

MONSANTO CHEMICAL COMPANY

E. M. Jones
Harry Keating

From Location: Texas City, Texas

Date : June 26, 1959

Subject : Acetaldehyde Explosion in Pressure
Cell No. 11

To : Mr. S. L. Hunter

At : Texas City, Texas

cc: Frank Ball - Spfld.
G. L. Gorbell - St. L.
Plant Manager Safety Board
R. J. Schatz - Spfld.
Research Group Leaders
Research Staff
Research File

PLAINTIFF'S EXHIBIT

MON-1126

SUMMARY:

On June 25, at 1312 hours, an explosion occurred in research pressure cell No. 11 during an experiment to determine the effect of adding excessive amounts of acid to plant product acetaldehyde (AcH). No one was injured. Damage to the pressure cell and equipment is estimated at \$5,000-8,000.

DISCUSSION:

Research had been requested by Production to define the hazards associated with AcH recovery and more particularly to determine the effect of acid contamination and its relationship to paraldehyde (PAcH) formation. Knowledge of the rate of pressure and temperature increase in the above reaction was required to determine if the presently installed relief devices were adequately sized. The required information had been obtained using acid concentrations up to 0.1% H_2SO_4 , which was estimated to be 20 to 100 times the amount which could be anticipated in the plant. Runs were then made at 1% and 3% H_2SO_4 for purely academic reasons to determine if an equilibrium between AcH and PAcH with a maximum calculated pressure of 100-150 psig could be reached regardless of acid content.

The experiment underway at the time of the explosion was the seventh and last of the series in which increasing amounts of H_2SO_4 were being added to AcH. Three percent by weight of concentrated H_2SO_4 was added to 30 lbs of AcH contained in a 24 liter thin walled vessel with an operating pressure of 200 psig. The vessel had been fitted with connections for acid addition and high speed pressure and temperature sensing devices. The vessel was mounted in the pressure cell and all instruments and valves were remotely operated from outside the cell.

Following the established procedure, the vessel containing the reaction mixture from the previous run at 1% acid concentration, was allowed to stand and cool overnight before draining and cleaning for the next run. After cleaning and drying, 30 lbs of fresh AcH from the AN plant was introduced into the vessel.

The necessary amount of acid needed to give a concentration of 3% in AcH was then placed in the acid feed section of the apparatus. The acid was then introduced into the AcH via the remotely operated quick opening valve. The pressure and temperature recording devices showed an immediate increase, of 53 psig in 0.5 sec and 56°C in 2 sec, which was less than had been anticipated from previous runs using lesser acid concentrations. There was no change in temperature or pressure after the initial surge noted above during the following 15 minutes. Previous runs had never indicated any further change after the initial reaction so the high speed recorders were shut off and the reaction mixture left to cool overnight. Approximately 15 minutes after the recorders were cut off and the technician had left the area, the explosion occurred. The explosion was followed by a small fire which was extinguished with dry chemical hand extinguishers. It was necessary to evacuate Research No. 2 since the fumes resulting from the explosion were drawn into the building through the air conditioning fresh air intakes.

The cell walls, constructed of two 3/8" steel plates with an inner layer of 2" oak timbers, received major damage. Both side walls and the front wall were broken loose from their mountings and moved several inches. The entire back wall, of which 1/3 was the blowout panel, was blown completely loose except for one bolt which kept it from falling. The blowout panel, consisting of two sheets of thin aluminum enclosing glass wool insulation was completely blown out. The major portion of the panel was found upwind approximately 200' near the west side of the pilot plant. Small fragments of the aluminum panel and insulation were found scattered over the entire area between the pressure cell and the pilot plant. In addition, several small fragments of the pressure vessel were also found in the vicinity of the pilot plant. Instruments used in the experiment were knocked from their stand but the extent of damage has not been determined.

The enclosed pictures are:

1. Outside view of the back wall and blowout panel.
2. Inside view from the cell doorway looking towards the back wall. Sections of the vessel are scattered on the floor. The white material in the pictures is from the dry chemical extinguishers.
3. Inside view from the back wall toward the corner of the front wall. Door out of picture to left. The bottom of the vessel was mounted 24" from the floor in the vicinity of the rope. Note the dark brown varnish like material on both walls. Walls were grey before the explosion.

