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RADIATION-POLYMERIZATION BINDER FOR Mk 48 DECOY FLARES

Clyde F. Parrish, et al

Naval Ammunition Depot
Crane, Indiana

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An alternate method for production of Mk 48 flares has been described. This method is based on the radiation polymerization of a binder/oxidizer system. Chlorotrifluoroethylene, the monomer used, is 100% polymerized by radiation doses less than five mega rads. Several grades of magnesium may be used including reclaimed magnesium. Because of the density involved, no special adjustment for concentration of either the oxidizer or fuel is needed. The voids in the magnesium are simply filled with the gaseous monomer. The units produced meet the required performance standards. The cost of radiation curing is less than five percent the cost of the monomer.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Radiation-polymerization						
Magnesium						
Trifluorochloroethylene						
Infrared						

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RADIATION-POLYMERIZATION BINDER
FOR
MK 48 DECOY FLARES

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James E. Short, Jr.
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The MK 48 flare is a thermal decoy which has strong emissions in the infrared. These units utilize the magnesium-fluorine reaction for the energy and usually carbon as the emitter. A simulated example of the application of one of these units is shown in Figure (1). Here in an artist conception is a missile being directed from a ship toward a decoy flare. The needs and applications of these units, however, are not what concerns us, but the methods of production do.

Presently the MK 48 flare is produced by blending magnesium, teflon (Polytetrafluoroethylene) and viton. This mixture is then extruded and cut to length. These units have been produced since 1970 and the methods are well documented (1). Production methods which require batch mixing where a catalyst is added have inherent problems, but in most cases satisfactory solutions exist. This has been one consideration in our design of an alternate production method. A second and possibly more important consideration has been to provide a requirement for an alternate set of raw materials. For the production of the MK 48 flare a specific grade of magnesium and teflon (DuPonts #1 or #7) had to be used along with the binder. The method described here may use either standard balled magnesium or a reclaimed magnesium from scrap and degraded MK 24 and MK 45 illuminating flares. The quality of the product and recovery of these units is described elsewhere in this document. The oxidizer selected also functions as the binder when polymerized. A non-catalytic method of polymerization has been selected which utilizes ionizing radiation as the source of energy. Although the application of radiation polymerization to produce pyrotechnique binders is not new (2) application of this technique to produce thermal decoys is.

It is this alternate method of production which we will describe and based on our present level of success we feel it warrants strong consideration as an alternate production method.

Techniques of Radiation Polymerization

The subject of radiation induced polymerization has existed for a number of years. Early studies date back to the 1940's, however, the body of knowledge relative to the subject has been somewhat confined. Only recently have there been commercial application of this technology. For example, the radiation polymerization of wood-plastic began in 1969. Today there are three companies (American Novawood, Atlantic Richfield, and Lockheed Georgia) using this method (3). Another application under consideration is the production of a concrete-polymer which has 300 to 500% improvement in strength over standard concrete with only a six percent polymer loading (4).

Since the technology of the radiation on polymer field has been limited, several questions immediately come to the mind of those outside the field, such as: What is ionizing radiation? What are its methods of use? What are the potential advantages? What are the hazards? Can it find economic commercial applications?

The answer to these and many other questions must be answered before an application is made of the process.

When a chemical system is exposed to ionizing radiation chemical bonds are broken. Although, this breakage of bonds is not as selective as those in photochemistry, there is some selectivity. This lack of selectivity comes from the fact that the ionization potential of organic molecules is of the order of 10 ev. while the energy from gammas is of the order of 1,000,000 ev. Since photochemical energies are sub ionization and gamma energies are much greater than the ionization potential, thus the name ionizing radiation.

The most probable initial event is the production of an ion-pair. These initial ions can either react directly to initiate a polymerization reaction or can recombine with its geminate pair to produce an excited molecule. (See Figure II) These excited molecules then can decompose to produce ions and/or free radicals.

Although there are two common classes of polymerization reaction, e.g., addition and condensation, here only addition polymerization reactions are common. Simply, these are reactions where a bond is formed for every bond broken and the repeating unit has the same emperical formula as the monomer. The mechanism for this type of reaction is shown in Figure III. There are three steps to the reaction mechanism: initiation - where reactive fragments start the polymerization chain; propagation - where the growing polymer chain adds to the monomer; termination - the polymer chain stops growing. This latter step may be complex for radiation polymerization reactions.

Experimental

The study reported here used chlorotrifluoroethylene as the oxidizer/binder. The material was standard commercial grade obtained from Matheson Gas; no attempt to remove inhibitors and no other purification methods were used.

Two cells were used during the course of this experiment. These are shown in Figures IV and V. The demountable cell illustrated IV had an interanal diameter of 1.78" and a length of 5.5". It was held together by standard radiator hose clamps. There was a filling port which was connected to the cell. Due to problems in removing the sample, plugs were inserted in the side of the sample cell. To remove the sample, the cell was attached to a supply of compressed air to blow the cell apart. Usually 150 to 160 psi was sufficient to achieve this. Several attempts were made to develop a release agent that would assist in the removal of this sample, however, no good candidate was found. Best results were obtained by a freshly cleaned aluminum surface. This required complete reconditioning of the cell between each run.

The second cell used was a standard aerosol can. See Figure V. No special liners were used for these cans. During the course of the study we found that it was necessary to remove all air from the sample before irradiation. This required the use of a vacuum crimper for the cans.

Sample filling was made easy due to the porous nature of the balled magnesium used. For example, the 30/50 mesh balled magnesium was used for the initial part of this study. The burning time was increased by the addition of five percent of a finer grade of magnesium. In both cases, the density was significantly less than the bulk density or the closest packing density for magnesium spheres. This made it easy to control the ratio of magnesium to oxidizer. Since the monomer is a compressible gas, the magnesium was added to the cell and followed with the monomer. Although this did not exactly equal the storchemetric point.

Several samples were prepared with various grades of reclaimed magnesium. In all cases satisfactory results were obtained. When the aerosol can was used for the sample, cell, a measured amount of magnesium was placed in the can. The can was then evacuated and sealed. The monomer was next forced into the can and an effort was made to assure the can was completely filled.

The aerosol can samples were rotated in the device shown in Figure VI. Here the cans were placed in the containers and the system rotated in the radiation field, this gave complete mixing and more uniform samples. The speed of rotation was 17 rpm. The demountable cells were irradiated in the center well of the source and was not rotated.

All irradiations were performed in a nominally 10,000 curie Co-60 irradiation cave. This facility is located at Indiana State University, Terre Haute, Indiana, is shown in Figures VI and VII and has been previously described in detail (5).

The Co-60 is housed on a platform which moves up and down into a well of water. The source provides a radiation dose of approximately 200,000 rads/hour depending on the sample position.

