, and a variety of materials presently used for damage control equipment were tested for their resistance to CTF. Armalon and neoprene showed the most promise, and, therefore, were subjected to the widest range of test conditions. Some other materials (paper, missile fuels, lubricants) that might reasonably be found in missile handling areas also were examined for their behavior toward dilute CTF vapor, either separately or in contact with candidate protective clothing materials.

Since water spray or fog undoubtedly will be used to dissipate spilled CTF and to extinguish any fires resulting from such spillage, wet samples of protective clothing materials also were tested for reaction with CTF.

EXPERIMENTAL TESTING

I. Reactivity of Various Materials with Liquid CTF and Undiluted Gaseous CTF

Test Methods and Apparatus

Most of the materials tested for compatibility with CTF were in either continuous sheet form, or they were polymer coated fabric. They will be described more fully along with the test results. Approximately 3/4 by 2-1/2 inch samples were cut from unused stock. These were freed from dust and lint by wiping with a dry cloth, followed by blowing with a jet of compressed air.

In carrying out the liquid phase tests, CTF was allowed to fall in a small steady stream onto the face of a sample placed horizontally on a clean stainless steel surface which had previously been rinsed with liquid CTF to burn off any foreign material which might act as a source of ignition. After initial coverage of the sample was complete, the CTF stream was operated intermittently to just keep the sample face thoroughly wet. If ignition did not occur in one minute, the test was recorded as negative. All specimens were at room temperature (70 to 90°F) at the start of a test. Likewise, the CTF supply was at room temperature. However, it was necessary that the CTF cool itself by partial evaporation to a temperature below its boiling point (53°F) to form the liquid.

Initially, gas phase compatibility tests were made by a jet of CTF vapor impinging on the sample material. The apparatus was simply a 1/4 inch copper tube from the supply tank, bent to discharge downward. The open end was held about 2 mm above the sample. (See Fig. 1). This arrangement released objectionably large amounts of CTF, so a second apparatus was devised in which samples could be immersed in CTF gas. One end of a stainless steel pressure tank was cut off to give a chamber 1-3/4 inches I. D. by 11-1/2 inches inside length. The bottom was connected to the CTF storage cylinder, and a perforated plate diffuser was placed near the bottom (Fig. 2). Air in the chamber was first displaced by CTF gas, and then the test specimen, held by an aluminum wire clip, was lowered well below the rim of the chamber. A slow flow of CTF vapor was maintained during the test. This apparatus permitted exposure of the specimens to undiluted CTF gas with a considerably lower flow of the gas than with the jet. When ignition did not occur in one minute, the test was recorded as negative. When ignition did occur, it was marked by a burst of flame without any preliminary glowing, and the burning area increased rapidly.

Results

Neoprene (black) Exposure

Samples of this material were obtained from black neoprene laboratory gloves. Dry samples exposed to liquid CTF, and to gaseous CTF in both the jet and immersion tests, did not ignite. The only visible effect was a change from shiny to dull luster where the neoprene and liquid CTF were in contact. A piece of the neoprene was wetted with a 0.1 cc drop of water which spread out to cover a 1/4 inch diameter circle, and a jet of CTF gas was directed onto the water. Ignition occurred in 4 or 5 seconds. The wetted portion was immediately destroyed and the remainder burned vigorously as long as it was held in the CTF. A strip sample was smeared over half its length with a thin film of water and immersed in CTF gas in the immersion tube. Ignition was immediate and the fire rapidly spread to the dry portion. A 0.1 cc drop of water was placed on the back of a complete neoprene glove and liquid CTF was poured on the glove at a point 2 inches away from the water so that a substantial part was wet with CTF before ignition occurred at the water spot. The flow of CTF was cut off at the moment of ignition. The fire flashed back quickly over the CTF wetted area of the glove, leaving a hole of corresponding shape. The preceding test was repeated, using a drop of light lubricating oil instead of water. The result was identical. In the same fashion, a drop of oil was placed on a strip sample which then was immersed in CTF gas. Ignition was prompt and the whole sample burned.

Neoprene (unfilled) Exposure

A sheet of neoprene which contained no filler or coloring agent was obtained. Two samples of this material were immersed in CTF vapor. Both immediately ignited along the edges and burned with a very sooty flame. However, the fire did not flash over the faces of the samples.

