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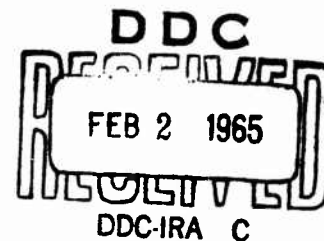


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SECOND QUARTERLY PROGRESS REPORT
OCTOBER - DECEMBER, 1964

FEASIBILITY STUDY OF FLOTATION OF
SUNKEN VESSELS BY INJECTION OF
FOAMED FLOTATION MATERIAL



FOR

BUREAU OF SHIPS
DEPARTMENT OF THE NAVY
WASHINGTON, D.C.

CONTRACT NObs-90437

January, 1965

ATLANTIC RESEARCH
CORPORATION

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January 26, 1965

Chief, Bureau of Ships
Department of the Navy
Washington, D. C. 20360

Attention: Mr. A. Winer, Project Monitor
Materials and Chemistry Branch
Code 634C 1

Reference: P.R. 634C1-49519/.1(s)

Subject: Transmittal of Second Quarterly Progress Report for
October through December 1964 on Contract NOBs-90437

Dear Mr. Winer:

Enclosed herewith are three (3) copies of the Second Quarterly Progress Report for Atlantic Research Corporation on the "Feasibility Study of Flotation of Sunken Vessels by Injection of Foamed Flotation Material" for the period October through December 1964. The material included here reports the progress under Contract NOBs-90437.

Very truly yours,

ATLANTIC RESEARCH CORPORATION

Charles B. Darley
Project Manager

CBD:mb
Enclosures

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Bureau of Ships
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SECOND QUARTERLY PROGRESS REPORT
OCTOBER - DECEMBER, 1964

FEASIBILITY STUDY OF FLOTATION OF
SUNKEN VESSELS BY INJECTION OF
FOAMED FLOTATION MATERIAL

Prepared by:

C. B. Darley

Approved by:

W. P. Jensen

For

BUREAU OF SHIPS
DEPARTMENT OF THE NAVY
WASHINGTON, D. C.

Contract NObs-90437
BuShips Identification No. 1013-6
Project Serial No. SR007-03-04-TASK 1013

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia

January 1965

ABSTRACT

Extensive laboratory tests of several foam formulations under both air pressure and water pressure have produced good foams of low density which are not affected by water environments, elevated pressures or low temperature. These foams have maintained adequate cell integrity and resisted cell rupture upon release of external pressure. Photographs are included which show the sequence of foam flotation events as represented by laboratory testing.

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1.0 SUMMARY

In continuation of the literature survey, two patents which basically describe the concept of raising sunken ships with a plastic foam have been discovered. Since they have added no new information, they have been relegated to a secondary interest.

In experimental work, Trident and Atlantic Research have continued their parallel, but separate, investigation of polyurethane foam systems. Trident has progressed to over 180 psig with the air pressure studies and Atlantic Research has (during the reporting period) continued its underwater tests to over 60 psig. Results of all testing have exceeded expectations. The Material Transport studies have not disclosed any insurmountable problems and the preliminary economic studies indicate the operating cost of a foam salvage operation to be one tenth that of conventional salvage.

The adverse conditions of an undersea salvage, those of environment, pressure, and temperature, have not had any considerable effect on the foams produced thus far. It has been recommended that some metering and mixing equipment be acquired and a subscale demonstration be performed in a diving school tank.

Tables and figures of the screening and laboratory testing are included in Appendices 7.2 and 7.3.

2.0 INTRODUCTION

This is the Second Quarterly Technical Progress Report which discusses the work accomplished during the period October through December, 1964, on the "Feasibility Study of Flotation of Sunken Vessels by Injection of Foamed Flotation Material".

This study, under Navy Contract, NObs-90437, is a nine-month program to ascertain the feasibility of raising sunken vessels by injecting foamed-in-place flotation material into the ballast tanks, and into the interior compartments of the vessel. The flotation material must then provide positive buoyancy for the vessel, and maintain this buoyancy after the vessel has surfaced to allow the vessel to be retrieved. In order to accomplish this required buoyancy, the foam must have characteristics of:

- a. Relatively low density.
- b. Mechanical and physical stability.
- c. Low water absorption rate at elevated hydrostatic pressures.
- d. Low volume decrease when exposed to hydrostatic pressures and low temperatures.
- e. Be easily foamed between 29° and 70°F.
- f. Have wet compressive strength to resist crushing at elevated hydrostatic pressure.
- g. Capability of displacing the water within the sunken vessel.

The hydrostatic pressure levels selected for this feasibility study involve the following:

- a. The pressure developed by the flotation material formulation, when introduced into the sunken vessel, must exceed 26 psig in order to displace water at a depth of 60 feet.
- b. The pressure developed by the flotation material formulation, when introduced into the sunken vessel, must exceed 66 psig in order to displace water at a depth of 150 feet.
- c. The pressure developed by the flotation material formulation, when introduced into the sunken vessel, must exceed 165 psig in order to displace water at a depth of 375 feet.

3.0 BACKGROUND

The First Quarterly Progress Report for this study was submitted in October, 1964. This report included a technical discussion of the motivations for attempting to raise a sunken vessel, be it military or commercial, of the inadequacies and complexities of our present antiquated salvage techniques and technology, and of the limitations imposed on a diver by the undersea environment. The need, therefore, is expressed for a new development which would speed up the salvage operation and simplify the underwater work to be done. This would constitute a major break-through in the art of marine salvage.

Of major concern in raising a sunken surface vessel was the consideration of deck loading. During a typical vessel salvage employing compressed air to provide buoyancy, special precautions must be maintained to prevent rupturing the vessel's bulkheads and deck plating by excessive differential pressure. In a vessel salvage, employing flotation foam for buoyancy, it was determined that if the worst conditions were assumed there would be an upward load on the vessel's deck of slightly over 4 psi. It was also anticipated that adherence of the foam to the bulkheads, stanchions, fittings, and machinery would be considerable and the actual upward deck loading would be appreciably less. These determinations were for a DD692 class destroyer in which the complete filling of the first platform deck compartment and of the two fire rooms and two engine rooms with an 8PCF foam would provide sufficient excess buoyancy to bring the vessel to the surface, with the upper portion riding slightly above the surface.

A literature survey was undertaken to obtain specific information concerning foam formation under water or at elevated pressures, but none was found. Although no specific information was disclosed, the survey verified certain conclusions regarding the foaming system requirements in this application. These were:

- a. The system must be easily handled.
- b. The components should be liquid.
- c. The foaming reaction should be highly exothermic.

- d. Gassing should be tied to polymerization in order to eliminate unequal temperature effects on the two reaction rates.
- e. The choice of blowing gas should be determined primarily by its solubility in the system.
- f. The properties of the components, and of the resulting foam, must be adequate to resist the effects of the environment.

Because of the great wealth of information available concerning polyurethane systems and it being among the relatively few types of systems in which foaming and polymerization are tied, this became a logical choice for study.

An experimental program was begun to investigate those ingredients which could be combined to yield a rigid or semi-rigid closed cell foam of low density, and with sufficient strength to resist the collapsing effect of the elevated pressures, and to resist cell bursting pressure of trapped gases when the external pressure was released. The resulting foam formulations were closely evaluated on the basis of texture, density, strength, reaction time, and cohesiveness. Qualitative comparisons were made on the strength of these results and the more promising of the prepolymer and one-shot formulations were singled out for additional studies in pressure and underwater tests.

In a series of tests made, using two formulations at pressures up to 75 psig, the resultant foam densities were plotted as a function of external pressure and compared with the density predicted by Boyle's Law. This plot indicated the possibility of maintaining a low density foam despite the high external pressure.

In the underwater tests, two formulations were tested at atmospheric pressure. The resultant foams were characterized by superior underwater behavior, high strength, resistance to water absorption, and stability. In these tests it was possible to raise a heavy walled resin pot, which had no buoyancy of its own, up to 12 to 15 inches from the bottom of a large beaker.

On the basis of these tests it was apparent that one or more polyurethane formulations could be developed which would meet all of the design requirements.

4.0 TECHNICAL DISCUSSION

4.1 Literature Survey

During this report period no specific information concerning foam formation underwater or at elevated pressures was obtained from the documentary sources, but very interestingly two United States patents were discovered which encompass the generalities of the concept of raising a sunken ship employing a plastic foam for buoyancy. In one patent, No. 3,091,205, dated May 28, 1963, the inventor, Mr. W. Watson, discusses a "Method of Raising Sunken Vessels." The invention relates to a method for raising sunken vessels and in particular to a procedure by means of which buoyancy is restored to the vessel itself without the use of pontoons. In the other patent, No. 3,057,694, dated October 9, 1962, the inventor, Mr. M. Kessler, discusses "Apparatus for Raising Sunken Ships." This invention relates to a method and apparatus for raising sunken vessels, and more particularly to a method for raising sunken vessels by pumping into them a mass of foaming plastic material to displace the water in such vessels.

In neither patent, do the inventors disclose specific details nor discuss the practicality and reduction-to-practice of their methods and underwater foam formulations. Therefore, no new or additional information was obtained from them. These two patents appear in this report in Appendix 7.1.

4.2 Experimental Program

Atlantic Research and Trident have continued their concurrent and parallel programs to further investigate the techniques and formulations considered promising during the first reporting period and investigate new ingredients and formulations in an attempt to optimize the resultant formulations. As before, the areas of study were allocated to:

- a. Screening studies performed by Atlantic Research Corporation and Trident.
- b. Pressure studies performed by Trident.
- c. Underwater studies performed by Atlantic Research.