Dosimetry was performed using the standard Fricke method for ferrous sulfate with a G for oxidation (Fe^{+2}---- Fe^{+3}) of 15.5 molecules per 100 ev. absorbed.

Results

A typical unit produced in the demountable cell is shown in Figure VIII. The white material at the end of the unit is the polymer of the oxidizer. The gray portion represents the area where the oxidizer and magnesium are bound together. A section of the radiation produced unit is shown in Figure IX. Here one can see the magnesium imbedded into the polymer matrix. A typical production unit is shown in Figure X. The most notable difference is the lack of the appearance of magnesium in the extruded unit. Cross sections of units produced in aerosol cans are similar. The physical strength of the radiation produced unit was quite good. In fact, the exterior of the radiation produced unit was smooth and hard.

Figure XI shows a MK 48 flare ready for test burning. Figure XII shows the burning of this unit. These tests gave burning characteristics similar to those of the standard production units.

We have now built and tested a large number of units produced by the technique described above. The specific data is classified, but may be obtained through the Research and Development Department, Naval Ammunition Depot, Crane, Indiana. With few exceptions all units produced passed the performance standards. A comparison of the relative performance of a group of the units built with 30/50 magnesium only is shown in Figure XIII. Here the burning standard production units is compared with the radiation produced units. As one can see these units meet the performance standards. Similar results were obtained when reclaimed atomized magnesium was substituted for the 30/50 mesh balled magnesium.

It is obvious that performance standards are of primary consideration, however, many other points must be examined before a method could be considered for production. One important consideration is the cost of the method.

Examination of the literature for information as to the cost of an irradiation process requires knowledge of several factors. A radiation dose of about five mega rads is sufficient for 100% conversion of chlorotrifluoroethylene to polymer. Based on current data, this would cost approximately three cents ($0.03) per unit for radiation processing (6). This cost is only a fraction of the cost of the monomer (current price is approximately $2.00 per pound). Several factors can operate to change the radiation dose needed for 100% conversion. First, it has been shown that the dose for 100% conversion tends to decrease as the dose rate is lowered (2). In some cases, this may change by an order of magnitude. Also it is possible to decrease the radiation dose with the addition of a radiation sensitive catalyst such as, benzoyl peroxide. Due to the stability of this peroxide system, the unit could be charged and stored before radiation.

Production methods have not been fully explored to date, although there are some immediate considerations. First, whether a demountable cell or aerosol can should be used. Second, what is the best type of magnesium? Once this is decided the monomer can be injected through some type of valving. At this point, the system may be stored for an indefinite period of time before radiation polymerization of the monomer. These filling methods are well known to the packaging industry and are easily automated. Such automation could reduce personnel exposure and increase the safety.

Summary

An alternate method for production of MK 48 flares has been described. This method is based on the radiation polymerization of a binder/oxidizer system. Chlorotrifluoroethylene, the monomer used, is 100% polymerized by radiation doses less than five mega rads. Several grades of magnesium may be used including reclaimed magnesium. Because of the density involved, no special adjustment for concentration of either the oxidizer of fuel is needed. The voids in the magnesium are simply filled with the gaseous monomer. The units produced meet the required performance standards. The cost of radiation curing is less than five percent the cost of the monomer.