4. Inside view of the rear wall and concrete support pillar.
5. View of the control room. Cell doorway at right.

The cause of the explosion is not specifically known. It would appear that if the AcH to PAcH reaction were responsible that the time lag observed would not have occurred. Also, earlier runs made in a stirred autoclave using from 0.2 to 1.0% concentrated H_2SO_4 indicated the AcH to PAcH reaction to be complete within 3 minutes as observed by the rapid decline in pressure. Vapor pressure curves for AcH and PAcH also indicate that for the temperatures and pressures recorded in the stirred autoclave and the thin wall reactor that the reaction mixture could only be primarily PAcH after the initial pressure surge. The literature also indicates that this reaction is essentially instantaneous.

Other possible causes in addition to the known reaction above are: 1) Lack of mechanical mixing, purposely omitted, (to simulate acid contamination of a plant storage vessel), could result in a highly concentrated acid - PAcH (or AcH) phase localized in the bottom of the vessel; 2) Oxidation of either the AcH or PAcH by H_2SO_4 (a weak oxidant).

Actually, the noticable amount of brown and black material obtained while cleaning the reactor between runs and the brown varnish material coating the cell wall after the explosion, indicates the strong possibility of oxidation and charring.

There is strong evidence to indicate that the explosion initiated at the bottom of the vessel. This was concluded from the fact that there were indentations in the cell walls both directly behind the vessel and at right angles in the side wall. Both were in the vicinity of the bottom of the vessel. This would further indicate that the acid had phased out and that the reaction was from the localized acid and either PAcH, AcH or both. Since a time lag had been observed (30 min) between acid addition and explosion it is most probable that the explosion was due to the more dense PAcH and H_2SO_4 rather than AcH and H_2SO_4 .

Examination of the vessel fragments indicated that the rupture of the vessel occurred when the internal pressure far exceeded its tensile strength. This can only happen when a very rapid pressure rise is obtained. Although the fragments were all sheered at a clean 45° angle with uniform edges the fragments were considered too large for a true detonation.

COMMENTS:

1. The inertia from the added weight imposed on the blowout panel by the glass wool insulation probably added materially to the damage to the cell walls.

Fox made the recommendation during construction that the insulation not be installed but it was installed without his knowledge at the recommendation of Engineering. Because of the aluminum covering the insulation was not noticeable after installation.

2. Although the blowout panels were located near the top of the back wall to provide protection to personnel in the area, no facilities were provided to stop flying fragments.
3. Although a pressure relief would have been of questionable value in this explosion, no relief had been installed because none were available. One was on order. Plans were originally made to install a relief device if early runs, made with low concentrations of acid, indicated a possibility of pressures greater than 100 psig.
4. An acetylene cylinder equipped with a pressure regulator and chained to the wall in the control room was knocked down. The main valve had been left open and acetylene was released into the area until noted on finally entering the area with an air mask.
5. The rear of the cells are tied together with a trench containing the utility piping which allowed the explosion and fire to be transmitted to the adjoining cells. This resulted in blowing out the blowout panel of the adjacent cell (No. 12).
6. Pipes with threaded ends extend through the face of cell to provide for controls and reach rods. None of the unused holes in the new cells have been capped. This allowed gas and flame from the explosion to spew out into the control room.
7. Wind direction and location of the air conditioning fresh air intakes necessitated evacuation of Research No. 2.
8. The area around the pressure cell was overrun with spectators even before the nature of the emergency could be determined. This hampered the necessary operations required to safeguard the area.
9. The cell was entered on two occasions fifteen minutes after the initial temperature and pressure surges were observed. It was assumed, because of data obtained from previous runs; that the reaction was complete. However, the vessel was still at the reaction temperature and pressure previously noted.

10. The cylinders chained to the control room side of the cell wall were knocked down from the force of the explosion. Instruments mounted on a table 12" from the wall were knocked to the floor.

ACTION TO BE TAKEN: (Research AN Process Group)

1. Identify the PAcH catalyst in the AN plant.
2. Repeat the experiments on the rate of pressure and temperature rise in the AcH to PAcH reaction in the presence of concentrated acids and bases (concentrated H_2SO_4 , anhydrous HCl , NH_4OH , and concentrated $NaOH$) but with the following equipment modifications:
 - a. Install agitator.
 - b. Install standard continuous pressure and temperature recorders in addition to the high speed brush recorders.
 - c. Install a rupture disc and relief valve.
 - d. Make use of one of the concrete cells designed with a much higher pressure rating.
3. Attempt to determine the cause of the explosion by investigating the reaction of: 1) concentrated H_2SO_4 on PAcH; 2) concentrated H_2SO_4 on PAcH containing 5-10% AcH; and 3) 1 and 2 above in presence of stainless steel; 4) reactions of concentrated H_2SO_4 and AcH to give products other than PAcH.
4. Preliminary experiments to be with smaller quantities of materials.