Close liaison was maintained to prevent any overlapping or duplication of efforts throughout this period and to keep abreast of the developments in the pressure and underwater experimental programs. The progress of the pressure studies performed by Trident are reported in Section 4.2.2. A summarization of the progress Atlantic Research has made in the underwater studies is reported in Section 4.2.4. Section 4.2.3 contains a discussion of the laboratory underwater pressure test apparatus which was constructed by Atlantic Research.

4.2.1 Screening Studies

A continuing effort at Atlantic Research has been made to obtain formulations that best suit the desired physical properties and characteristics for a foam flotation material and be economically produced. Recipes of formulations have been investigated which vary the isocyanates, both crude and refined, the polyethers and polyols, silicone surfactants, blowing agents, catalysts, and nucleating agents.

A number of existing formulations were modified in order to improve their physical properties, increase the heat of reaction, and minimize water logging. An attempt was made to obtain a closed, small cell foam by nucleating the polyol mixture with Cab-O-Sil (M-5), as in Formulation XV-D. The use of Cab-O-Sil was optimized at a level of 0.5 per cent of total formulation. A lesser amount was not quite enough to yield a uniform small cell foam, and a larger quantity tended to gel the solution. Cab-O-Sil added to the polyol produced the best results. This formulation was found to perform equally well without using Freon. In that case the polyol had to be heated to 140°F to reduce the viscosity. The use of a water dispersed silicone (L5310) also improved the formulation handling characteristics. The silicone is a solid at room temperature and must be dissolved in 110°F water.

To keep the viscosity of Quadrol formulations within workable limits, a Freon level of no greater than 5 per cent per total formulation was needed. The level of silicone oil recommended by most manufacturers is 0.9-1.5 per cent. No effective results were experienced above 1.5 during the screening tests.

When formulating XXIV-B, it was found to be essential to have both water and Freon present in order to take maximum advantage of gas formation. The TDI will react rapidly with water, whereas Mondur MR has little reaction. Therefore, some Freon is necessary to produce additional blowing to obtain a better foam rise. However, too much Freon reacted adversely. Its vaporization tends to drop the reaction temperature, and at higher pressures this presents considerable problems. Since the higher pressures suppress the boiling of Freon, more heat of reaction is needed to vaporize it. Two Freon formulations, VII and XV, were tested under elevated pressures. Formulation VII did not produce a foam at 75 psig but formulation XV, which is more exothermic, produced a very good foam density \approx 6PCF at this pressure. At higher pressures it was considered necessary to abandon the Freon solvent technique and concentrate on water (CO₂) blown foams.

Of the several formulations prepared, only two prototypes were remaining on the shelf after the screening studies were made. One of these, XV-C, is a modification of XV. The modification consists in the fact that it uses water in lieu of Freon 11, thus producing a CO₂ blown foam. The other formulation is a variation of VII using diethylene glycol to produce a hotter reaction, thus making it possible to use Freon under certain conditions.

An attempt was made to formulate a composition which would sustain its reaction under a severe heat sink. Such a formulation necessarily had to yield a high exotherm upon reaction to overcome the environmental water temperature of approximately 35°F and enable the Freon to vaporize. Besides the effect of temperature, the reaction time had to be very short to prevent the ice water from quenching the "pre-foam" cell. Nacconate 80, otherwise ideally suited for high exotherm reactions, was proven to be unsuitable for underwater foaming. A modified polyisocyanate Nacconate 4040 (Allied Chemical) was used instead. The reaction of this product with Quadrol is one of the "hottest" reactions in the field. Quadrol is an amine containing tetrol, which functions as its own catalyst, precluding the need of adding a catalyst to the formulation. The internal temperature of the reaction product of Quadrol with Nacconate 4040 (under Freon) was recorded at 110°C maximum. The reaction

reached 70°C in less than ten (10) seconds with one formulation of XV. This compares with a maximum temperature of 60°C in thirty (30) seconds with formulation VII. However, the reaction time of formulation XV is very fast and hard to control. Diluting Quadrol with less reactive polyols in formulations XIII and XIV did slow down the reaction time, but also yielded a poorer foam in ice water.

Qualitative comparisons of the various formulations were made and are presented as Table I of Appendix 7.2.¹ The results of these screening tests appear in Table II. In Table III, the more promising formulations studied and selected for further studies are shown.

In addition, a number of new ingredients were evaluated with the hope of improving the physical properties and the processing of the foam. None provided any improvement from the previous existing formulations. The results of these additional tests are presented in Table IV.

In the Trident screening tests during this reporting period, two basic formulations were tested. These are Formulations No. T-7 and T-11. Each of these basic formulations was prepared with varying proportions of water and isocyanate to give Formulations T-8, thru T-10, T-15 and T-12 thru T-14. The increase in H₂O-NCO content was designed to provide an increase in the quantity of blowing agent (CO₂) produced in the over-all foam reaction. This increase in blowing agent decreases the density of the foam produced. The basic formulations and their variations were subjected to a series of pressure tests to deduce the change in density with applied pressure.

Carbon dioxide, considered the best blowing agent available at this point, has its primary advantage in the nature of the CO₂ generating reaction which is coupled to the polymerization reaction, thus diminishing the effect of external variables such as temperature and pressure.

¹All Tables are presented in Appendix 7.2.

Freon systems have been tried on a modest scale. In the formulations selected for study by Trident, the sensitivity to pressure of the Freon release mechanism made this blowing agent unusable.

The formulations investigated by Trident are summarized in Table V.

4.2.2 Pressure Studies

Investigations in the Trident laboratory, during this report period, have been primarily aimed at studies of the effect of pressure on the formation of urethane foams.

The apparatus employed was essentially as previously described in the First Quarterly Progress Report. The pressure chamber itself was, however, a lucite tube supplied by Atlantic Research Corporation and is a duplicate of their reaction chamber as shown in Figure I. A one-shot system was employed -- two pre-mixed components of the one-shot formulation being mixed magnetically under pressure.

The results of pressure-density studies, both from the previous low pressure work and the latest investigations at higher pressure, are summarized in Figures II and III. All successful tests are tabulated in Table VI. Also shown in the figures are the formulations used for each set of acquired data. No tests free of mechanical difficulty (mixing failure, etc.) have been omitted. The linear relationship within this range is evident.

Figure IV is a representation of the above data. It has been used to determine the water content required to produce a given density foam under a specified pressure. Water content, in this case, is used as a parameter representative of amount of blowing agent.

Several tests were conducted to determine the gross effect of surfactant concentration on cell structure. Tests 218-220 showed no change in cell structure with surfactant concentration which could be isolated from variations in stirring efficiency.

A preliminary investigation of the factors which influence rate of water absorbance was conducted. Samples of foams blown with each of the two

basic formulations at comparable pressures were submerged at one atmosphere. Samples were tested as blown. Qualitative aspects alone were appraised; volume to surface area effects were ignored. Results are summarized in Figure V which shows that Formulation T-10 is more resistant to water absorption than Formulation T-13. Furthermore, the effect of high pressure blowing seems negligible.

4.2.3 Laboratory Test Apparatus

Two types of delivery systems have been designed, fabricated, and employed in the experimental laboratory tests. They are a pressurized reservoir system, and a batch feed system.

The pressurized reservoir system, as shown in Figure VI of Appendix 7.3,¹ was used in the early phases of the experimental work. In this system, the foam components were poured into their respective reservoirs with the metering valves VM-1 and VM-2 in the closed position. The reservoirs were then pressurized by opening valves V-1 and V-2. The metering valves VM-1 and VM-2 were then set to the predetermined orifice area to properly meter the two components. With the mixing head motor drive "on," valves V-3 and V-4 were opened, thereby causing the foam components to be mixed and pumped into the reaction chamber. A large volume surge tank prevented overpressures from developing within the reaction chamber. The pressurized reservoir system was used primarily with the cylindrical paddle mixer.

The batch feed system, as shown in Figure VII, was used in the underwater tests and proved effective in evaluating foam formulations. In this system the pre-weighed components were poured directly into the mixing head. The mixing head was then pressurized and the motor drive started. When the components were thoroughly mixed they were pumped, via the feed tube, into the reaction chamber. In most cases a 5 to 30 psi differential pressure was used to pump the foam out of the mixing head into the reaction chamber. Upon complete expulsion of the components from the mixing head, a solvent flush

¹All Figures are presented in Appendix 7.3.

with methylene chloride cleaned the head and the feed tube. This type of system was used exclusively with the cone mixer, as shown in Figure VIII. In those tests to evaluate foams under pressure, but not underwater, a system shown in Figure I was used. The reaction chamber in both the pressurized reservoir system and the batch feed system consisted of an 18-inch long by 6-inch diameter by 1/2-inch wall thickness acrylic tube with aluminum end closures. This construction permitted visual observation of all foam reactions.

An 11-1/2-foot high \times 6-inch diameter chamber has been constructed and will be used to simulate the travel of foam through an expanse of water, as would be encountered if foaming into the bottom of a ship compartment. This chamber consists of a ten-foot section of steel tubing with an 18-inch long section of acrylic tubing on top for visual observation. See Figure IX.

The cylindrical paddle mixer, as shown in Figure X, was constructed with an aluminum housing with a 1/2-inch bore. The length of the housing was four inches. A 1/4-inch shaft with 1/16-inch round blades pressed into it, extend through a seal in the rear of the housing. The inlet ports were located 180 degrees apart just forward of the shaft seal. Because of the short residence time of the foam components in the mixing head, the size and shape of the paddles proved inadequate.