Four samples of the unfilled neoprene were placed in a horizontal position and a stream of liquid CTF was applied near the center of each sample. One ignited immediately at the point of impact of the CTF and burned outward. One ignited immediately at the edge and burned rapidly inward. The other two remained wet with CTF for 3 and 5 seconds, then ignited at an edge and fire flashed over the surface. In all trials the flames were very sooty.

Armalon Exposure

Armalon is a laminate composed of a woven teflon (tetrafluoroethylene polymer) fabric bonded to a continuous sheet of FEP (fluoroethylenepropylene polymer) which may also have a thin aluminum or other metallic coating on its outer surface. Both the teflon and FEP sides of dry samples of uncoated Armalon, and the aluminum side of metallized Armalon, were subjected to a jet of CTF gas without producing any visible effect.

A 0.1 cc drop of water was placed on the FEP face of uncoated Armalon and a jet of gaseous CTF was discharged over the water and surrounding Armalon. (Since water does not wet Armalon, the water retained its drop shape.) In two trials out of six, the water burned away, leaving the Armalon slightly curled. (Curling was subsequently found to be the normal result of heating Armalon.) In the remaining four trials, the water ignited, and a few seconds later the Armalon ignited and continued to burn vigorously as long as the CTF flow was maintained. The preceding tests were repeated on aluminum coated Armalon with similar results. Ignition failed to occur in one trial, and did occur in two trials. It was noted that the drop of water often moved about on the Armalon during a test. When the Armalon was lightly creased in two directions to form a shallow pocket the water drop was held stationary, and the application of gaseous CTF invariably resulted in ignition of the Armalon.

A specimen of uncoated Armalon was placed in a horizontal position with the FEP face upward. This face was kept thoroughly wet with CTF for one minute without any sign of reaction. The same result was obtained when liquid CTF was applied to the aluminum face of metallized Armalon. However, a piece of paper dropped on one end of the CTF-wetted Armalon served as an ignition source; the samples ignited immediately and burned briskly.

Samples of both uncoated and aluminum coated Armalon were held horizontally, FEP layer upward, and a 0.1 cc drop of water was placed on each. Liquid CTF was then applied. In one trial (uncoated sample) the drop of water slid off the edge of the sample and there was no ignition. In two more trials with uncoated material, and in two with aluminum coated material, ignition took place in a few seconds and the Armalon continued to burn briskly in the CTF.

In the foregoing tests on Armalon, the flow of liquid CTF was shut off, or the samples were removed from the CTF immersion chamber, before the samples were completely consumed. Combustion stopped immediately, i.e., there was no tendency of the samples to continue burning in air alone.

Oxygen Breathing Apparatus Materials of Construction

Samples of the outer covering, liner, and seam reinforcement strips of the breathing bag of the Navy oxygen breathing apparatus (OBA, types A-1 and A-2) were subjected to a jet of CTF gas. The outer coverin and the seam reinforcing strip ignited immediately and continued to burn vigorously until the CTF flow was stopped. The elastic liner of the breathing bag, when dry, appeared unaffected after one minute exposure to a CTF vapor jet. The same material, moistened with water, ignited immediately and burned vigorously. These materials were ignited immediately by a stream of liquid CTF. A small sample of the material used in the breathing bag of the OBA model A-3 was available for testing. This material is a laminate consisting of rubber impregnated cotton sheeting on the outside and a neoprene layer on the inside. Liquid CTF ignited the test sample immediately. It was not apparent which of the components was most sensitive to ignition. Since the construction of the OBA exposes a cross section of laminate at some points, liquid CTF can cause its ignition.

Butyl Rubber Exposure

Samples of butyl rubber impregnated cloth, cut from "guided missile handlers protective clothing" (Federal stock number 8415-753-6210) were exposed to a stream of liquid CTF and to a jet of gaseous CTF. In both circumstances the material ignited immediately.

Vinyl Coated Cloth Exposure

Samples cut from an "acid and fuel resistant propellant handlers protective suit" (MIL-C-12527A (QMC)) made of vinyl polymer impregnated glass cloth, ignited immediately and burned briskly when exposed to either liquid or gaseous CTF.