RECOMMENDATIONS:

1. Review the present cells and their construction to determine the necessary corrections or additions to further safeguard this area. (Fox, Henslee and Jones with the Engineering Dept.)

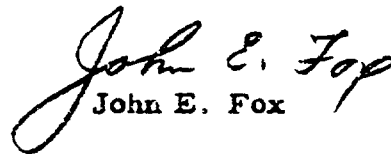
We suggest the following as a starter:

- a. Replace the present blowout panels on the new cells with a thin light weight material.
- b. Block the utility trench between each cell.
- c. Cap all unused holes through the cell walls.

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- d. Installation of a blowout retaining mat or wall.
 - e. Consider enlarging the blowout panels.
 - f. Use welded construction to tie all cell walls together. (While all welds held, practically all bolts pulled out or were sheared off.)
- 2. All pressure reactors are to be equipped with a rupture disc or relief valve. Safety Manual so states. (All Group Leaders responsible for their equipment)
 - 3. Reactors should be mounted out away from the cell wall to reduce the force of the explosion. (All Group Leaders responsible for their equipment)
 - 4. Relocate the airconditioning fresh air intakes for Research No. 2. (Henslee and Jones responsible.)
 - 5. Personnel are not to enter a pressure cell while the reactor is at operating temperature and pressure. Safety Manual so states. (All Group Leaders responsible.)
 - 6. All personnel not directly associated with the emergency or being of aid should stay away from the area. (Staff and Group Leaders responsible.)
 - 7. Consider the necessity of equipping each pressure cell with automatic fire extinguishing equipment. (Fox and Staff responsible.)
 - 8. Review of Dept. 20 plant piping to determine whether the possibility exists for inadvertent addition of concentrated acid or base to the AcH facilities. (Dept. 20 Supervision responsible.)