The cone mixer employs a conical mixing blade of the type used in standard Atlantic Research cone vertical mixers, as shown in Figure XI. A batch feed system was used in all tests with this mixing head. In most tests the mixing blade was rotated between 1500 and 2500 rpm which provided excellent mixing. The shape of the mixing blade tends to force the components toward the bottom, or apex, of the mixing head. This aids in the extrusion of the foam through the feed tube into the reaction chamber. While providing effective mixing, this unit might prove awkward for hand-held or portable mixing operations.

4.2.4 Underwater Studies

A step-wise test procedure was used in which each formulation was first tested on the bench, then under pressure, and finally underwater. The bench tests were run first to obtain base line data for each formulation.

In these tests the equipment setup was the same as for other tests, but instead of pumping into the reaction chamber the foam was pumped into containers on the bench. Atlantic Research Corporation Formulations XXI, XV-C, XV-D, and Trident Formulations T-7, and T-8 were tested underwater at elevated pressures. The foams were collected inside containers, either vented beakers, acrylic tube with wire mesh closures, or wire mesh baskets, located over the feed tube outlet in the bottom of the reaction chamber. See Figure VIII. In most of the underwater tests, the water level in the reaction chamber was within 4 or 5 inches of the top of the chamber. After the foam had been pumped into the reaction chamber, the pressure was vented and the foam specimen removed. Motion pictures were made of several of these tests in an attempt to determine what the foam characteristics were during discharge into the water environment. An attempt was made to provide a foam at discharge that had undergone primary nucleation and gas generation of "cream time" and was beginning self-nucleation or "rise time." One of the photographically documented tests is shown in a sequence of pictures from the film in Figure XII. This series of pictures depicts a 600 ml beaker which had four holes ground in its base to vent the fluid and supported by a wire tripod several inches above the bottom of the reaction chamber. These scenes were photographed in color so that it was possible, under close observation of each frame, to readily distinguish the foam particles from the air bubbles. To further clarify the discharge characteristics, examine the foam dispersal, and observe the foam expansion, a high-speed motion picture was also made during an underwater foaming test. A series of pictures from these high-speed movies is shown in Figure XIII. As a result of these photographs, it was determined that although the foam is greatly dispersed during discharge, either by the differential mixing and extruding air pressure or by its own inherent gas generation, there is little major effect on the resultant foam produced. This is easily seen by referring again to Figures XII and XIII. Both of these films were taken of Test 25. Scene B of Figure XII and Scene C of Figure XIII were taken at the same moment during the foaming discharge. The resultant foam shown in Scene F of Figure XII was a very good quality foam of 4.9 PCF.

To dispel the concern for the supposed problem of a glass or other solid containers lending a protective skin to the foam during its formation, thus not truly foaming underwater, several tests were made in an acrylic tube with a wire mesh (10×10) which would naturally expose the foam both from above and below to the water environment. Figure XIV shows several pictures of such a test documented on motion picture film. This test, No. 27, was made underwater at atmospheric pressure and produced a foam of 1.9 PCF. After solving this problem, the question arose as to how would the foam in a damaged hull be contained. In a similar test as before, the entire foam receptacle was made of wire mesh, again 10×10. If the foam would form and remain within this wire basket the resultant would be twofold. It would further acclaim the ability of the formulation to foam underwater and provide a logical means of preparing a ruptured vessel or jammed hatch for salvage by foam flotation. Figure XV is a sequence of pictures taken from such a test. In this test, No. 23, a 5.9 PCF foam was obtained, at 66 psig, which had exceptional desirable characteristics.

At this time, densities were taken and water absorption and compression tests made. Since the amount of water absorption is dependent upon the surface area to volume ratio of the specimen, the small laboratory specimens produced a higher percentage of absorption than would be encountered in service applications. Figure XVI shows the results of these preliminary water absorption tests taken at atmospheric conditions. Extended tests are being made at higher pressures to determine long duration effects on water absorption rates.

The laboratory experimental test data, Table VIII, records the conditions met by each of the formulations tested. In each test a prime goal was set to determine the effects of one or more of the following criteria:

- a. Effect of water on formulation.
- b. Effect of pressure on formulation.
- c. Effect of temperature on formulation.
- d. Effect of mixer design.

- e. Effect of agitator speed.
- f. Effect of differential pressure.

The results of the laboratory experimental tests are shown in Table VIII by comparisons of the quality of foam produced in each test.

A pressure versus density curve was made for the two most promising formulations, XV-D and T-8, with a comparison with the density curve which is plotted as a function of Boyle's Law. This curve, shown in Figure XVII, for Formulation T-8 blown underwater, depicts an 8 PCF foam for a pressure of 60 psig. This compares very favorably with the 6 PCF foam, reported in Figure II, produced by Formulation T-8 blown under 60 psig air pressure. Formulation XV-D, however, produced a 10.6 PCF foam when blown under 60 psig air pressure and a 15.5 PCF foam blown underwater at that same pressure.

Although preconditioning of materials was not required in most cases, Formulation XV-D did require preheating the components to 130°F. All other formulations were mixed at room temperature. The chemicals involved seemed to have no adverse effect upon system hardware; however, those valves which isocyanate came in contact with did require a solvent flush after use to prevent binding. In most tests the foam was pumped into a wire mesh container in the bottom of the reaction chamber. Removal of this foam was quite easy, particularly Formulation T-8. By inserting a wooden spatula between the foam and the screen, the two were easily separated.

4.3 Material Transport Studies

If a ship salvage method utilizing foamed-in-place material is to be used, there must obviously be developed a simple, economical method of delivery to the compartments of the sunken vessel. Some of the considerations involved in this problem are listed below:

- a. The system must be economical.
- b. The foam injection device must be readily handled by a diver.
- c. There must be provision for keeping the formulations at proper temperatures.

- d. Equipment to be lowered to the bottom should be kept at a minimum.
- e. Equipment must be capable of delivering formulation continuously or intermittently without gumming up.
- f. The formulation should not be such that it will solidify in the delivery lines when the delivery nozzle is shut off.
- g. Since the foam is to displace water, a means must be provided for egress of water when foam expands.
- h. Amount of foaming mixtures to compartments should be calculated with a fair degree of accuracy to prevent overflowing compartment, thereby inhibiting the expansion of the foam. (Economics to be considered here too.)
- i. Formulation must be introduced either close to the bottom of the compartment, or fast enough so that all of the formulation needed in a particular compartment is placed in the compartment before the foaming action prevents the introduction of additional formulation.

Several methods have been suggested for delivery of formulation to the vessel:

- a. A diving-bell (similar to a submarine escape chamber) containing tanks of formulation, to be lowered to the bottom with delivery hoses running from this apparatus to the chamber to be foamed. This method would not appear to be practical because of the difficulty of placing this apparatus accurately on the bottom and the inherent danger to operating personnel.
- b. Delivery through integrally heated hoses which would keep formulation at a usable temperature until delivery. Formulation would be pumped through these hoses from tanks located aboard the support vessel. This would appear to be a workable solution; however, it would require special (probably expensive) delivery hoses fabricated with integral heating elements and effective insulation to retain the heat, and would probably require a fairly large supply of electrical current for heating. It has the advantage of providing precise thermostatically controlled temperature of the delivered

mixtures. Insulation and heating elements would have to be designed so that the hose diameter would not be appreciably increased and the hose flexibility would not be appreciably reduced. The hose must be one that could be handled effectively by a diver.

c. The formulation could be heated aboard the salvage vessel to a temperature high enough so that on delivery to the sunken vessel it will have dropped to approximately the optimum temperature for forming the desired foam. This method would have the advantage of using a fairly standard hose without special insulation and heating elements. Disadvantages may include the necessity for obtaining temperature gradient at the site by a bathythermograph or similar device; the necessity of experimentally determining temperature drops in the specific hose to be used; and problems which may occur because of variations in rate of flow (e.g., the diver may shut off the flow in order to move the delivery nozzle to a new location causing the stagnant formulation in the hose to lose heat more rapidly).

d. Another possibility which might be worthy of consideration is a system in which containers of the formulation could be lowered to the divers, placed in the correct location, and then connected to a mixing nozzle at the compartment and to compressed air hoses to pressurize the containers. This would involve the handling by the diver of additional pieces of apparatus, but the tanks of formulation could be made sufficiently buoyant to enable them to be easily handled. Serious problems in handling could be encountered if there were any appreciable current present.

4.4 Preliminary Economic Feasibility Studies

For the purpose of comparing the possible salvage of vessels using a foam flotation method with salvage by ordinary means, an attempt has been made to analyze the steps required in each of the methods.

a. First Step - Decision to Study Possibilities for Salvage. This first decision, considering the possibility of salvage, will no doubt be parallel for both methods. It will be predicated on the desirability of attempting salvage based on the probable condition of the vessel, the probable

depth at which the wreck lies, the economic aspects, as well as demand for or value of the vessel itself, its cargo, or important equipment aboard it.

b. Second Step - Location of Wreck. Obviously, determining the location of the wreck must be accomplished, and its position adequately buoyed or otherwise marked to show exact location. Equally obvious is the fact that method of salvage will not be a consideration at this stage.

c. Third Step - Survey of Wrecked Vessel (Preliminary). A diving survey must be made to determine position of vessel, extent of damage, and general condition of vessel and/or cargo. If the cargo is of prime importance, it may be discovered that this could be salvaged without raising the complete vessel.

d. Fourth Step - Decision to Go Ahead With Salvage Operation. Depending on the results of the initial diving survey, a decision must be made on whether or not to attempt salvage of the vessel. An affirmative decision here would be heavily dependent on the methods available for salvage and on the condition of the wreck.