Fire Hose Exposure

A 30 inch long section of Navy cotton covered, rubber lined, fire hose was subjected to both liquid and gaseous CTF. The CTF was applied to the outside of the hose, near the center, so as to avoid contact between the CTF and the cut and somewhat frayed ends of the sample. Brief (approximately 1 second) application of a stream of liquid CTF resulted only in slight scorching of the surface of the cotton jacket. The application of a steady stream of liquid CTF for one minute produced a scorched circle about 4 inches in diameter. The cotton jacket was deeply charred at the point of impact of the CTF, but the rubber liner appeared little damaged. A jet of gaseous CTF scorched a circle 1-1/2 inches in diameter and burned a 1/2 inch diameter hole through the cotton cover and almost through the rubber. The remaining rubber was so weakened that it was easily punctured with the blunt end of a pencil.

II. Reactivity of Various Materials with Dilute Gaseous CTF

Materials Tested

Since a 100% concentration of CTF vapor would be encountered only close to a vapor leak, or close to spilled liquid CTF, protective clothing would most likely be exposed to CTF vapor more or less diluted with air. Therefore, the behavior of some of the candidate protective clothing materials with dilute CTF was examined. Samples of Armalon, black neoprene, butyl rubber impregnated cloth, and vinyl polymer impregnated glass cloth were the same as those described in the foregoing section of this report. In addition, fuel and fuel constituents (hydrazine, UDMH (unsymmetrical dimethyl hydrazine), MHF-3 and MHF-4 (hydrazoid or mixed hydrazine fuels)), and paper were exposed to dilute CTF vapor, since these materials also might be present in case of a missile handling mishap.

Test Methods and Apparatus

CTF-air mixtures of the desired concentrations were prepared in the apparatus shown in Figure 3. This apparatus comprised a 34 liter stainless steel tank, a pressure gage having a range of 2 atmospheres absolute in 0.002 atmosphere divisions, and an exposure chamber, assembled as shown in the figure. Copper tubing, brass flare fittings, and bellows-sealed brass valves were used in connecting the parts. The exposure chamber is the 1-3/4 x 11-1/2 inch stainless steel chamber described for the earlier tests with 100% CTF. CTF-air mixtures were prepared by the method of partial pressures. That is, the system was first evacuated, then CTF vapor was let in to a predetermined pressure, and finally dry compressed air was admitted to the appropriate pressure between 1 and 2 atmospheres absolute. The gases were allowed to stand for at least one hour to permit mixing by natural convection and diffusion. The volume concentration of CTF was taken as the ratio of CTF pressure to the total pressure.

In carrying out a test with a solid sample, a CTF-air mixture of the desired strength was prepared and the exposure chamber was connected to the reservoir and supported in a vertical position, except as noted for Armalon. When tests were made with water drops in contact with Armalon, it was necessary to turn the immersion chamber so that the test samples could be held horizontally. Otherwise, the water drops, which do not wet Armalon, would quickly slide off the samples. The CTF-air mixture was allowed to run through the chamber to flush out air and then a 3/4 x 2-1/2 inch strip of the material being tested was immersed in the still flowing gas mixture until ignition occurred, or for at least one half minute when there was no ignition. Liquid fuel samples were supported on glass wool wrapped around a glass rod. The samples were held well below the top of the exposure chamber to insure that they were in gas which had not been diluted by air currents at the mouth of the chamber.

Results

The reaction of the various materials with dilute CTF is given in Table I, along with results found in earlier tests with undiluted CTF.