John E. Fox


R. G. Roth

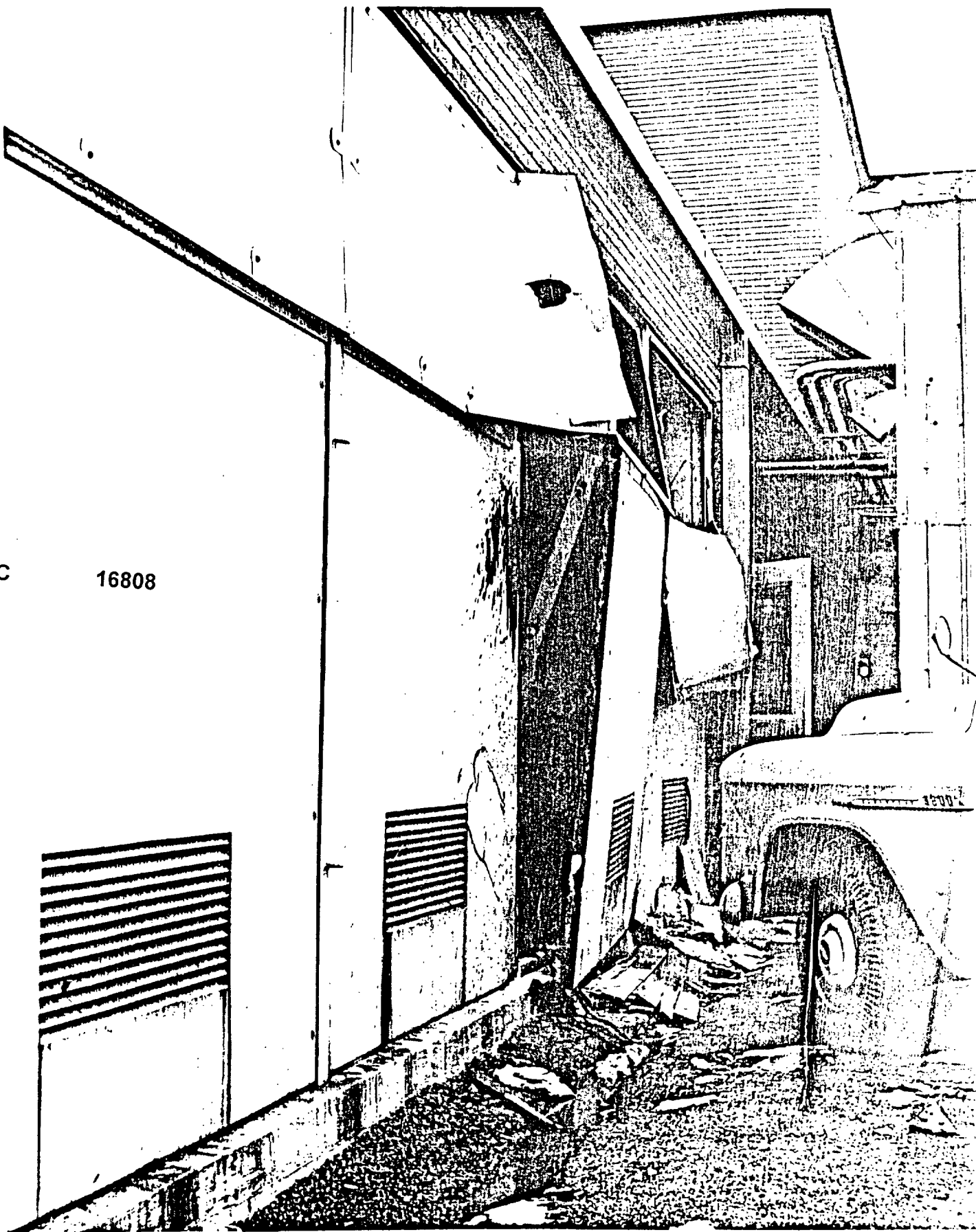
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