4.4.1 Salvage by Conventional Methods

If the decision is to be based on present day conventional salvage methods (using compressed air to displace water in compartments or using pontoons as a medium to raise the ship), many problems present themselves. With the use of compressed air: (1) all compartments to be blown out must be made airtight; (2) adjacent compartments must be shored up or strengthened; (3) it probably would be necessary to reinforce bulkheads and decks by underwater welding of reinforcement members; (4) damage to compartments and closures must be temporarily repaired with patches or cofferdams, and means provided for blowing out the water and sealing in the compressed air; and (5) the difference between air pressure in compartments and ambient pressures at the depth of the vessel while it is being raised will increase considerably, so means should be provided to vent some air pressure as the ship rises to prevent destruction of compartments by the rising pressure differential.

Pontoon raising of vessels is probably not practical, except in cases where the vessel is comparatively small. It is highly likely that consideration of the conventional salvage methods available would indicate a negative decision on salvaging in practically all cases.

4.4.2 Salvage by Foam Methods

Provided that a suitable foam is available (i.e., a foam which has the required low density, can be foamed underwater and under the pressures being considered, and has a low rate of water absorption), there will be a much larger percentage of sunken vessels that can be successfully salvaged. There are problems, to be sure, but none of them at this stage seem insurmountable. Considerations involved in this method of salvage are preparation of the wrecked vessel and exterior equipment required for the salvage operation. Details on these two considerations are as follows:

a. Preparation - There is no particular need to make compartments airtight in the foam method, and patching of compartments so that foam might be contained could be accomplished with light material such as plastic screening, small mesh nets, light wooden forms, etc. These need only have a strength and configuration required to keep the foam in place while it is expanding and hardening. It would not be necessary to keep patches in place after the foam has hardened. Preparation must include the provisions of fairly large openings in the lower regions of the compartment so that, as the foam expands, the water may be allowed to escape quickly enough to prevent the build-up of back pressure in the compartment. Such back pressure, if present, would considerably inhibit the expansion of the foam, and if high enough would prevent complete expansion and cause a foam of unsatisfactory density to be formed. Openings also must be provided so that the foam formulation may be introduced into the lower section of the compartment. It can readily be seen that, if the mixture were introduced at the upper part of the compartment, the compartment could never be filled, as that foam which formed first would harden at the top of the compartment and prevent the entrance of any more of the mixture. If sufficient opening for ready egress of the water is provided, there should be no need to

do any shoring of decks and compartments, as the hardened foam will exert no outward pressure except for upward buoyant pressure. Strength of decking (considering decking to be that plating on the upper surface of the submerged vessel) will probably not have to be very great, as it is highly likely that the plastic would harden around beams and stringers and stanchions as well as anchored equipment so that there would not be a large buoyant pressure exerted uniformly upward against the decking alone. There is a possibility that some inner bulkheads would have to be removed to eliminate the necessity for divers to have to work in the interior of the ship to foam small interior compartments.

b. Exterior Equipment - Diving equipment needed would be somewhat the same as that required for conventional salvage, except that far fewer divers need be employed since most of the laborious shoring and patching work will have been eliminated. A salvage ship must be available and equipped with decompression chambers, diving gear, stages, line, cable, chain and compressed air, as well as the necessary equipment, hoses, chemicals, etc., which will be needed for the introduction of the foam formulation into the vessel. It will probably be advantageous to have pumping and repair facilities available for use when the sunken vessel is raised, permitting it to be pumped out and repaired sufficiently so that it can be trimmed and towed to land.

4.4.3 Equipment Requirements

a. Conventional Salvage.

- (1) ARS or other diving vessel completely equipped with compressors, air banks, decompression chambers, etc.
- (2) Complete deep-sea diving gear for numbers of divers to be employed.
- (3) Repair vessel for manufacture of patches, strongbacks, cofferdams, braces, reinforcements, air fittings, etc. (This vessel plus a diving barge could replace the ARS.)
- (4) Compressed air equipment with sufficient capacity for blowing out compartments.

- (5) Moorings for diving barge.
- (6) Underwater welding and cutting equipment.
- (7) If pontoons are to be used -- pontoons, tugs, chains, cables and chain handling equipment, shackles, air lances for tunneling, etc.

b. Foam Salvage

- (1) ARS or other diving vessel completely equipped with compressors, airbanks, decompression chambers, etc.
- (2) Complete deep-sea diving gear for numbers of divers to be employed.
- (3) Light patching materials sufficient to hold foaming plastic in place until it is hardened.
- (4) Moorings for diving vessel or barge.
- (5) Small amount of underwater welding and cutting equipment.
- (6) Vessel for handling components of plastic foam, delivery equipment (hoses or tanks), and mooring equipment for this vessel.
- (7) Chemicals, tanks, hoses, nozzles, and other equipment associated with foam equipment.

In the matter of equipment necessary for each of the separate methods, it is believed that they are more or less comparable economically, with no particular advantage to either method, considering only value of basic equipment.

Economic advantages of the foam method of salvage are, however, readily apparent when the time element is considered.

Assuming that an average size surface vessel has suffered sufficient hull damage to cause it to sink, and assuming (unrealistically) that the compartments could be sufficiently repaired and braced to hold the air pressure necessary to displace the sea water -- it is conservatively estimated that it would require at least ten times as long to prepare the vessel for compressed air salvage as it would to prepare it for foam salvage.

This area of work (preparation of vessel) is considered to be the major economical advantage of the foam method. Time required for introducing the foam would probably be about equal to the time required for blowing out by compressed air.

There is little purpose to be served at this time in attempting to compute an actual dollar saving involved in the use of the foam method, as there are so many variables involved.

The actual cost involved in either method would depend on the parameters of each specific salvage job and could only be actually determined by experience.

It is extremely doubtful that the cost of either method would be low enough to completely justify its use for raising a vessel for the value of the vessel alone. If it is desirable to raise a vessel because of other considerations, it is considered that the saving involved in the foam method could be roughly estimated by multiplying by ten the operating cost of all the equipment used during preparation for foaming.

Other than the economic consideration, there is the likely probability that in 99 per cent of all cases it would prove impossible to raise the vessel at all with conventional methods, while in most cases it would be possible to successfully conduct the salvage operation using foam.

Deck loads (heretofore considered to be one of the limiting factors in raising a surface vessel by blowing out with compressed air) are not a serious consideration in foaming as the solid foam would form around beams, machinery, bulkheads, etc., relieving much of the upward strain against the decks. Because of the fact that the foam, being rigid, would assume the shape of the compartment, the foamed plastic would in all probability remain in place if the deck above were carried away entirely after the foam had hardened.

5.0 CONCLUSIONS

Progress to date permits drawing some positive conclusions regarding the feasibility of the foamed-flotation scheme. Many of the primary considerations which originally seemed insurmountable have, during this reporting period, been met, investigated, and found to be within the scope of present foamed plastics technology. The adaptation of this technology to that of existent salvage technology appears feasible at this time. Only adverse and contradictory test results during this next quarter, January thru mid-March 1965, could disprove this conclusion.

Conclusions have been reached pertaining to each requirement necessary for a foam flotation material. These are:

a. Effect of water on formulation. When properly formulated, the resultant foams have shown little, if any, adverse effects from the aqueous environments. Although only a few tests have been run using a seawater environment (most tests used tap water), the salinity has not greatly affected the foam formation.

b. Effect of pressure on formulation. Experiments conducted in the first months of this study indicated that a linear relationship might be expected between pressure and density for a polyurethane system blown in air or water. Recent improvements in apparatus have now extended the range of investigations up to 200 psig. The linear relationship, intimated earlier, is now a proven reality, as shown by Figures II, III, and XVII.

It is now anticipated that with the curves of Figure IV, a series of formulations may be made that will produce foam densities whose variation is not linear with pressure, but less than linear.

c. Effect of temperature on formulation. Few investigations have been made in the laboratory at reduced water temperatures. Those that have been made indicated very little affect on the resultant foam. The screening tests under low temperature conditions performed very satisfactorily.

d. Effect of mixer design. The mixer was found to be important for producing a desired foam. Mixing was easily accomplished by hand, magnetic, cylindrical pin, and cone vertical mixers. It was determined that a good mixer must provide adequate blending of ingredients, retain the ingredients in the mixer for the proper residence time, be easily operated and handled, and be easily cleaned.

e. Effect of agitator speed. This was found to be allied with the effectiveness of the mixer blending action and could well range from 1000 to 6000 rpm.

f. Effect of differential pressure. No real adverse effects were noted by the differential pressure between the mixing bowl and reaction chamber. It was found that a minimum of 10 to 15 psi differential was necessary to extrude or motivate the "creamed" foam from the mixing bowl.

g. Effect on the cell structure. The effect on the cell structure of the foam of blowing under pressure has been of primary importance in this investigation. Observations made at all phases of foam formation and aging, coupled with microscopic examination of cured foams, indicate that cell integrity is not reduced by blowing under pressure. Initial concern that cell rupture might be encountered upon pressure release was proved unfounded. Only large surface cells ("health bubbles") have been observed to burst. Pressure changes of over 200 psi over a period of less than one minute cause no rupture of body cells.