TABLE I

Exposure of Various Materials to Gaseous CTF and Air Mixtures

Material	Reaction
	100% CTF
ARMALON, UNCOATED	
Dry	No reaction in 1 min
With 0.1 cc drop of water	Water ignited in less than 2 sec in all tests; Armalon ignited at 5, 7, 9, 9 and 13 sec and continued to burn progressively
ARMALON, ALUMINUM COATED	
Dry	No reaction
With 0.1 cc water drop on aluminum face	Water ignited in less than 2 sec; Armalon ignited in 6, 7, 8, 9 and 22 sec and continued to burn progressively
With 0.1 cc light lube oil on aluminum face near end of strip	Oil and Armalon both ignited immediately, and Armalon continued to burn progressively
NEOPRENE	
Dry	No reaction in 1 min
Wet with 0.1 cc of water near end of sample strip	Wet portions ignited in 2, 3, 4 and 5 sec and samples continued to burn progressively
BUTYL RUBBER IMPREGNATED CLOTH	
Dry	Ignited in 2 sec and continued to burn rapidly
Wet with 0.1 cc of water near end of sample strip	Ignited immediately at one edge and continued to burn progressively

VINYL COATED GLASS CLOTH

Dry	Ignited immediately and continued to burn rapidly
Wet with 0.1 cc of water near end of sample strip	Ignited immediately and continued to burn rapidly

ARMALON, ALUMINUM COATED — 75% CTF

Dry	No reaction
With 0.1 cc drop of water	No reaction

NEOPRENE

Dry	No reaction
Wet with 0.1 cc water near end of sample strip	Ignited and continued to burn progressively

ARMALON, ALUMINUM COATED — 50% CTF

Dry	No reaction in 1 min
With 0.1 cc drop of water	No reaction in 1 min
Face near end smeared with 1 drop of light lube oil	Ignited in 2 sec and continued to burn progressively

NEOPRENE

Dry	No reaction
Wet with 0.1 cc drop of water near end of sample strip	Ignited in 6, 6, and 7 sec

BUTYL RUBBER IMPREGNATED CLOTH

Dry	Ignited in 2 and 3 sec at edges of sample and continued to burn slowly

VINYL COATED GLASS CLOTH

Dry	Ignited in 1 and 2 sec at edges and continued to burn slowly

ARMALON, ALUMINUM COATED	25% CTF
Dry	No reaction in 2 min
With 0.1 cc drop of water	No ignition in 4 min; back (Teflon) layer of the sample was partly bleached underneath the water drop
Smeared with 0.1 cc light lube oil near end of coated face	Oiled portion smoked lightly, but no other apparent reaction in 1 min
With scrap of paper in contact with aluminum face	Paper ignited in less than 1 sec, followed immediately by ignition of the Armalon, which burned progressively with a sooty flame
NEOPRENE	
Dry	No reaction in 2 min
Wet with 0.1 cc of water near end of sample strip	One sample ignited in 11 sec; second sample dried, but showed no other reaction in 1 min
BUTYL RUBBER IMPREGNATED CLOTH	
Dry	No reaction
Wet	Ignited in 7 sec
PAPER	
Dry	Ignited immediately

ARMALON, ALUMINUM COATED	10% CTF
Dry	No reaction
With 0.1 cc drop of water	No reaction
Oily	No reaction
In contact with a piece of paper	Paper ignited; Armalon did not react

NEOPRENE	
Dry	No reaction
Wet with 0.1 cc of water near end of sample strip	No reaction
Face, near end, smeared with drop of lube oil	No reaction
In contact with a piece of paper	Paper ignited immediately, setting fire to the neoprene, which continued to burn rapidly
BUTYL RUBBER IMPREGNATED CLOTH	
Dry	No reaction
Wet	No reaction
PAPER	
Dry	Ignited immediately
PAPER	**3% CTF**
Dry	No reaction
PROPELLANT FUEL	
MHF-3	Fumed; ignited in 4 sec
MHF-4	Fumed; ignited in 20 sec
UDMH	Fumed; ignited in 4 sec
Hydrazine	Fumed; ignited in 4 sec
PROPELLANT FUEL	**2.5% CTF**
MHF-3	Fumed; ignited in 12 sec
MHF-4	Fumed; no ignition in 1 min
UDMH	Fumed; ignited in 6, 8 sec
Hydrazine	Fumed; ignited in 18 sec in 1 trial, failed to ignite in 2 trials lasting 30 sec
PROPELLANT FUEL	**2% CTF**
MHF-3	Fumed lightly; no ignition in 30 sec
MHF-4	Fumed lightly; no ignition in 30 sec
UDMH	Fumed; ignited
Hydrazine	Fumed lightly; no ignition in 30 sec