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LIST OF FIGURES

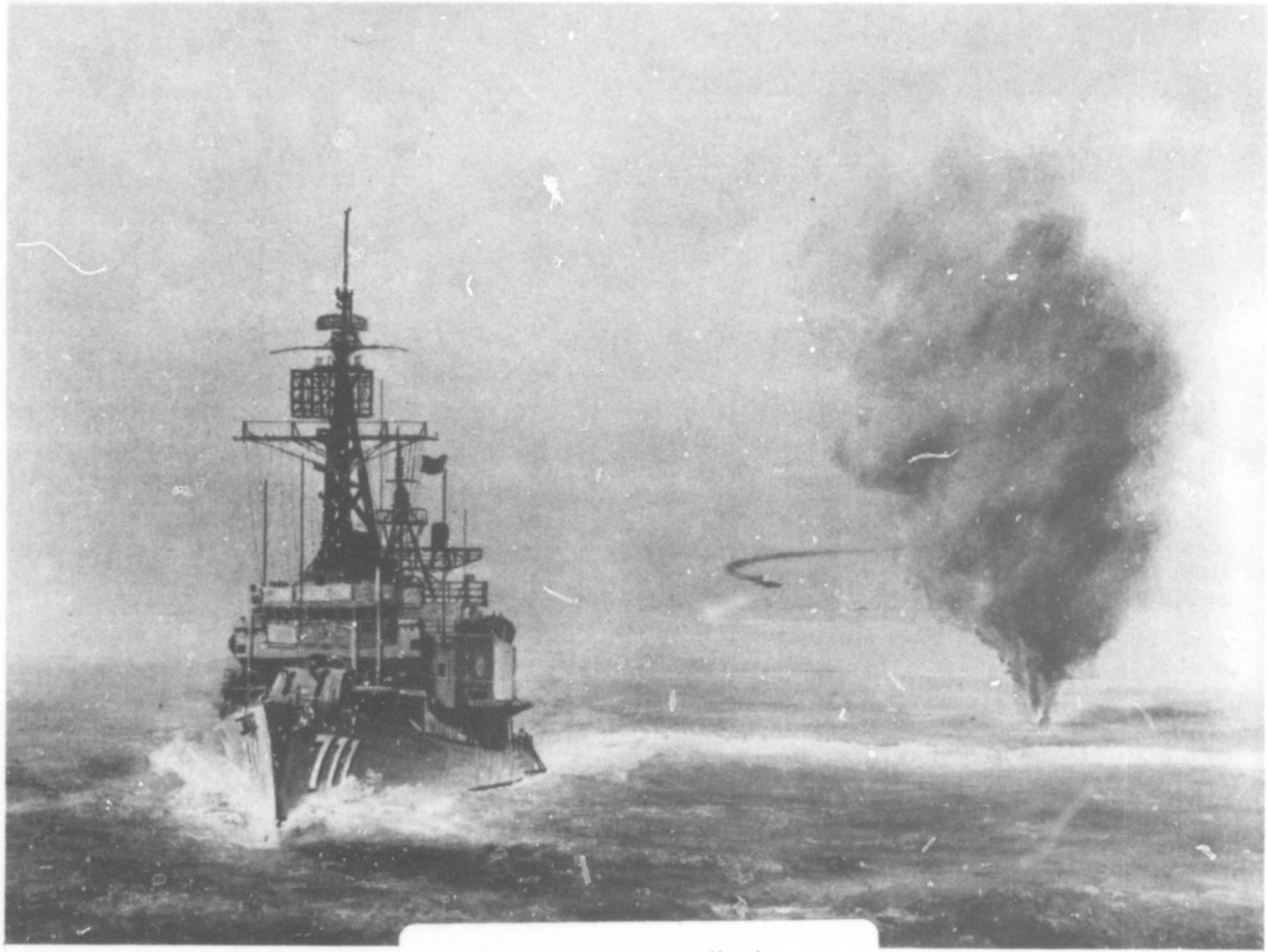
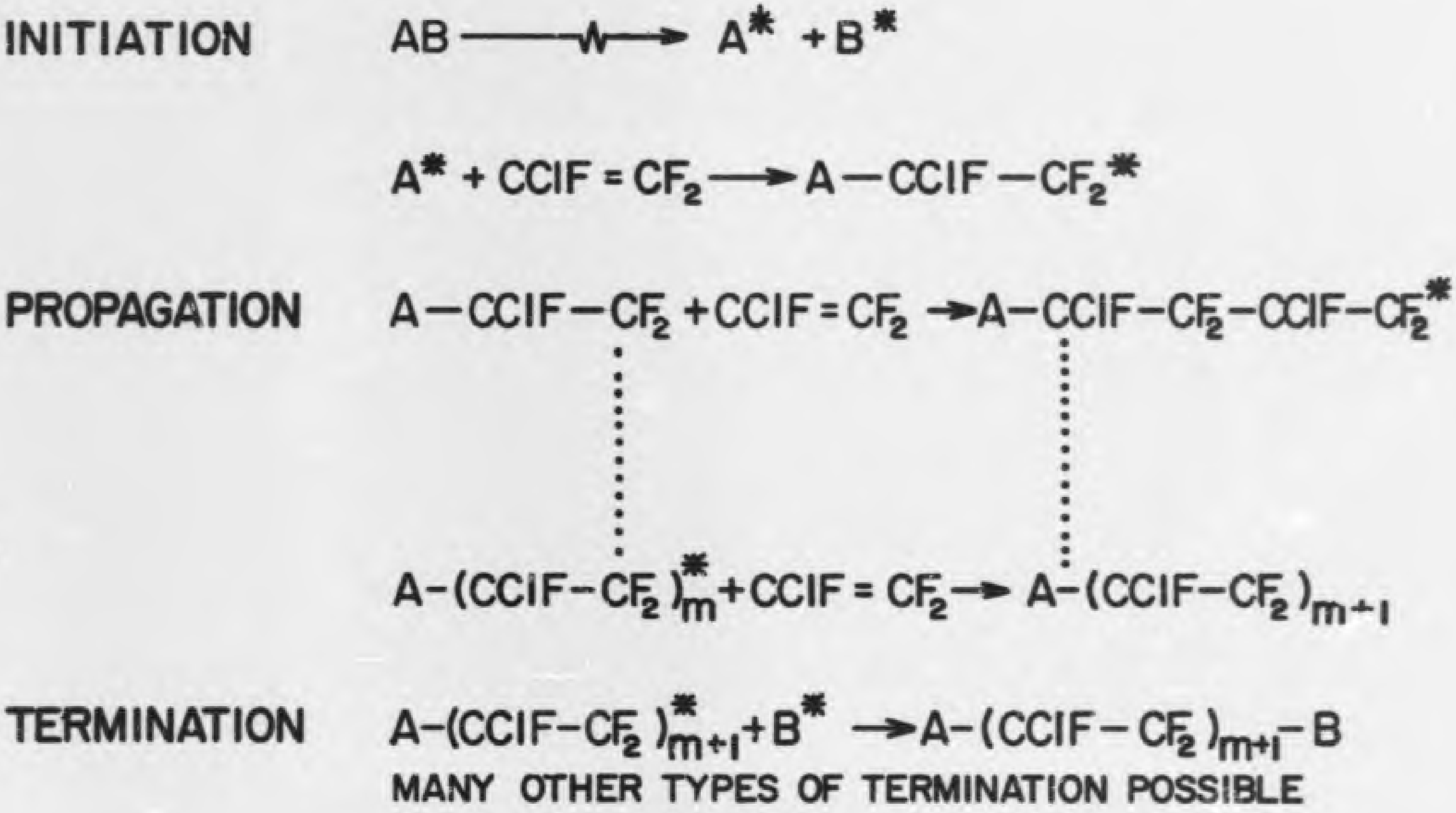


Figure 1 - Simulated application
of MK-48 decoy

$$\begin{aligned}
AB &\longrightarrow AB^{+} \quad e^{*} \\
AB^{+} \; e^{*} &\longrightarrow AB^{*} \\
AB^{*} &\longrightarrow A^{\bullet} + B^{\bullet} \\
& \qquad\; A^{-} + B^{+} \\
& \qquad\; A^{+} + B^{-}
\end{aligned}$$