6.0 RECOMMENDATIONS

It is felt that upon the conclusion of this feasibility study, in mid-March 1965, the feasibility will have been conclusively demonstrated and some aspects of the technical and economic practicability will have been reviewed in preliminary form. It will be apparent then that a subscale prototype salvage mission should be attempted. It has been suggested previously that such a mission might be simulated within the training tanks at the U.S. Navy Divers Training School. It is again strongly recommended that this salvage demonstration be considered. Not only will a well planned demonstration of this nature provide a more realistic simulation of an actual salvage operation, but also it will provide invaluable suggestions and criticism from the Navy salvage operators performing the test. It might be an opportune time, also, for others interested in underwater salvage, such as DSSP, to become acquainted with what appears to be the salvage technique of the future.

A commercial metering and mixing unit is recommended to accomplish the necessary continuous feed. This metering unit could be attached to the mixing head designed by Atlantic Research or to a modified commercially attachable mixing head. A list of commercial metering and mixing equipment manufacturers will be presented in the Final Report. Modifications necessary to adapt these commercial mixing heads for foaming underwater will be enumerated.

APPENDIX 7.1

1. United States Patent No. 3,057,694, M. Kessler,
"Apparatus for Raising Sunken Ships", October 9, 1962.
2. United States Patent No. 3,091,205, W. Watson,
"Method of Raising Sunken Vessels", May 28, 1963.

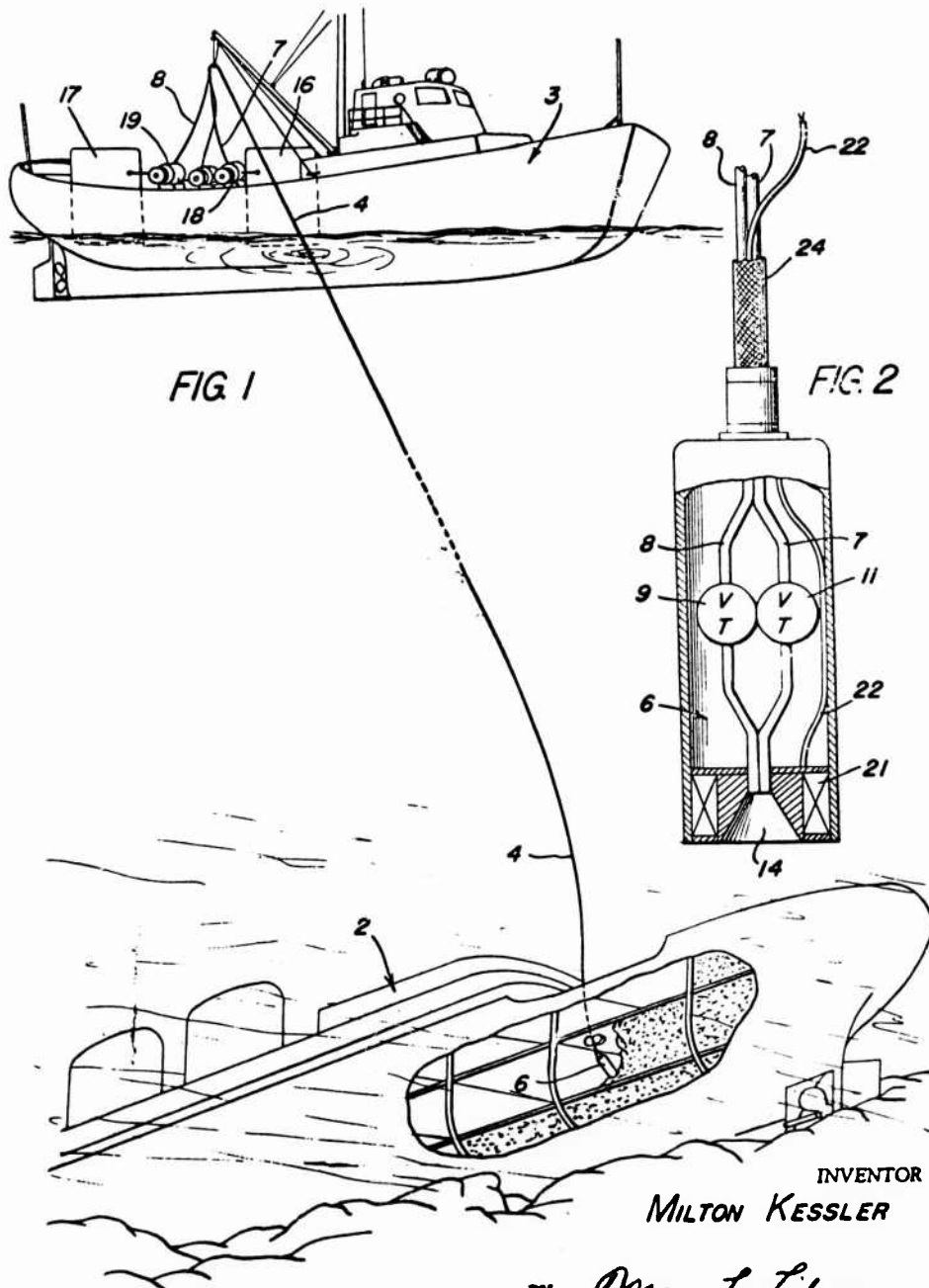
Oct. 9, 1962

M. KESSLER

3,057,694

APPARATUS FOR RAISING SUNKEN SHIPS

Filed Dec. 15, 1958



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3,057,694
APPARATUS FOR RAISING SUNKEN SHIPS
 Milton Kessler, 4535 Grove Drive, Youngstown, Ohio
 Filed Dec. 15, 1958, Ser. No. 780,475
 2 Claims. (Cl. 23-252)

This invention relates to a method and apparatus for raising sunken vessels, and more particularly to a method for raising sunken vessels by pumping into them a mass of foaming plastic material to displace the water in such vessels.

It has been proposed to raise sunken ships by various methods, including the attachment of tanks to the sunken vessel and the subsequent pumping out of the water (or pumping in of air) from the attached tanks until their buoyancy is sufficient to raise the vessel, which can then be towed to a convenient harbor or dock for salvage or repair. All of the prior art methods of which I am aware have the disadvantage of being very expensive, dangerous to carry out in waters which are often very rough, and requiring a considerable amount of submarine operation. To date, no generally satisfactory method of raising sunken ships has been evolved.

It is a major object of the invention to provide a method and apparatus for raising sunken ships which obviates the disadvantages of the prior art methods and apparatus in being relatively inexpensive, simple to apply, and not requiring extensive underwater work or special treatment of the sunken vessel, such as fastening on tanks under water, etc.

Foamed plastics, similar to foam rubber except for being relatively rigid, have been developed and are available. By mixing the plastic material in a soft plastic or liquid condition with gas-evolving chemicals, a foam material can be produced which has an extremely low specific gravity. For example, it is possible to produce a foam material having a weight per cubic foot of less than one-half pound. This means that each cubic foot of the material can produce approximately sixty pounds of buoyancy, and it will be apparent that a relatively small amount of this material will be sufficient under most conditions to provide sufficient buoyancy to raise the sunken vessel. This material is widely used for thermal insulation, as a bulk material, and as a low specific gravity material. It resembles the well-known foam rubber except for the strength and rigidity which it acquires on setting. According to the invention, the material is produced in situ in the hold or other enclosed compartment of a sunken vessel to raise it. I have discovered that foam plastic can be successfully produced under water, even at a pressure in the order of 100 p.s.i., and that it can be used to displace water when so produced. By carrying out this process directly in the hold of a sunken ship, all of the openings which have been closed sufficiently to retain the foamed plastic mass, the vessel can finally be made sufficiently buoyant to rise to the surface and to float thereon.

It is also an object of the invention to provide improved apparatus for applying the foamed plastic from a surface boat to the sunken ship. This apparatus includes means for mixing the ingredients on the surface boat, and hose means for piping the plastic material to the point where it is to be used, and including means for keeping the plastic material at the optimum condition by heating it as it is being produced.

The specific nature of my invention as well as other objects and advantages thereof will clearly appear from a description of a preferred embodiment as shown in the accompanying drawing, in which:

FIG. 1 is a schematic diagram showing the manner in which the invention is applied to the raising of a sunken ship; and

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FIG. 2 is a schematic diagram, partly in section, showing a nozzle used in the ship to produce the plastic foam under water.

Referring to FIG. 1, the sunken vessel 2 is depicted lying on the bottom, at a depth that can be reached by divers. A surface vessel 3, which may be the same vessel from which the divers are working, or a vessel specially equipped for the plastic foam operation, is provided with any conventional means (not shown) for supplying the foam ingredients to a hose 4, which is preferably provided with a special mixing nozzle, 6, shown in FIG. 2.

The hose 4 is preferably composed of two separate hose lines 7 and 8, respectively provided at their free ends with throttle valves 9 and 11, which can be manually controlled by the diver operating the equipment. Alternatively, the throttle valve at the free end of the hose can be dispensed with, and the control of the plastic ingredients can be accomplished from the vessel where the ingredients are pumped into the two hoses. However, there is an advantage in providing the valves at the bottom end, which insures that both of the major ingredients flow together into the mixing nozzle 14, to minimize wastage of the ingredients. One of the hoses, for example, hose 7 is fed from a tank 16 containing, for example, a mixture of the following ingredients: No. 1.—Nacconate 1080-H, Witco 77-86 and water; and the other hose 8 is fed from a tank 17 with the following: No. 2.—a material known as N-Methylmorpholine. Both of these ingredients are manufactured by the Barrett Division of Allied Chemical and Dye Corporation, Toledo, Ohio.

One form of spraying installation suitable for this invention is shown in U.S. patent to Bauer, No. 2,860,856, issued November 18, 1958.