PROPELLANT FUEL	1.5% CTF
MHF-3	Fumed lightly; no ignition in 30 sec
MHF-4	Fumed lightly; no ignition in 30 sec
UDMH	Fumed; ignited in 7 and 15 sec
Hydrazine	Fumed lightly; no ignition in 30 sec

PROPELLANT FUEL	1% CTF
UDMH	Heavy fumes were evolved for 90 sec, after which fuming decreased. The UDMH had disappeared in 120 sec without igniting

SUMMARY AND DISCUSSION

Some materials which are now used in making protective clothing and other damage control gear for use in case of spills of liquid missile propellants were tested for their resistance to both liquid and gaseous CTF. Two other materials which have been proposed for this use also were tested.

Samples of butyl rubber impregnated cloth, taken from coveralls intended for protection against nitrogen tetroxide, were self-igniting in contact with liquid CTF, and with CTF gas diluted to 50% concentration with air. Samples of this material when wet with water, were self-igniting in 25 percent CTF vapor.

Vinyl coated glass cloth from coveralls intended for protection against fuming nitric acid was self-igniting on contact with liquid CTF, and with CTF vapor as low as 25 percent. When wet with water, it was self-igniting in 10 percent CTF-air mixture.

Samples of the materials used in making the breathing bag of the Navy oxygen breathing apparatus (OBA types A-1 and A-2) were ignited immediately by liquid CTF. The outer covering and the seam reinforcement strips of the OBA were ignited by undiluted CTF vapor. The inner liner, when dry, resisted undiluted CTF vapor, but was readily ignited when wet with water. These materials were not tested against dilute CTF vapor, but it is reasonable to expect the assembled OBA would ignite in dilute CTF since it has exposed cotton cloth reinforcements which are sensitive to dilute CTF, and which would act as ignition points.

Neoprene samples, obtained from black laboratory gloves, were considerably more resistant to CTF than the materials now used for propellant handlers protective clothing. When the neoprene samples were clean and dry, they did not ignite on being kept wet for one minute with liquid CTF, nor when subjected to undiluted CTF vapor for one minute. However, contamination with water or oil rendered the neoprene very sensitive to CTF. Both liquid and undiluted gaseous CTF caused practically immediate ignition of the wetted samples. A 25 percent mixture of CTF vapor in air caused the ignition of one sample of wet neoprene after 11 seconds exposure, but failed to ignite a second sample. A lower concentration of CTF (10%) did not show any reaction with wet neoprene.

Armalon, a laminate of woven polytetrafluoroethylene (teflon) cloth and polyfluoroethylenepropylene (FEP) sheet, showed the greatest resistance to CTF of any of the materials tested. Clean, dry Armalon was unaffected by liquid CTF or CTF vapor. It could be ignited, however, when it was in contact with a more reactive material. Water drops caused ignition and continued burning of Armalon in undiluted CTF, but not in 75 percent or weaker CTF. A smear of lube oil caused Armalon to ignite in 50 percent CTF vapor, but not in 25 percent CTF. A piece of paper in contact with Armalon ignited immediately in 25% CTF vapor and promptly ignited the Armalon which continued to burn after the paper was consumed. Finally, a piece of paper in contact with Armalon ignited in 10 percent CTF, but the Armalon was unaffected.

Although the foregoing tests demonstrate a wide range of CTF concentrations in which Armalon will burn, it should be noted that the methods of ignition were extreme. The avoidance of easily ignitable material, such as grease or oil, on protective clothing is mandatory regardless of the kind of material of which it is made. Undoubtedly water may be present in damage control operations, but water does not wet Armalon and droplets very easily move around, even on nearly horizontal surfaces. Thus, it appears unlikely that a drop would stay in place long enough to cause ignition. The neoprene, in contrast, was readily wetted, and, thus, is more likely to be ignited by the presence of water. One possible source of ignition is contamination with fuel which might be spilled from a damaged missile. It was found that as little as 1.5 percent CTF in air could cause self-ignition of UDMH and that 3 percent CTF would ignite any of the hydrazoid fuels or fuel components that were tested.