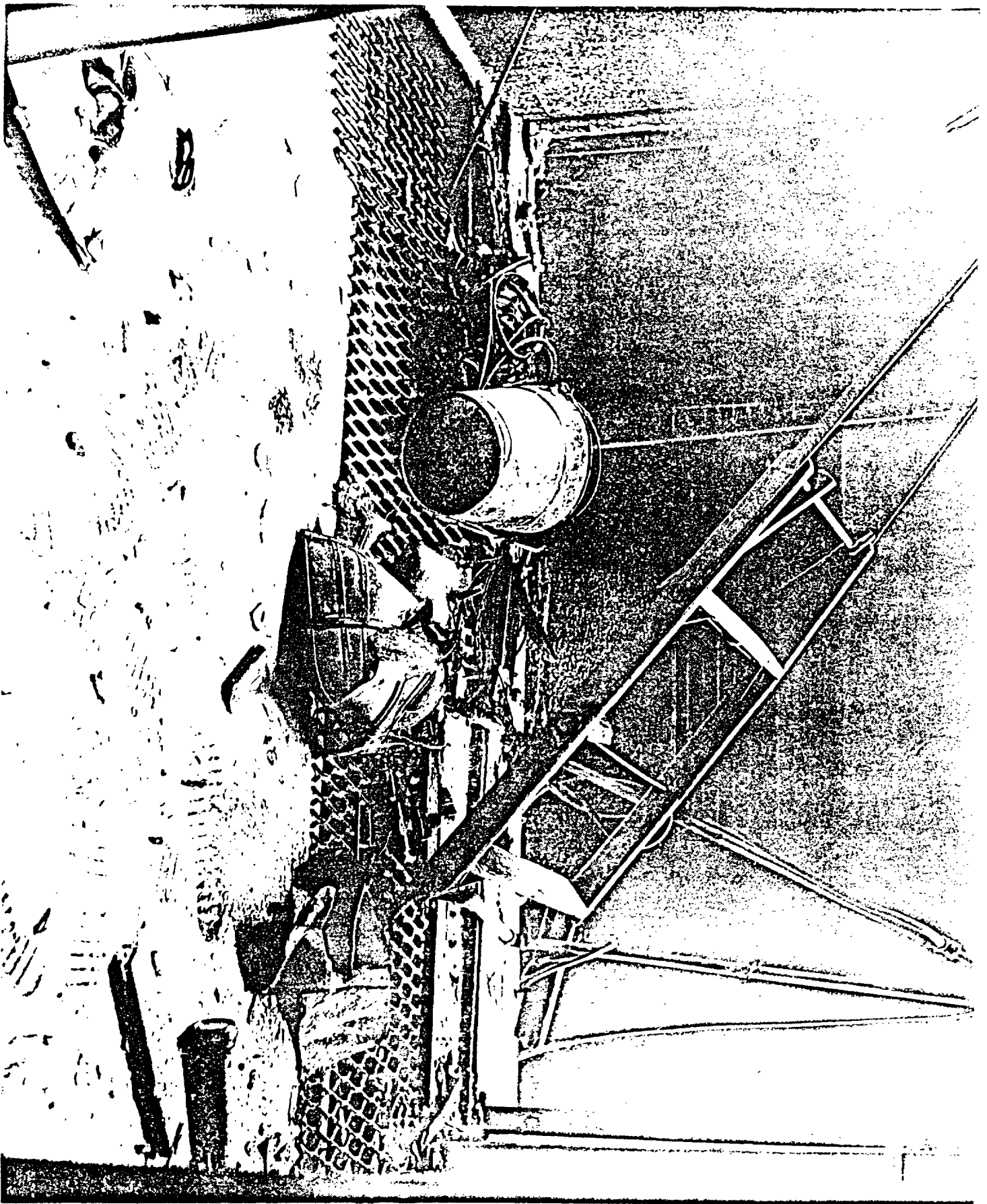
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