FIGURE II
EARLY EVENTS DURING INTERACTION OF RADIATION WITH MATTER



INITIATION $AB \xrightarrow{\quad} A^{*} + B^{*}$

$A^{*} + CClF = CF_2 \longrightarrow A-CClF-CF_2^{*}$

PROPAGATION $A-CClF-CF_2 + CClF = CF_2 \rightarrow A-CClF-CF_2-CClF-CF_2^{*}$

$A-(CClF-CF_2)_m^{*} + CClF = CF_2 \rightarrow A-(CClF-CF_2)_{m+1}$

TERMINATION $A-(CClF-CF_2)_{m+1}^{*} + B^{*} \rightarrow A-(CClF-CF_2)_{m+1}-B$

MANY OTHER TYPES OF TERMINATION POSSIBLE

FIGURE III
MECHANISM FOR ADDITION POLYMERIZATION REACTION

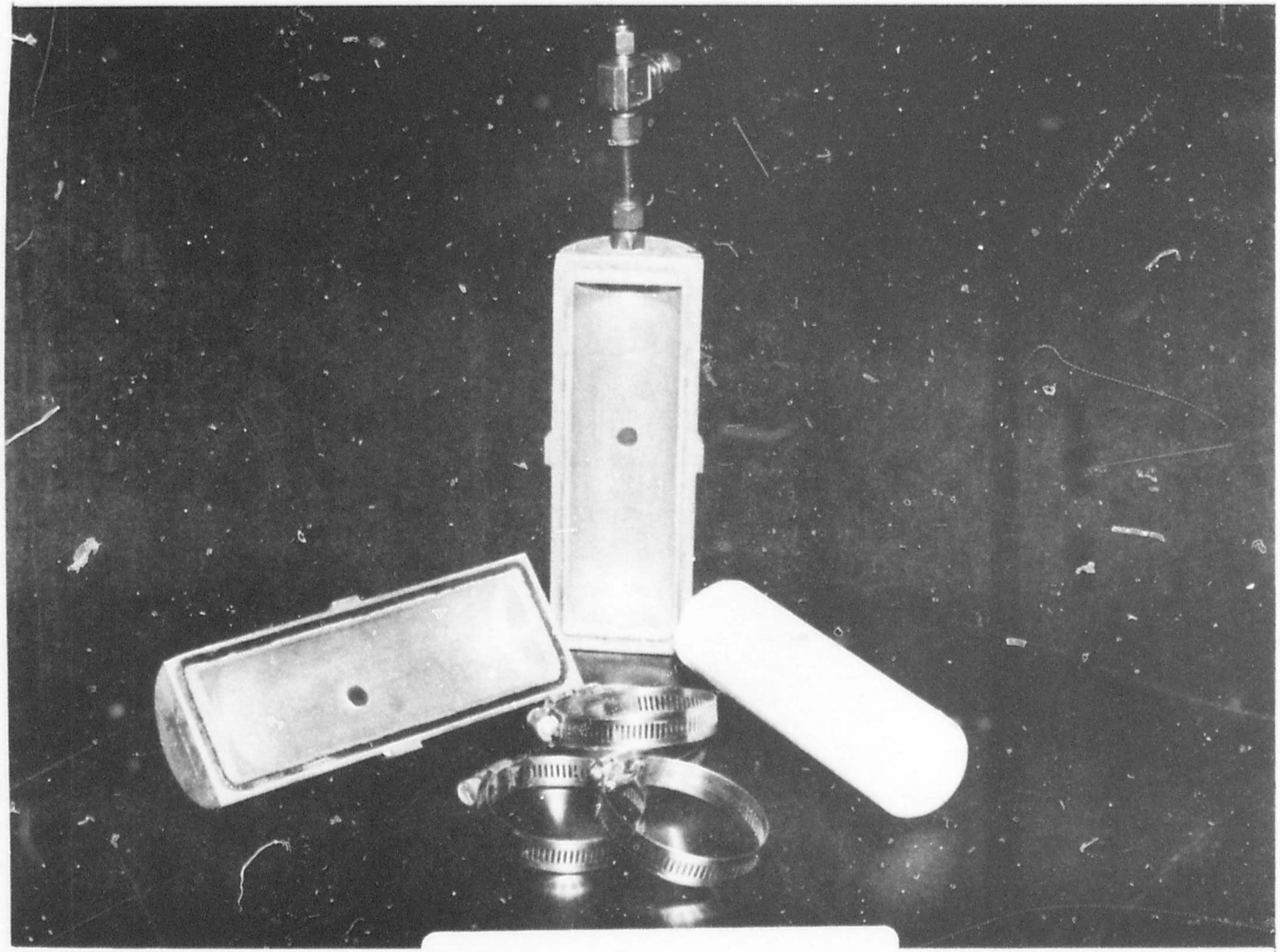