A pump 18 is shown connected to hose 7 for forcing mixture No. 1 into hose 7, and a similar pump 19 is used for ingredient No. 2. Alternatively, a dual pump can be used, since the two mixtures must be pumped down together. It is necessary to pump each mixture down a separate hose to prevent interaction of the ingredients in the hose, which would not only clog the hose but probably also rupture it. At the far or under water end, the two hoses are combined in a single nozzle 6, which is preferably provided with an electric heating coil 21, fed from a surface generator through a power cable 22, which must, of course, also be properly insulated and water-proofed. The foaming reaction is greatly accelerated by heat, and tends to be retarded by the low temperatures usually found in large bodies of water, and the heating coil is therefore provided in order to establish the optimum foaming temperature at the nozzle just as the ingredients are being mixed.

In the practicing of the invention, the nozzle is carried by a diver to the sunken vessel, which ordinarily contains many compartments which are sufficiently intact so that it is a simple matter to insert the nozzle into one of them, and commence the production of plastic foam into the interior. The foam material should be started on the far side of the aperture from which it is introduced, and the nozzle moved backward as the foam material is produced, rapidly displacing the water in the compartment. The material adheres to itself, forming a coherent mass of fairly rigid material, which also tends to adhere to surfaces with which it comes in contact, even when the surfaces are wet. It is therefore possible to rapidly fill the desired components one by one, until the vessel begins to recover its buoyancy. In order to obtain the proper "trim" of the vessel as it is rising, and when it is afloat again, it is desirable to begin with the uppermost compartment of the vessel and to judiciously manipulate the nozzle so that the vessel finally tends to float in an upright position. Of course, it is not necessary that the vessel be given anything like its original buoyancy, but only

sufficient buoyancy so that it will rise to the surface, after which it can be towed away to a suitable location for further work. After the recovered vessel has been grounded or docked, the spongy plastic material can be readily removed, as it is of sufficiently soft consistency so that it can easily be cut with a knife or any similar implement, the foamy plastic produced by the mixture described herein is not particularly resilient, but, on the other hand, is rather pliable, and therefore can be removed in large chunks with relative ease.

In the event the vessel to be raised has been seriously damaged, or where the compartments which it is desired to fill with foam have too many apertures, it may be necessary to rig some temporary barricades in the apertures, which can be readily done by the divers in order to retain the plastic material where it is needed. It will be apparent that by judiciously distributing the plastic material throughout the vessel, a concentration of strain at any one point on the vessel can be avoided, and at the same time, the vessel can be given any desired "trim" so that it will float in a convenient position for easy handling.

For use in cold water, it is desirable to also heat the ingredients before they are combined, to insure sufficiently rapid foaming. This may be done on the vessel, and well insulated hose can be used, or alternatively, the power cable 22 can be made as a heater cable of well known type, to keep the hoses 7 and 8 at a suitable temperature. In either case it is desirable that the outer covering 24 of the cable be of reasonably good thermal insulating material.

It will be apparent that the embodiments shown are only exemplary and that various modifications can be made in construction and arrangement within the scope of my invention as defined in the appended claims.

I claim:

1. Apparatus for raising sunken ships comprising at least two containers for respective ingredients of a foaming plastic, a separate hose line connected to each such container, pump means for pumping fluid ingredients from said containers into said hose lines against a pressure head corresponding to the depth of a sunken ship, combining nozzle means at the free ends of said hose lines for combining said ingredients by chemical action solely within the nozzle at the point of exit from said hose lines to produce a foamed plastic material, and means for applying heat to said ingredients mounted adjacent said nozzle means to raise the temperature of said ingredients to maintain the chemical activity thereof.
2. The apparatus according to claim 1, said last means comprising electric heater means mounted on said nozzle means and water proof electric cable means supplying said heater means with current, said cable means and said hose means being fastened together along their length to form a unitary supply line.

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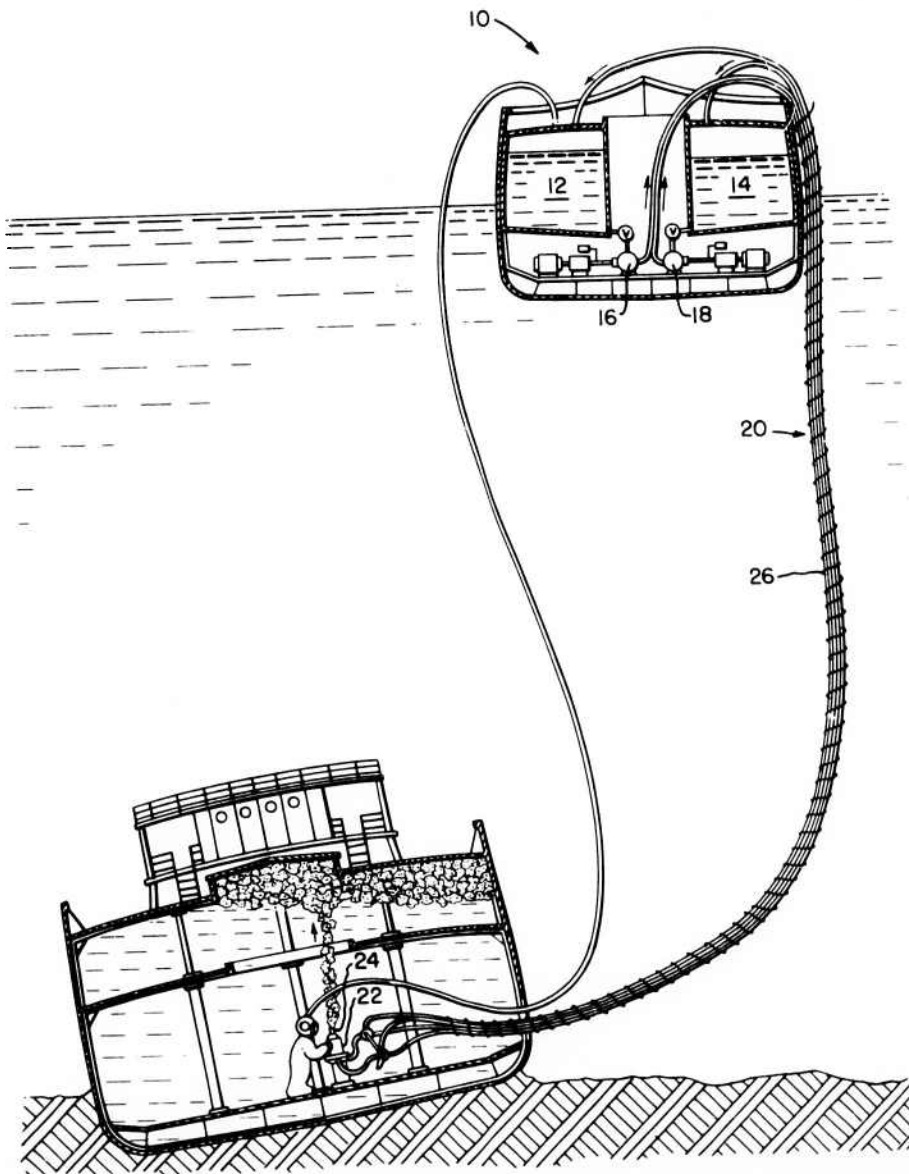
May 28, 1963

W. WATSON

3,091,205

METHOD OF RAISING SUNKEN VESSELS

Filed Aug. 16, 1957



INVENTOR.
WILLIAM WATSON

BY *Kennedy, Jenney,
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ATTORNEYS

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3,091,205

METHOD OF RAISING SUNKEN VESSELS
William Watson, Bradlee Road, Marblehead, Mass.
Filed Aug. 16, 1957, Ser. No. 678,554
2 Claims. (Cl. 114-50)

This invention relates to a method for raising sunken vessels and in particular to a procedure by means of which buoyancy is restored to the vessel itself without the use of pontoons.

In the past sunken vessels have been raised from the sea bottom by a combination of two methods. If the vessel has compartments which are or can be made watertight, the water may be pumped out from such compartments and replaced with air, the process being repeated until the total volume of air-filled watertight compartments is sufficient to impart buoyancy to the vessel as a whole. It has also been the practice to sink pontoons into position where they can be moored to the vessel, the pontoons being subsequently filled with air in order that they may exert lifting force on the vessel. While such methods are often satisfactory, they have severe limitations. The lifting capacity to be secured from pontoons is not great enough to raise a sizeable ship, and many vessels are not equipped with watertight compartments of sufficient volume to impart the desired degree of buoyancy to the ship.

In accordance with my invention I form within the interior of a sunken ship a quantity of plastic foam of closed cell form which displaces the water and imparts buoyancy to the vessel. The foam is formed in situ, and the operation of the method does not require watertight compartments in view of the fact that it is the buoyancy of the foam which operates to lift the vessel and not the effect of an air-filled watertight compartment.

In practicing the method of the invention I provide a salvage vessel equipped with tanks adapted to contain the two fluids which are to be mixed to form the foam, pumps for handling the fluids, a multi-conduit hose terminating in a mixing head and nozzle and adapted to be inserted in the interior of the sunken vessel, and the necessary auxiliary apparatus as will hereinafter more specifically be described.

These and other aspects of the invention will be more readily understood and appreciated from the following detailed description of a preferred embodiment thereof selected for purposes of illustration and shown in the accompanying FIGURE.