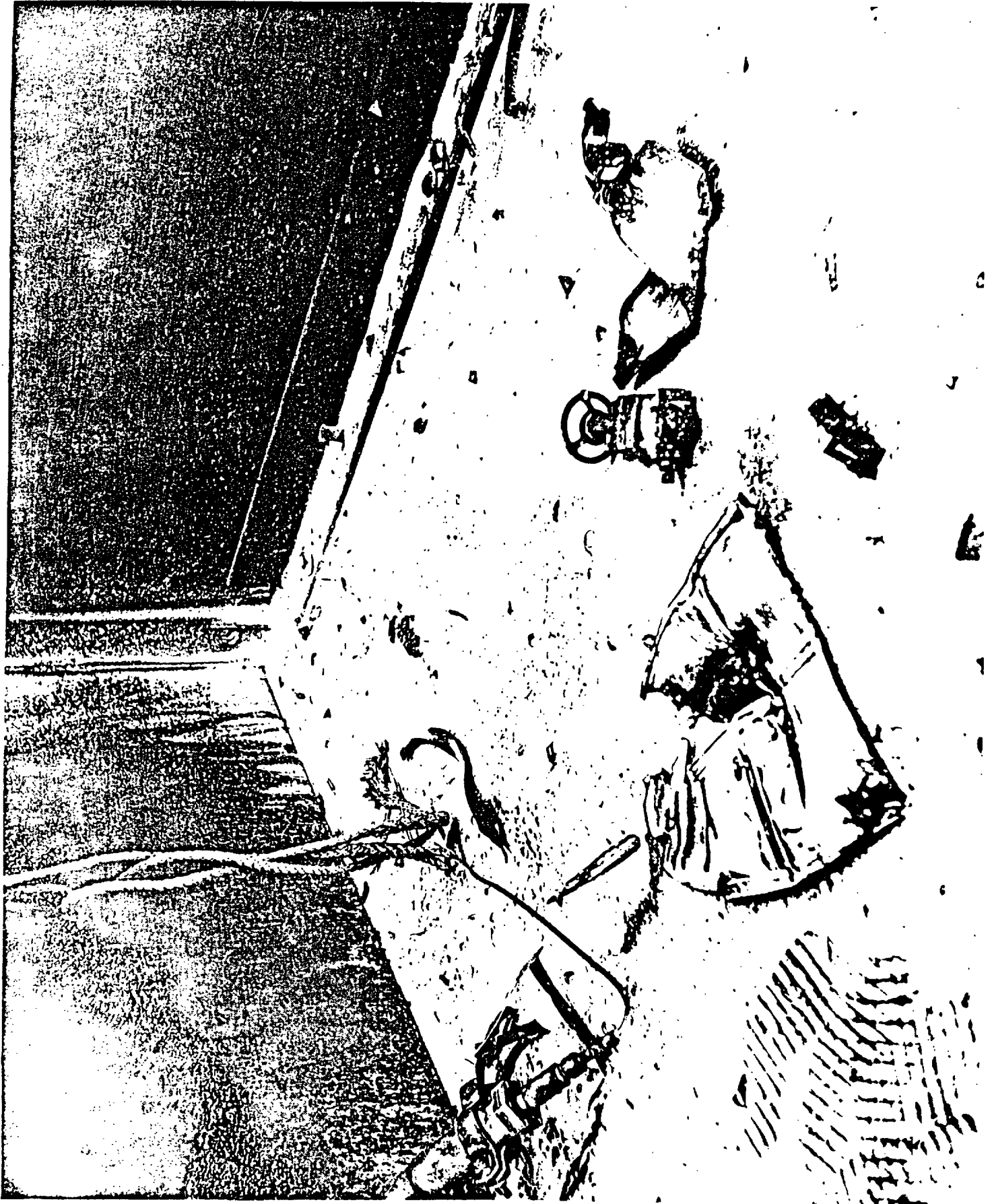
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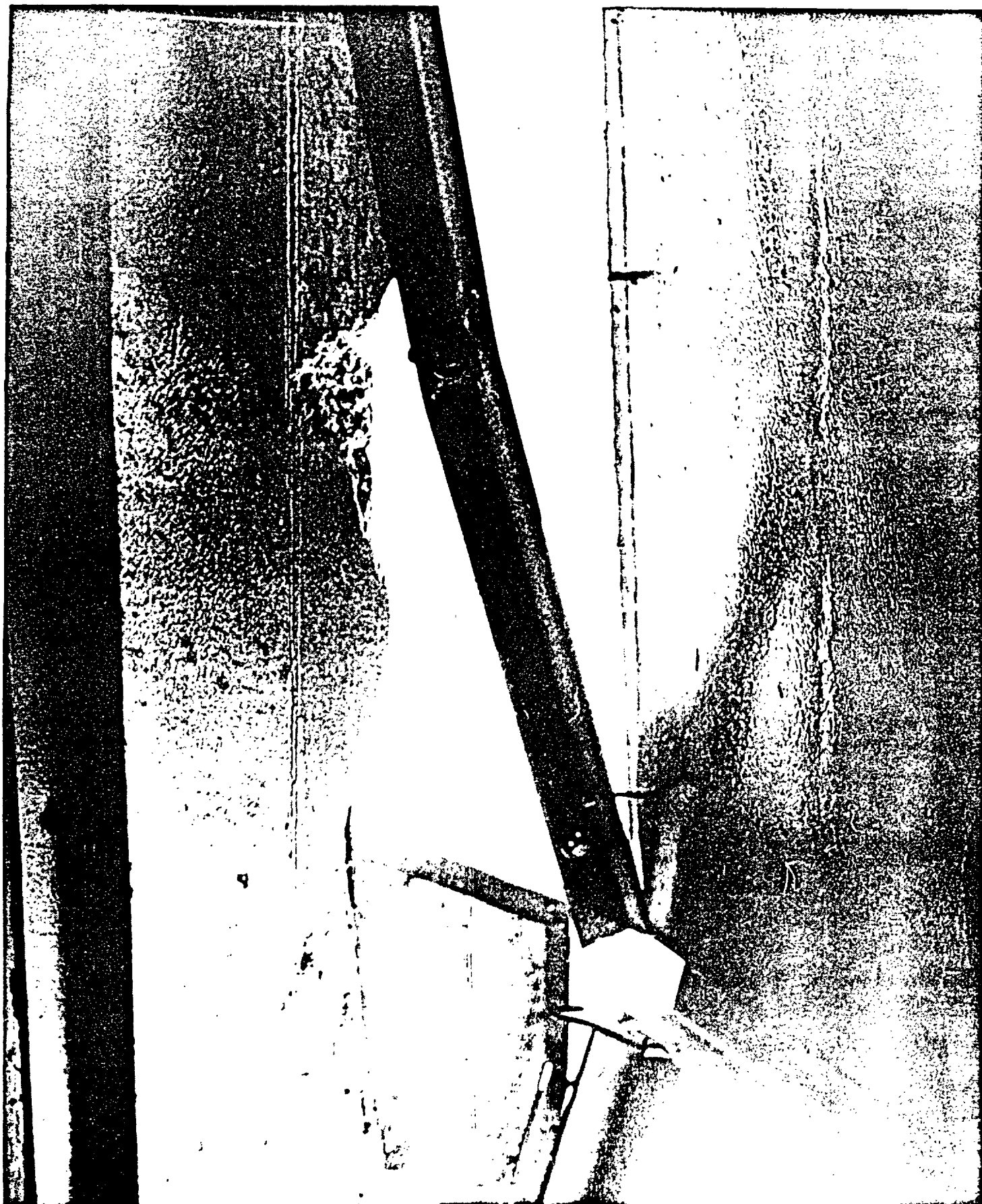