Figure 4 - Demountable cell used
for samples irradiation

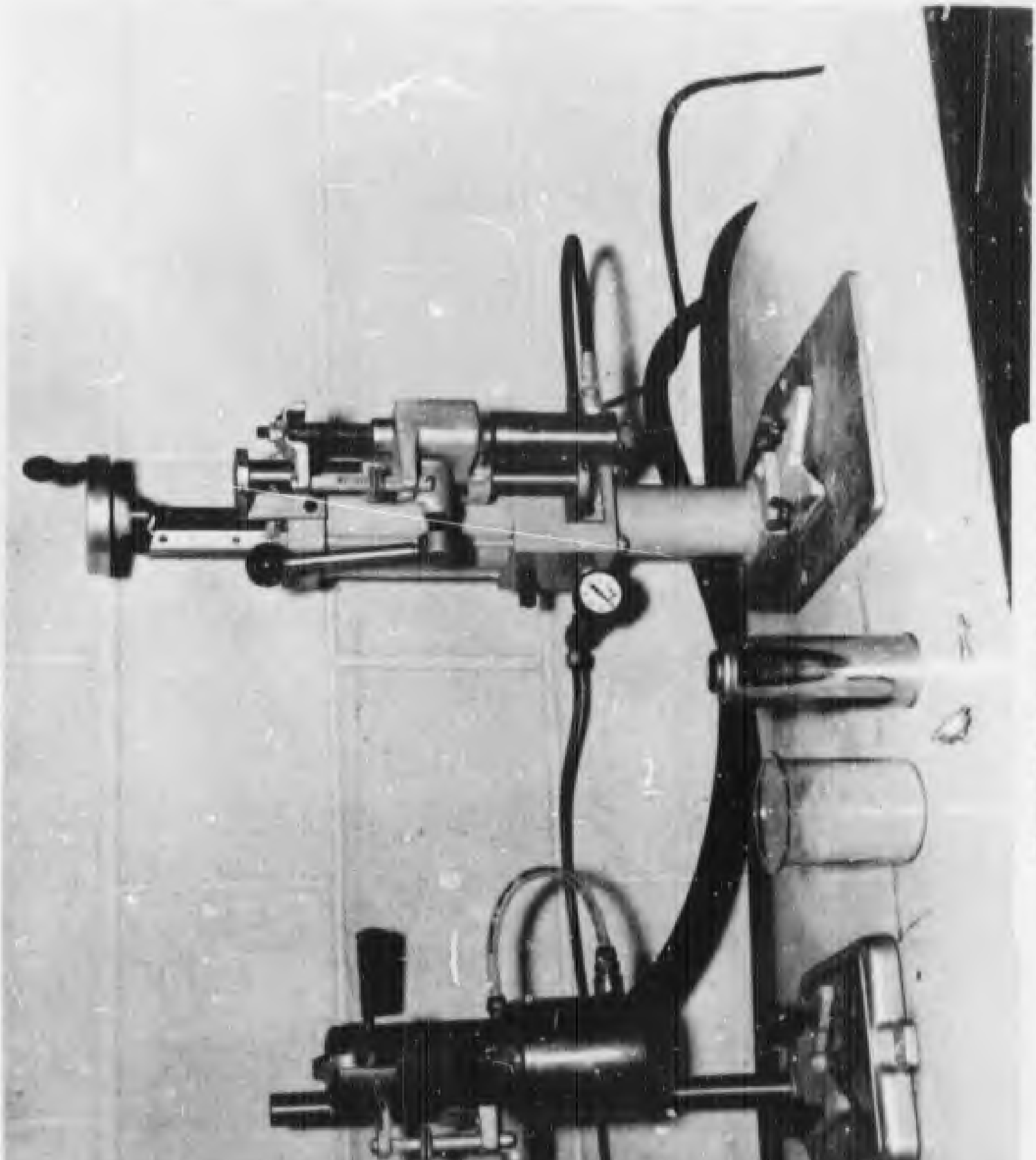


Figure 5 - Aerosol cell and monomer filling equipment

Figure 6 - Sample spinner and radiation chamber

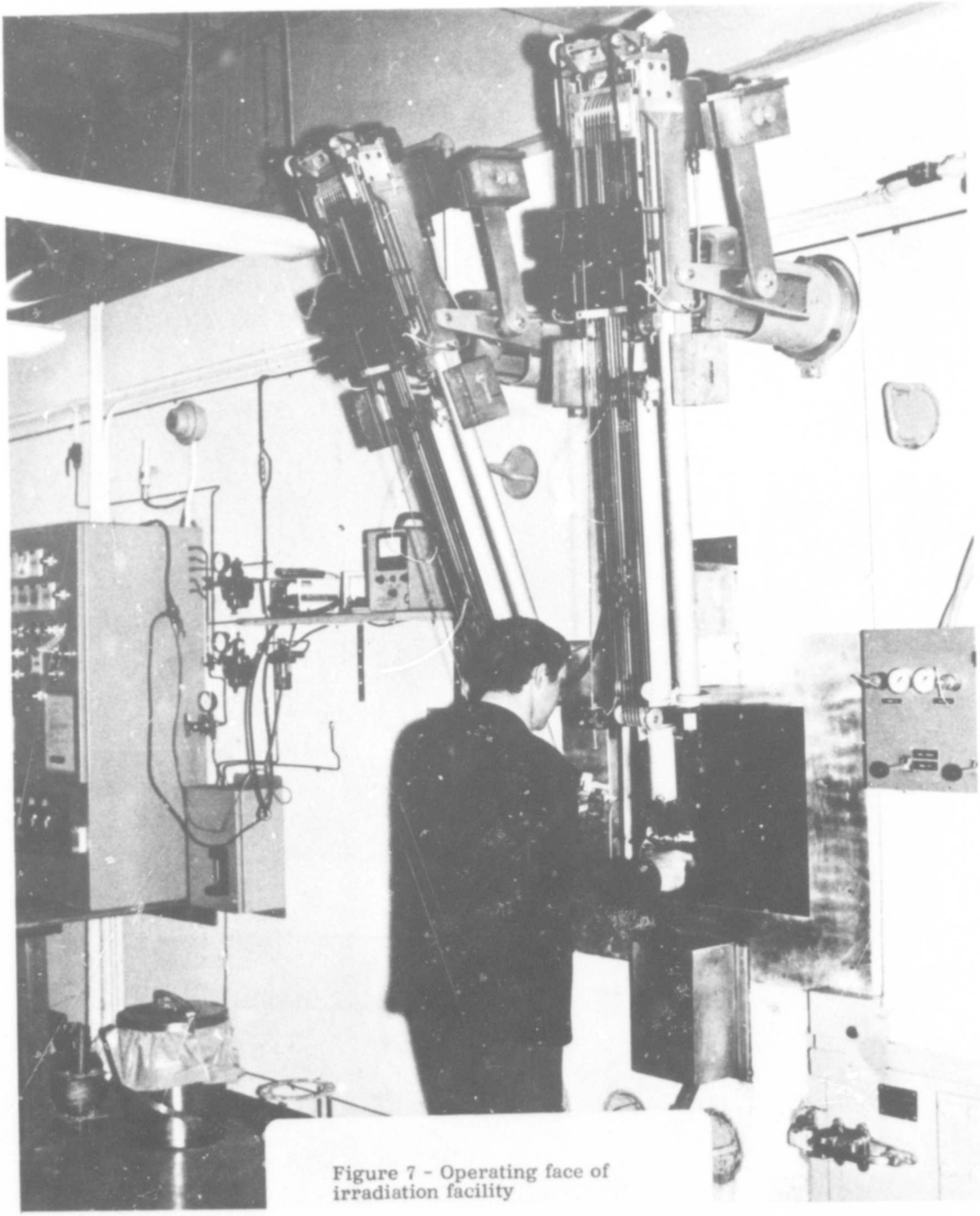


Figure 7 - Operating face of irradiation facility