This invention does not relate to any particular plastic foam, since there are many formulations suitable for use in practicing the method of the invention. Those skilled in the art will readily appreciate the commercial availability of suitable materials and the factors which must be taken into consideration in selecting the foam to be used. As an example of a suitable material, there may be employed a mixture of a polyisocyanate and a resinous polymer. One suitable series of satisfactory foaming materials is currently sold by Nopco Chemical Company under the trademark "Nopco Lockfoam," and other types are currently on sale by E. I. DuPont de Nemours & Company and Monsanto Chemical Company. The foam selected must have relatively low water absorption characteristics, be of the closed cell type as opposed to the interconnecting cell type, and be capable of formation by the mixture of two fluids under pressure.

As shown in the drawing there is provided a salvage vessel 10 equipped with a pair of tanks 12 and 14, one of which contains a liquid resinous material such as a polyester resin, an epoxy resin, an alkyd resin, or a phenolic resin. In the other tank there is a catalyst, generally one

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of the amines or peroxides. A pair of pumps 16 and 18 serve the tanks 12 and 14 and are arranged to pump fluid from the tanks into a multi-conduit hose 20 suspended over the side of the vessel and terminating at its lower end in a valve controlled mixing head 22 where the two fluids are mixed and discharged through a nozzle 24. The hose 20 has four conduits, two of which are connected to the pumps 16 and 18 at their upper ends and at their lower ends to three-way valves by means of which the fluids may either be directed into the mixing head 22 or returned through the other two conduits of the hose 20 back into the tanks 12 and 14. Some types of foams require that the materials be heated prior to mixing, and in such cases the hose 20 is provided with a coiled heating element 26 connected to a suitable source of current on the salvage vessel 10.

In connection with the equipment thus far described useful detailed information will be found in a sales bulletin published by Gabriel Williams Co., Inc. of Freeport, Long Island, describing "Kluder Williams Foam Machines." The invention contemplates the use of similar hoses and mixing head, although the equipment used in practicing the method of the invention will necessarily be constructed to withstand the higher pressures involved.

In applying the foam to the interior of a second vessel, a diver inserts the nozzle in an opening in the hull and operates the valve to direct the two fluids into the mixing head for intimate mixing and discharge through the nozzle 24. It is of course necessary that the pumps develop sufficient pressure to overcome the hydrostatic pressure, the pump pressure being dictated by the depth to which the sunken vessel lies.

If the compartment of the vessel into which the foam is directed is reasonably tight, though it need not be watertight, nothing more is required. If, however, it is desired to introduce the foam into a compartment having a relatively large opening at the top, such as a compartment opening into a companionway, divers must first cover the upper openings with a barrier of screening or boards. Inasmuch as the foam is buoyant after it has formed, it will rise to lodge against the barrier and conform exactly to the configuration of the compartment being filled.

The process described is repeated in various compartments of the sunken vessel until sufficient water has been displaced by the buoyant foam to render the vessel as a whole sufficiently buoyant to become lifted from the sea bottom. Of course, the "bottom" suction may be overcome in conventional fashion, as by hydraulically washing away mud from the ship's bottom.

After the vessel has been brought to the surface, or sufficiently near it, it may be towed to dry-dock. After the vessel has been dry-docked, the plastic foam may then be cut out very easily. The removal of the foam from the interior of the ship presents no problem.

Those skilled in the art will readily appreciate that there are many variations and alternatives to the specific operations described above, and the scope of the invention is not limited by the foregoing but is rather measured by the claims appended hereto.

Having thus disclosed my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of imparting buoyancy to a sunken ship comprising the steps of pumping a fluid resin into a water-filled compartment of the ship from a salvage vessel, through a first hose, the hydrostatic pressure in the compartment being substantially above atmospheric pressure, pumping a fluid catalyst capable of acting on the resin to form a closed cell buoyant foam into the ship from the salvage vessel through a second hose, mixing

APPENDIX 7.2

TABLES

<u>Number</u>	<u>Description</u>
I	Tabulation of Ingredients (by gram weight) of Formulations Investigated by Atlantic Research.
II	Results of Atlantic Research Screening Tests.
III	Formulations Selected for Further Study.
IV	Tabulation of Additional Formulations Investigated by Atlantic Research.
V	Tabulation of Ingredients (by gram weight) for Formulations Investigated by Trident.
VI	Tests to Determine the Effect of Pressure on Foam Characteristics.
VII	Laboratory Experimental Test Data .
VIII	Results of Laboratory Experimental Tests Performed by Atlantic Research Corporation.

Table I. Tabulation of Ingredients (by gram weight) for Formulations Investigated by Atlantic Research.

	XII	XIV	XIV B	XV	XV B	XV C	XV D	XVIII		XIX	XX	XXI	XXII	XXIII	XXIV	XXIV B
								PPM	15							
NCO/OH Ratio	1.04	1.03	1.34	1.03	0.73	0.73	1.1	1.03	1.09	1.03	1.03	1.03	1.1	1.1	1.1	1.1
PREPOLYMER								15								
ISOCYANATES																
NACCONATE 4040	14.3	15.1	16.5	15.5	15.0	15.0	16.9	81.8%	11.1	16.5	16.4	16.1	8.0	10.2	10.5	
NACCONATE 80													8.0	4.3	4.5	
MONDUR MR																
POLYOLS																
QUADROL	5.7	3.2	2.7	10.4	14.2	14.2	10.6		9.1	9.0		8.7	13.4	12.1	12.5	
LA 475																
ATPON G2410	5.7	7.6	6.4					18.2%	9.1	4.4	4.4	4.4				
PG 11 - 80																
LS 650																
DEG ^a																
SILICONES																
DC 201	0.3	0.3	0.3		0.3	0.3	0.5	0.3	0.36	0.3	0.3	0.3	0.3	0.4	0.5	
L 520																
L 5310																
CATALYSTS																
DABCO																
T-12, drops																
T-9, drops																
FREONS																
FREON 113	4.0	3.8	4.1				1.5	4.0		4.2	4.2			3.0	1.5	
FREON 11				4.1												
WATER																
H ₂ O					0.4	0.5 ⁺	0.5		0.36				0.5 ⁺	0.45	0.5	
NUCLEATING AGENT																
CAB-O-SIL (M-5)							0.15								0.15	

^aDiethyleneglycol

^bT-12 Solution - T-12/FREON 113, 1:5

NOTE: Formulation XI, XII, XVI, and XVII deleted.

TABLE II. Results of Atlantic Research Screening Tests.

<u>Formulation</u>	<u>Remarks</u>
XI	Deleted.
XII	Deleted.
XIII	Very brittle foam.
XIV	Added two drops of T-12 to each formulation. Foam was not as good as generated by Formulation VII.
XV	High exotherm. Foam in ice water (34-38°F). Relatively poor structural strength when compared to Formulation VII. A good silicone stabilizer for this formula has not been found yet.
XVB XVC	The amount of water will control the density of the foam. This is a very hot reaction. Tack free time for B, five (5) seconds; for C, ten (10) seconds. Must be heated to 60-65°C for viscosity control.
XVD	Excellent reaction and foam rise. Nucleation yields smaller cell foam, and hopefully closed cells.
XVI	Deleted.
XVII	Deleted.
XVIII	Prepolymer type formulation. Very long tack free time. Extremely brittle foam.
XIX	Excellent, fast reaction. Good foam rise. Density of foam is controlled by amount of water and excess isocyanate (nacconate 80) added. Freon 11 did not perform in this formulation. Use in underwater foaming doubtful due to higher reactivity of nacconate 80 with water. Also ingredients are more expensive.

TABLE II. (continued)

<u>Formulation</u>	<u>Remarks</u>
XX	Fair reaction. Mondur is not as reactive as nacconate 4040, and should not be used in this type of formulation.
XXI	Best reaction of all Mondur type foams. Very fast and hot. Good foam rise. Foam is more rigid than Formulation VII. Fairly uniform cell formulation. Should be used for foaming in cold water.
XXII	Reaction slower than XVC. Quadrol does not have to be heated, but it helps. Foam has better physical properties than XV series. Good reaction and foam rise. Better rise when using Freon 11.
XXIV	Poor reaction. Phase separation of the two NCO carriers.
XXIVB	Excellent foam rise. Good exotherm. No phase separation of isocyanates. A few large voids were present in the foam. They can be eliminated by increasing the viscosity of solution during foam rise (by reducing Freon content or increasing T-12 concentration or both).

TABLE III. Formulations Selected for Further Study.

Formulation XV-D		<u>Gram Weight</u>
Quadrol		10.6
L5310/H ₂ O 1:1		1.0
Freon 11		1.5
Nacconate 4040		16.9
T-12 Solution	(2 drops)	
Cab-O-Sil (M-5)		0.15
Formulation T-8		
TD 1		104
NIAX-LA 475		50
Pluracol TP 340		50
Dabco		0.4
T-9		0.1
Water		4
Silicone 201		2

TABLE IV. Tabulation of Additional Formulations Investigated by Atlantic Research.

<u>Formulation</u>	<u>Isocyanate</u>	<u>Polyol Ratio</u>	<u>NCO/OH</u>	<u>Remarks</u>
1A1	Mondur MR	LS 650/LHT 42 = 4:1	1.03	LS 650 has very poor miscibility with Freon.
1A2	Mondur MR	LS 650/LHT 42 = 2:1	1.03	LS 650 has very poor miscibility with Freon.
1A3	Mondur MR	LS 650/LHT 42 = 1:1	1.03	LS 650 has very poor miscibility with Freon.
1A4	Mondur MR	LA 475/LHT 42 = 4:1	1.03	Poor foam rise.
1A5	Mondur MR	LA 475/LHT 42 = 2:1	1.03	Poor foam rise.
1A6	Mondur MR	LA 475/LHT 42 = 1:1	1.03	Poor foam rise.
1A7	Mondur MR	LS 490/LHT 42 = 4:1	1.03	Fair foam rise.
1B	Nacconate 4040	LA 475/LHT 42 = 4:1	1.04	Slow reaction.
2		LS 650/PG 11-80 = 4:1	1.03	Could replace G2410 except for poor miscibility with Freon.