The results of the tests indicate that a reasonable amount of protection against CTF can be obtained from a gas-tight coverall made from Armalon. Such a coverall would be designed to completely cover the damage control man and to permit his carrying oxygen breathing apparatus on the inside. It is anticipated that the wearer would be further protected by the cooling and cleansing effects of water spray from an L-11 fog nozzle or a Navy high velocity fog nozzle. Neoprene appeared useful for a coverall for protection against moderate concentrations of CTF but was reactive, especially when wet, with liquid CTF and higher concentrations of the vapor. Thus, coveralls made of neoprene would place much more dependence on a continuous, thorough wash-down with water spray than would Armalon.

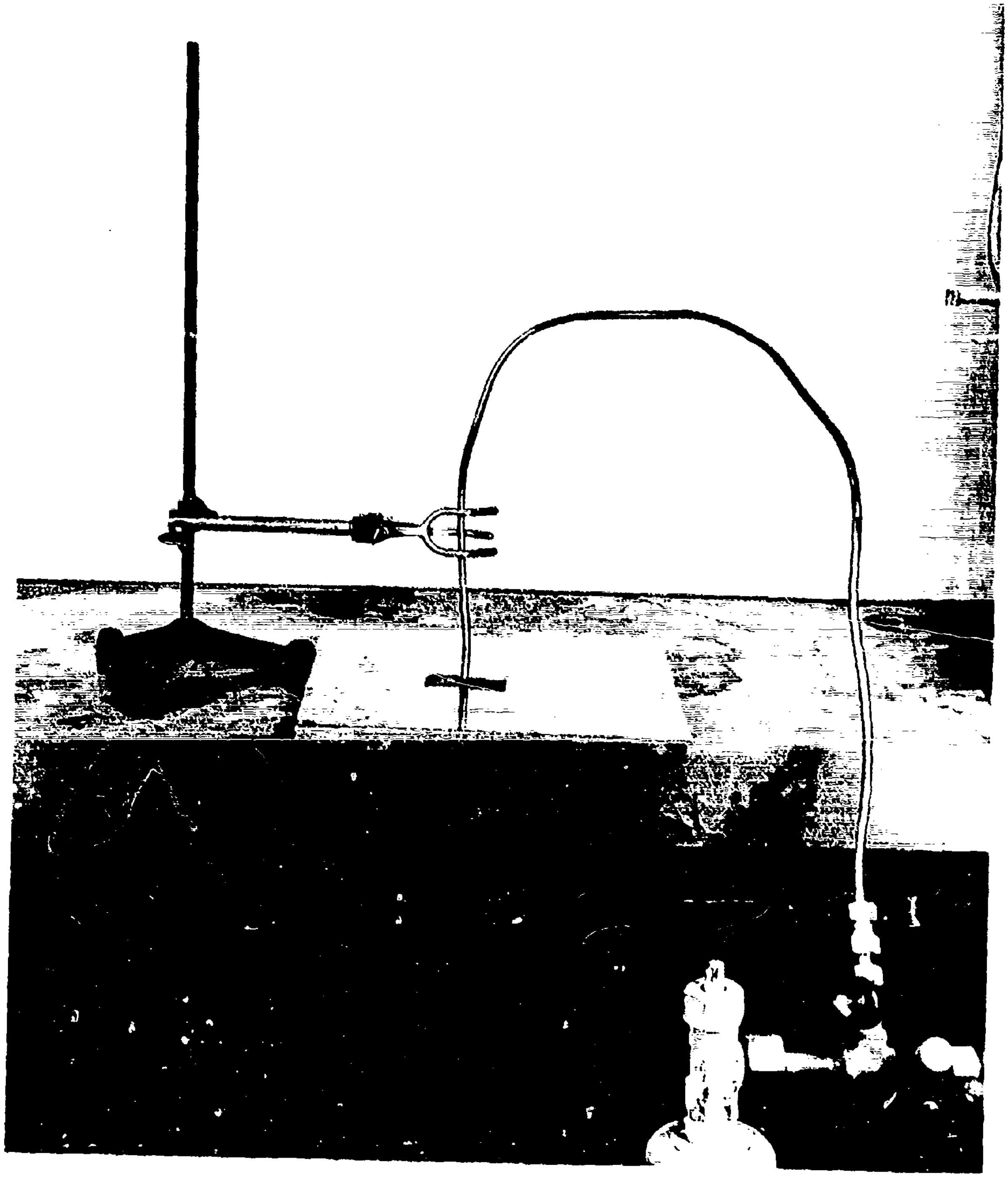

Figure 1 - Apparatus for exposing samples to a jet of undiluted CTF

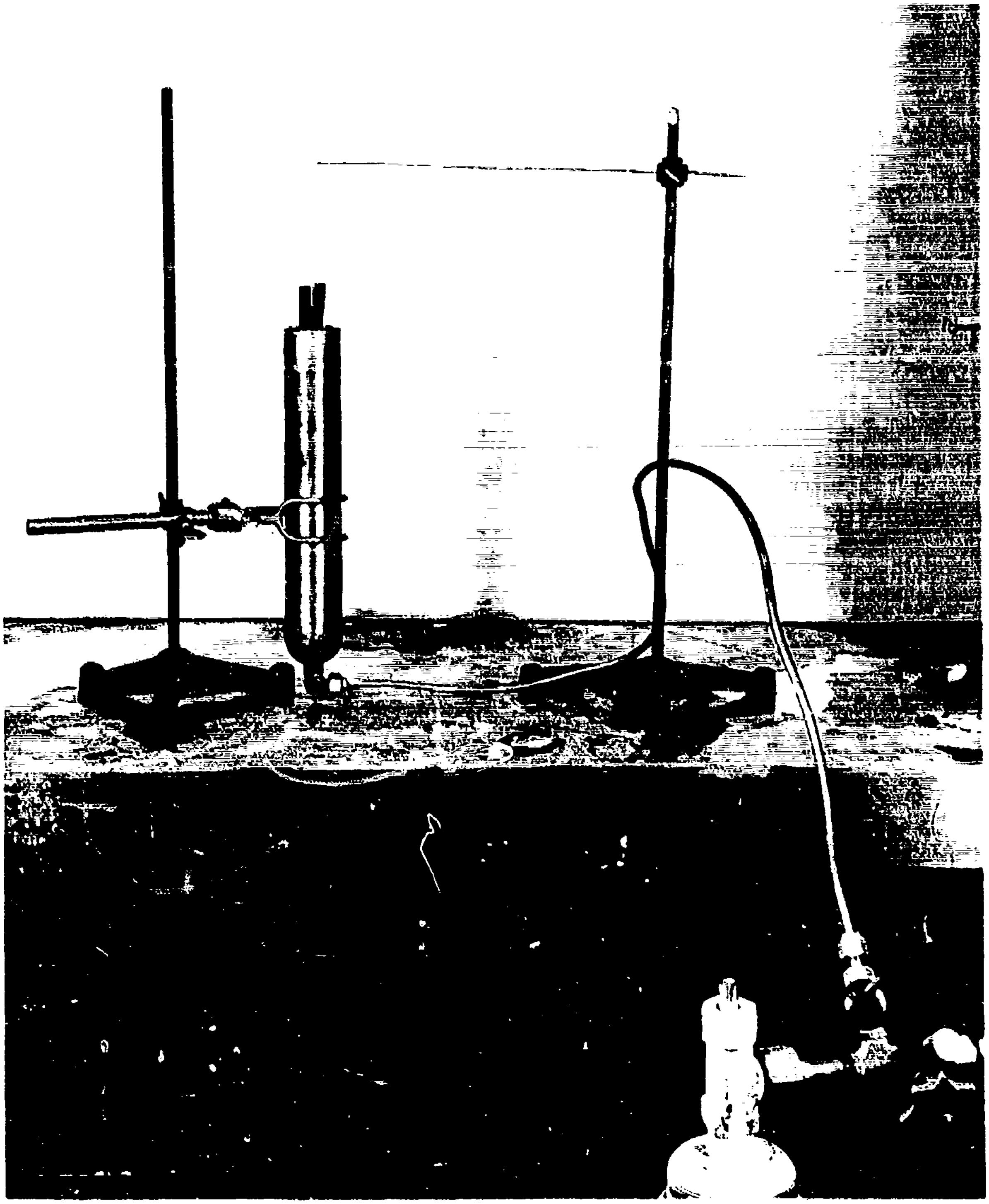

Figure 2 - Apparatus for immersing samples in undiluted CTF gas (In actual tests the sample is lowered well below the rim of the immersion chamber.)