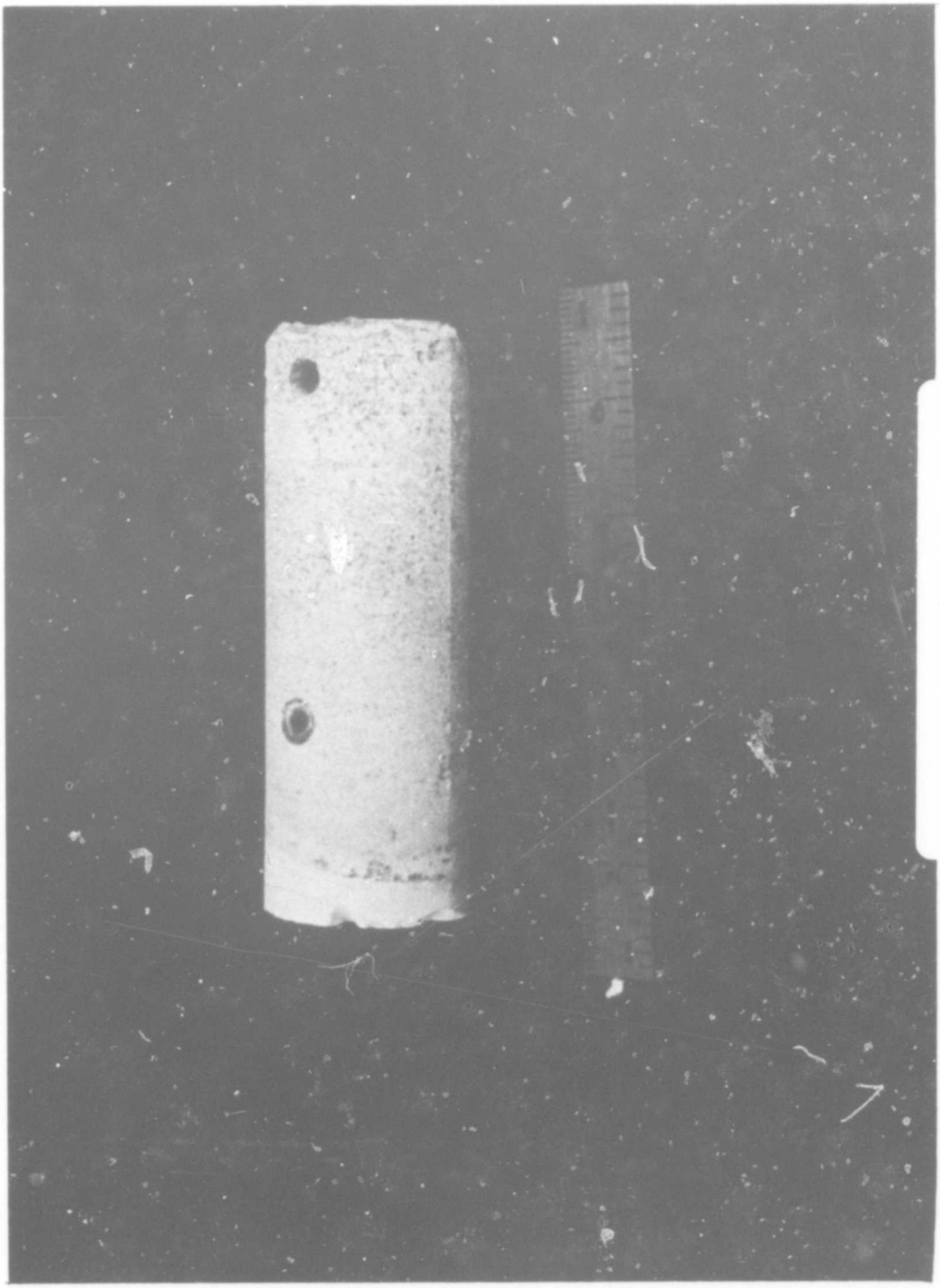


Figure 8 - Flare produced in demountable cell

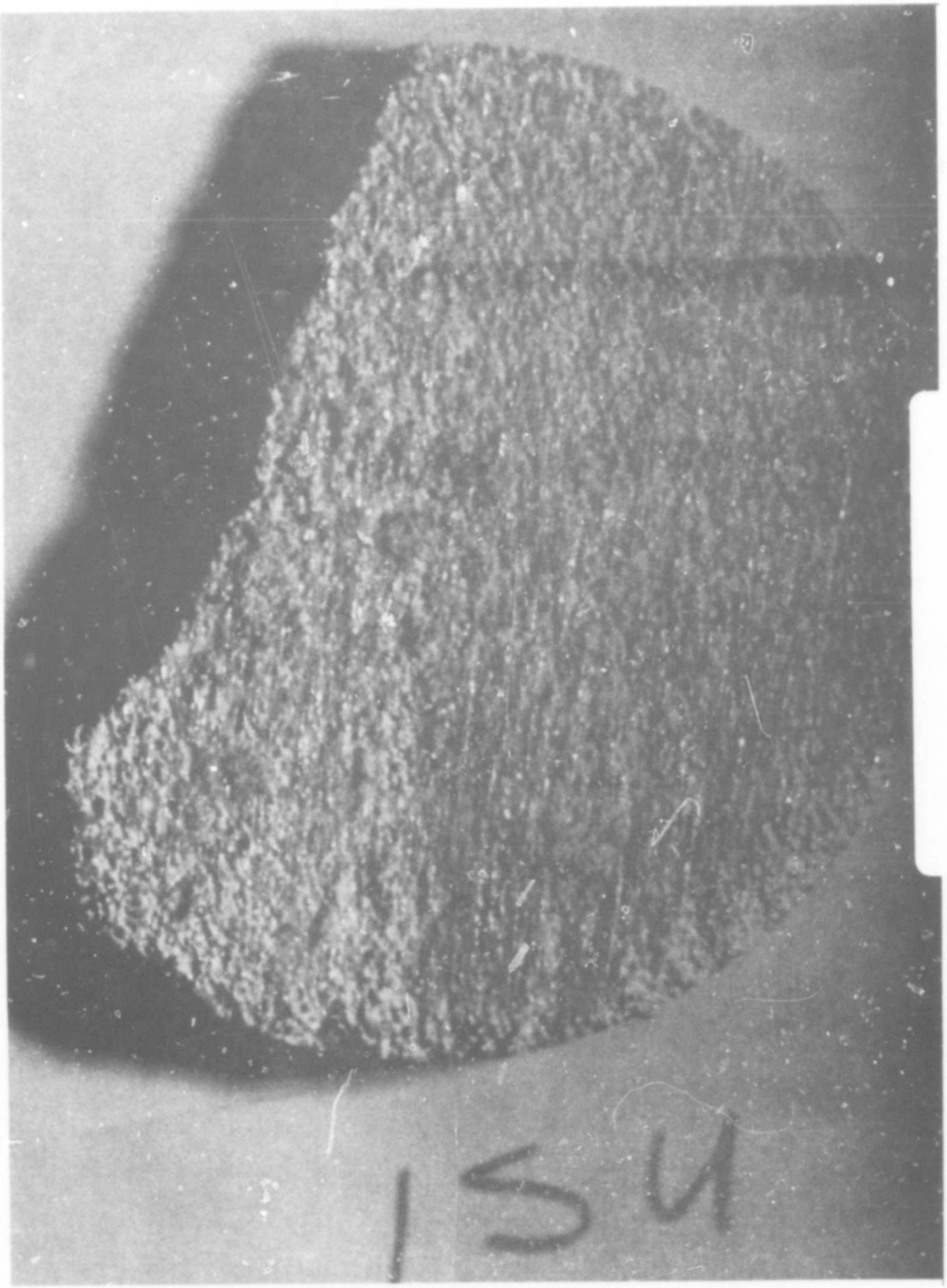


Figure 9 - Cross section of radiation production flare

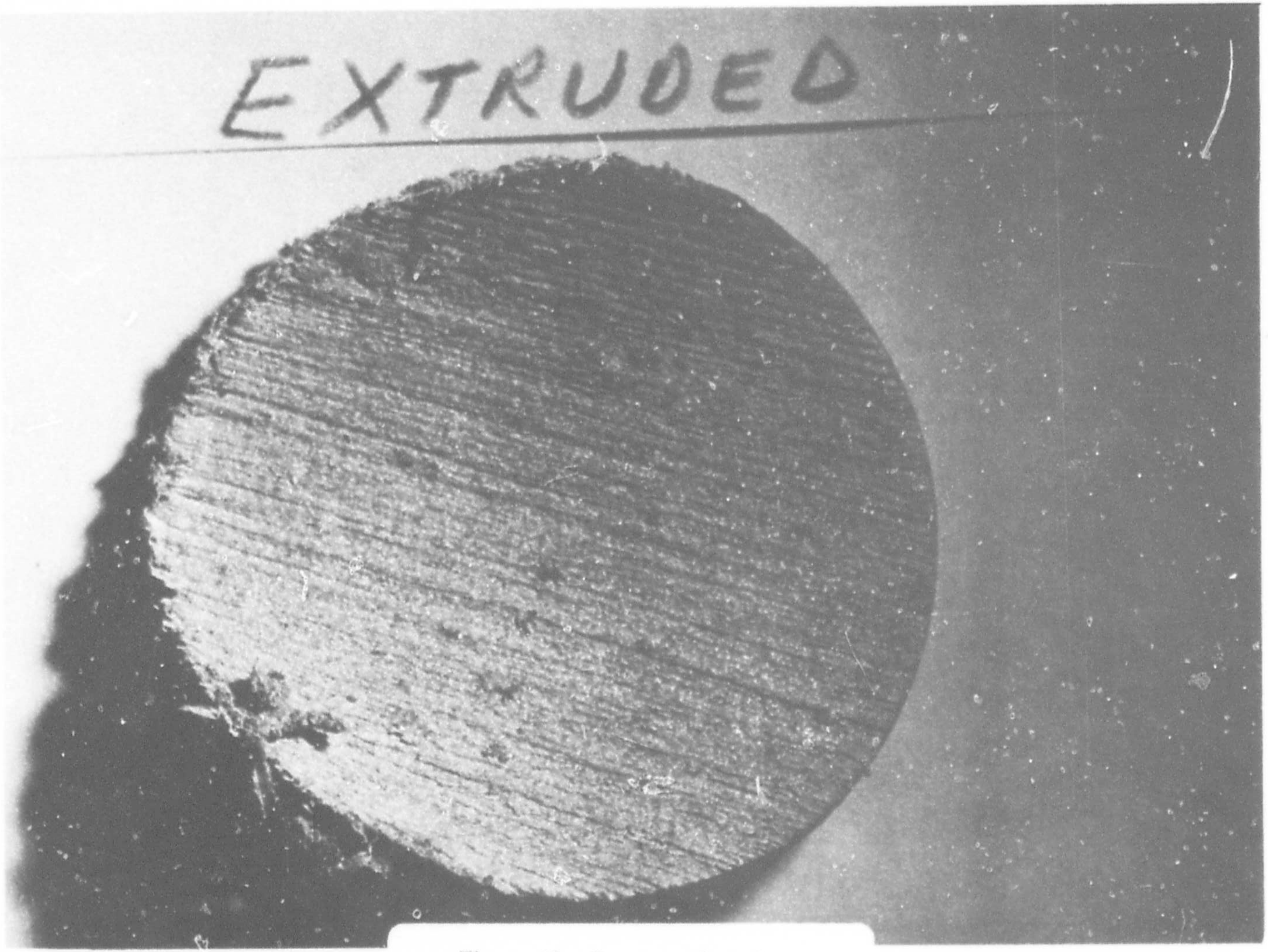


Figure 10 - Cross section of standard production flare