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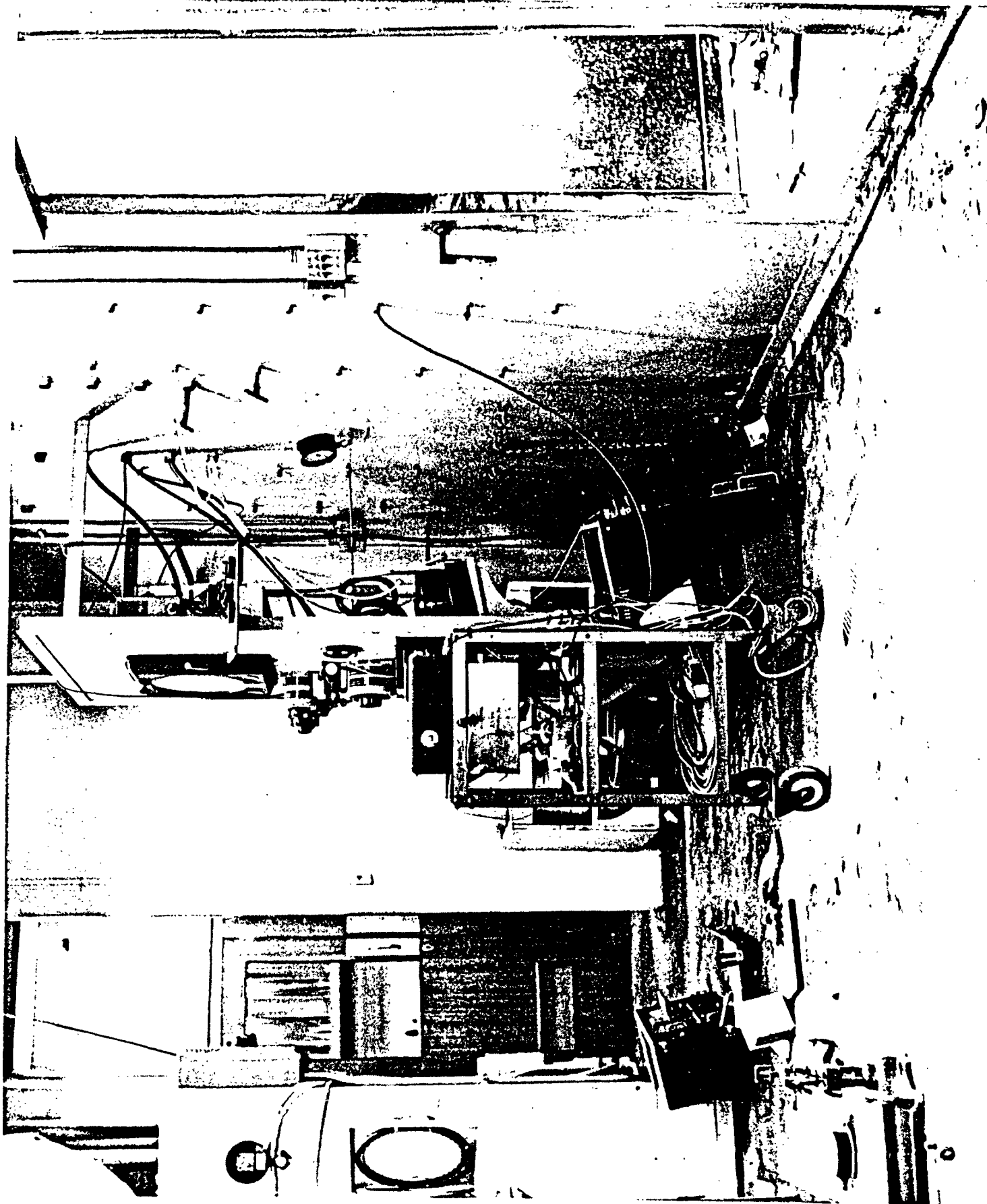




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