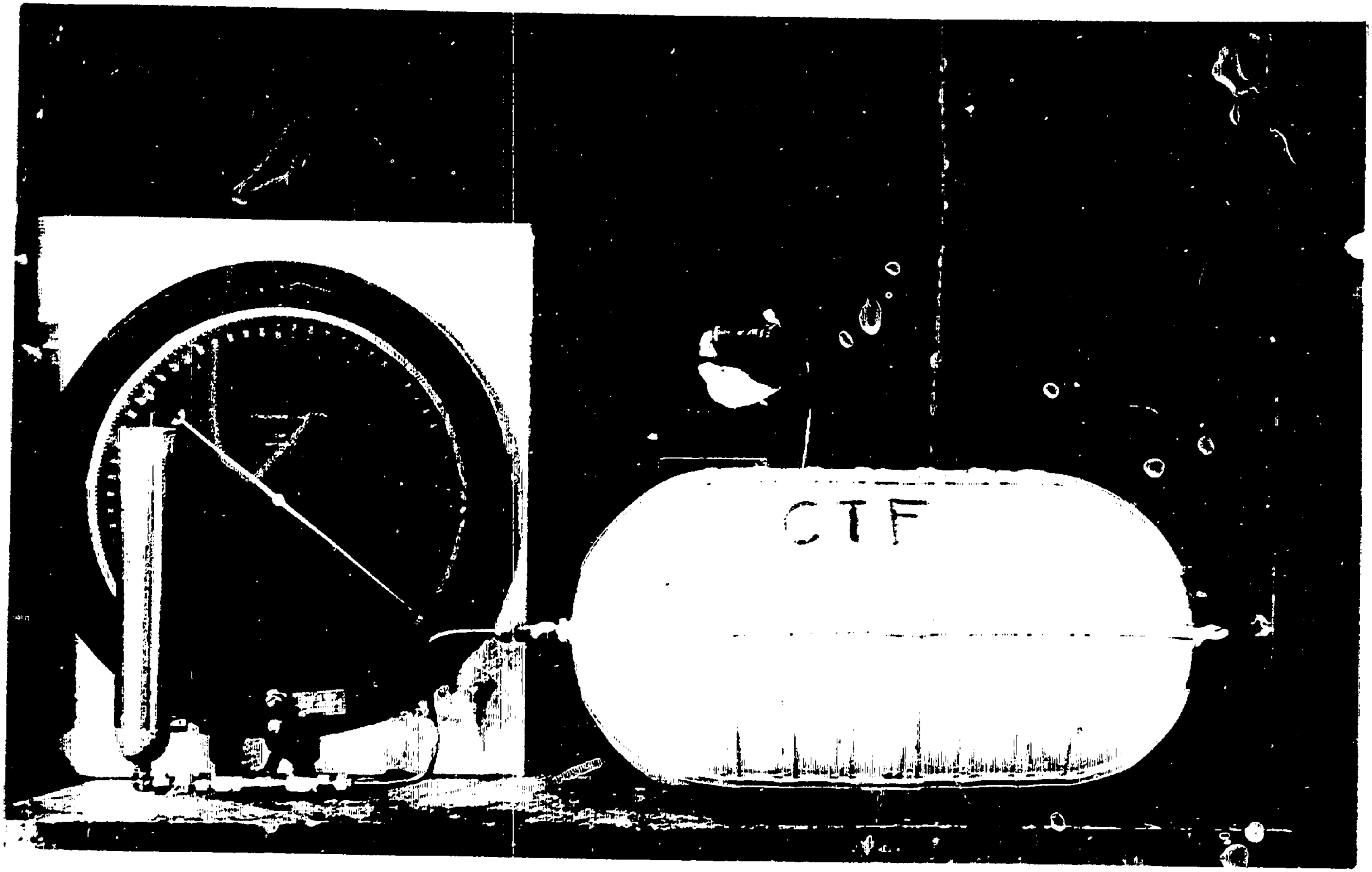

Figure 3 - Apparatus for making CTF-air mixtures and for exposing samples to the dilute CTF