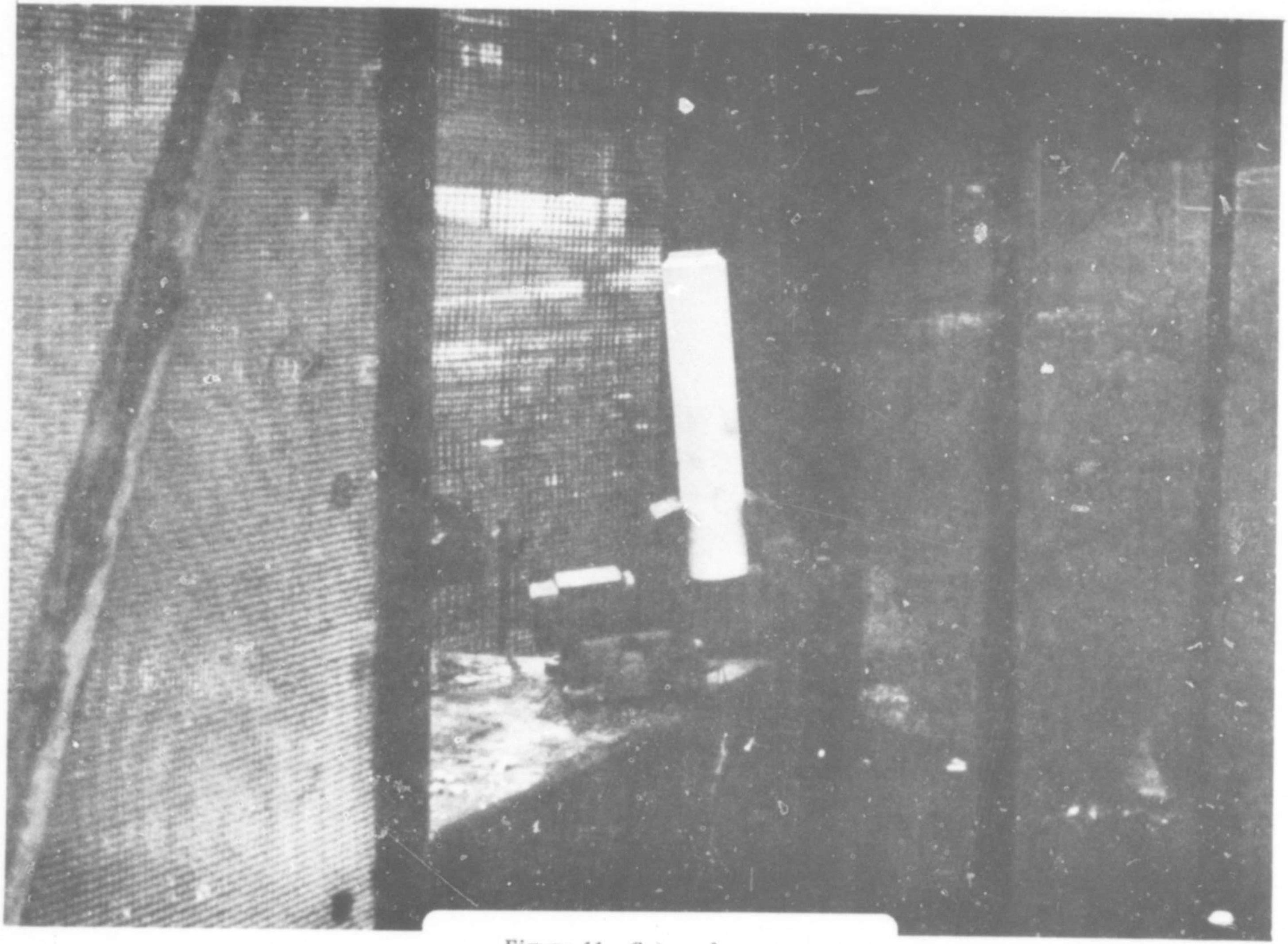


Figure 11 - Set-up for test burning flare

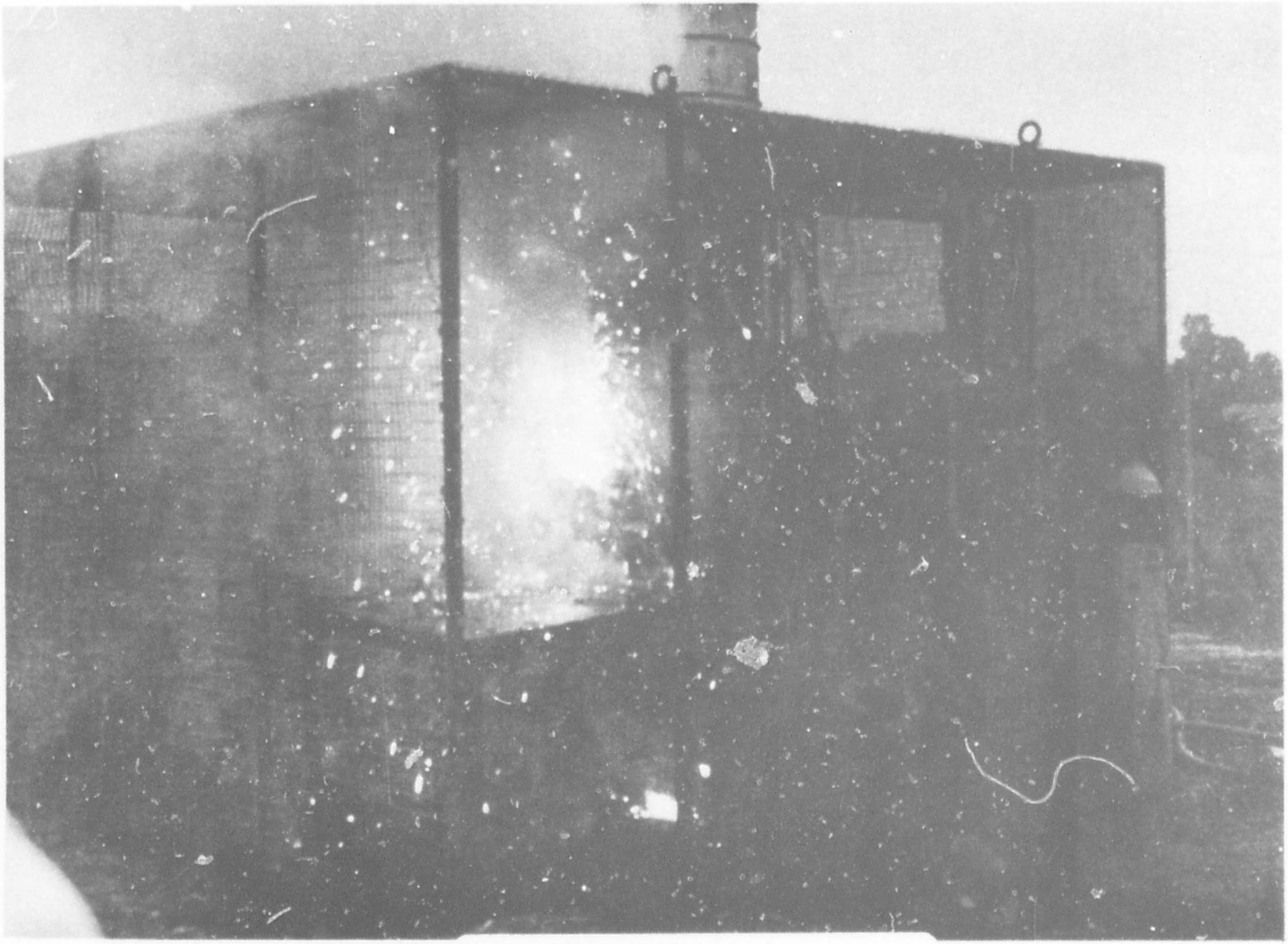


Figure 12 - Burning of radiation produced flare

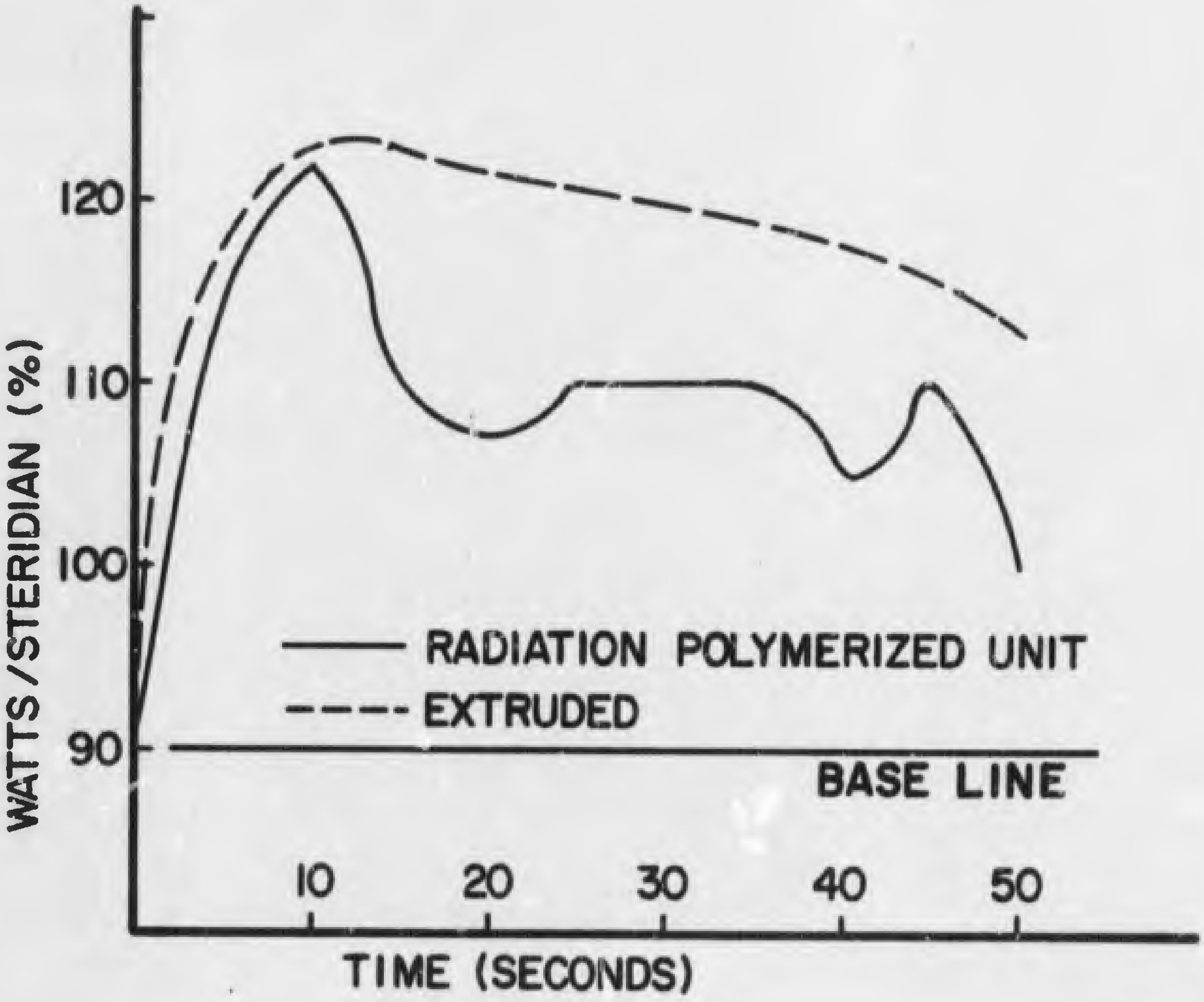


FIGURE XIII
RADIANT OUTPUT VS
FUNCTION OF TIME