TABLE V. Tabulation of Ingredients (By Gram Weight) For Formulations Investigated by Trident.

Formulation Number	T-7	T-8	T-9	T-10	T-11	T-12	T-13	T-14	T-15
Component									
Niax IA-475	50	50	50	50	-	-	-	-	50
Pluracol TP-340	50	50	50	50	-	-	-	-	50
Pluracol Pep 450	-	-	-	-	50	50	50	50	-
Pluracol EDP 500	-	-	-	-	50	50	50	50	-
TDI	88	104	127	148	103	117	144	68	68
DABCO (ml) ^a	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.2	0.5
T-9	-	0.1	0.1	0.1	0.8	0.8	0.8	-	-
H ₂ O	2	4	6	8	2	4	8	-	-
D.C. 201 (ml) ^b	2	2	2	2	2	2	2	2	2
Freon 11	-	-	-	-	-	-	-	20	22

^aBased on a 20% aqueous solution per 100 gm polyol.

^bml/100 gm polyol.

TABLE VI. Tests to Determine the Effect of Pressure on Foam Characteristic.

<u>Test Number</u>	<u>140</u>	<u>141</u>	<u>142</u>	<u>143</u>	<u>144</u>	<u>145</u>	<u>146</u>	<u>146a</u>
Formulation	T-8	T-8	T-8	T-9	T-9	T-9	T-9	T-9
Pressure, psig	54	36	70	0	52	26	75	99
Density, ^a lb/ft ³	5.68	4.45	6.64	1.67	4.25	2.98	5.60	6.71
Time at Pressure, min.	10	11	11	--	10	12	10	12
Cream Time, sec	15	20	20	10	20	15	15	15
Rise Time, sec	35	45	60	30	60	35	60	60

Comments: General - Temperature measurements made on interior of foaming sample were discontinued due to erratic results. Variation in thermocouple placement could not be controlled well enough to isolate a meaningful temperature reading.

^aAll density measurements are average density.

<u>Test Number</u>	<u>147</u>	<u>148</u>	<u>202</u>	<u>203</u>	<u>204</u>	<u>205</u>	<u>206</u>	<u>207</u>
Formulation	T-10	T-10	T-10	T-10	T-10	T-11	T-11	T-11
Pressure, psig	0	56	106	140	175	0	25	50
Density, lb/ft ³	1.34	3.41	5.42	7.07	8.07	2.27	6.20	14.7
Time at Pressure, min.	10	10	5	8	10	--	10	8
Cream Time, sec	15	20	15	15	15	15	15	15
Rise Time, sec	45	60	25	30	30	30	30	30

<u>Test Number</u>	<u>208</u>	<u>209</u>	<u>210</u>	<u>211</u>	<u>213^a</u>	<u>214</u>	<u>215</u>	<u>216</u>	<u>218</u>	<u>219</u>	<u>220</u>
Formulation	T-12	T-12	T-12	T-12	T-13	T-13	T-13	T-13	T-13 ^b	T-13 ^c	T-13 ^d
Pressure, psig	0	28	51	77	0	175	125	63	105	103	108
Density, lb/ft ³	1.45	3.83	5.65	8.05	1.25	8.40	6.53	3.85	6.35	5.95	6.48
Time at Pressure, min.	--	10	11	10	--	10	12	10	10	10	10
Cream Time, sec	15	15	15	15	15	15	15	15	15	15	15
Rise Time, sec	25	25	25	25	25	25	25	25	25	25	25

^aFriable foam under these conditions.

^b4 ml DC 201/100 gm polyol.

^c6 ml DC 201/100 gm polyol.

^d8 ml DC 201/100 gm polyol.

These tests were run with formulation T-13, except with surfactant concentrations altered as indicated.

Table VII. Laboratory Experimental Test Data of Formulations Investigated by ARC.

Test No.	Form No.	Feed	Qty. MB (gr)	Qty. 150 (gr)	Temp. MB (°F)	Temp. 150 (°F)	Type Test	Reaction Chamber Pressure (psig)	Mixing Head Press. (psig)	Water Temp. (°F)	Mixing Speed (RPM)	Mixing Head	Time Under-water (min)	Density (lb/ft ³)
1	XXI	Pressure Reservoir	45	55	74	74	U.W.	75	105	73	2500	Cyl. Paddle	1	
2	XXI	Pressure Reservoir	45	55	73	73	U.W.	75	95	73	2500	Cyl. Paddle	1	27.9
3	XXI	Pressure Reservoir	45	55	74	74	U.W.	75	105	73	2500	Cyl. Paddle	1	9.2
4	XV-C	Batch	52.5	47.5	76	76	Bench	-	30	-	1000	Cone	-	4.0
5	XV-C	Batch	52.5	47.5	74	74	Bench	-	30	-	1000	Cone	-	3.7
6	XV-C	Batch	52.5	47.5	77	77	Bench	-	5	-	1000	Cone	-	-
7	XV-C	Batch	52.5	47.5	75	75	Bench	-	15	-	1000	Cone	-	2.9
8	XV-C	Batch	52.5	47.5	76	76	U.W.	30	45	72	1000	Cone	½	12.3
9	XV-D	Batch	40.5	59.5	130	130	Bench	-	15	-	1500	Cone	-	1.8
10	XV-D	Batch	40.5	59.5	130	130	Press.	30	45	-	1500	Cone	-	6.2
11	XV-D	Batch	40.5	59.5	130	130	U.W.	30	45	72	1500	Cone	½	8.7
12	XV-D	Batch	40.5	59.5	130	130	Press.	60	80	-	1500	Cone	-	17.3
13	XV-D	Batch	40.5	59.5	130	130	Press.	60	75	-	2000	Cone	-	10.6
14	XV-D	Batch	40.2	59.8	130	130	U.W.	60	80	70	2000	Cone	½	15.5
15	XV-D	-	30.1	44.8	130	130	Bench	-	-	-	-	Magnetic	-	2.64
16	XV-D	-	30.1	44.8	130	130	Press.	30	-	-	-	Magnetic	-	-
17	XV-D	-	40.2	59.8	130	130	Bench	-	-	-	-	Hand	-	3.0
18	T-7	Batch	30	23.25	75	75	Bench	-	15	-	1500	Cone	-	11.3
19	T-7	Batch	30	23.25	75	75	Bench	-	5	-	2500	Cone	-	8.0
20	T-7	Batch	50	44	75	75	U.W.	0	10	64	2500	Cone	1	2.0
21	T-8	Batch	50	52	75	75	U.W.	60	75	64	2000	Cone	10	6.6
22	XV-D	Batch	40.3	59.7	130	130	U.W.	60	75	64	2000	Cone	1	16.0
23	T-8	Batch	50	52	74	74	U.W.	66	80	66	2000	Cone	1	5.9
24	T-8	Batch	50	52	75	75	U.W.	30	45	68	2000	Cone	1	5.3
25	T-8	Batch	50	52	75	75	U.W.	66	80	71	2000	Cone	2	4.9
26	T-8	Batch	50	52	74	74	U.S.W.	165	180	45	2000	Cone	1	11.3
27	T-8	Batch	50	52	74	74	U.W.	0	15	71	2000	Cone	1	1.9

U.W. = Underwater
 Press. = Air pressure
 U.S.W. = Under salt water

Table VIII. Results of Laboratory Experimental Tests Performed by ARC.

Test No.	Friability	Surface Condition	Cohesion	Yield	Resistance to Exothermic Degradation	Congelment Celerity	General Comments
1			3	3			Complete dispersion.
2	1	3	2	2	1	1	Surface cracks.
3	1	3	2	2	1	1	Surface cracks.
4	2	1	1	1	1	1	Uniform texture.
5	2	1	1	1	1	1	Uniform texture.
6	-	-	-	-	-	-	Expansion took place in mixing head before foam could be expelled.
7	2	1	1	1	1	1	Uniform texture.
8	3	2	2	2	1	1	Surface voids - dispersion.
9	2	1	1	1	3	1	Uniform texture in area not charred.
10	1	1	1	1	3	1	Uniform texture in area not charred.
11	1	1	2	2	1	1	Some dispersion - uniform texture.
12	1	1	1	1	3	1	Incomplete mixing at start of run.
13	1	1	1	1	3	1	Incomplete mixing at start of run.
14	1	1	2	2	1	1	Same as Test 11.
15	2	1	1	1	3	1	Magnetic stirrer.
16	-	-	-	-	-	-	Not enough power to mix after MB was added. Magnetic stirrer.
17	2	1	1	1	3	1	Hand stirring.
18	2	1	1	1	1	3	Long cream time on formulations 7 and 8.
19	2	1	1	1	1	3	
20	2	1	1	1	1	3	Quite spongy.
21	2	1	1	1	1	2	Excellent underwater yield. Easy foam system to work with.
22	1	1	2	2	1	1	Some dispersion.
23	2	1	1	1	1	2	Same as 21.
24	2	1	1	1	1	2	Same as 21.
25	2	1	1	1	1	2	Same as 21.
26	3	3	1	1	1	3	Completely saturated with water.
27	2	1	1	1	1	2	Same as 21.

1 - Good
2 - Fair
3 - Poor

APPENDIX 7.3

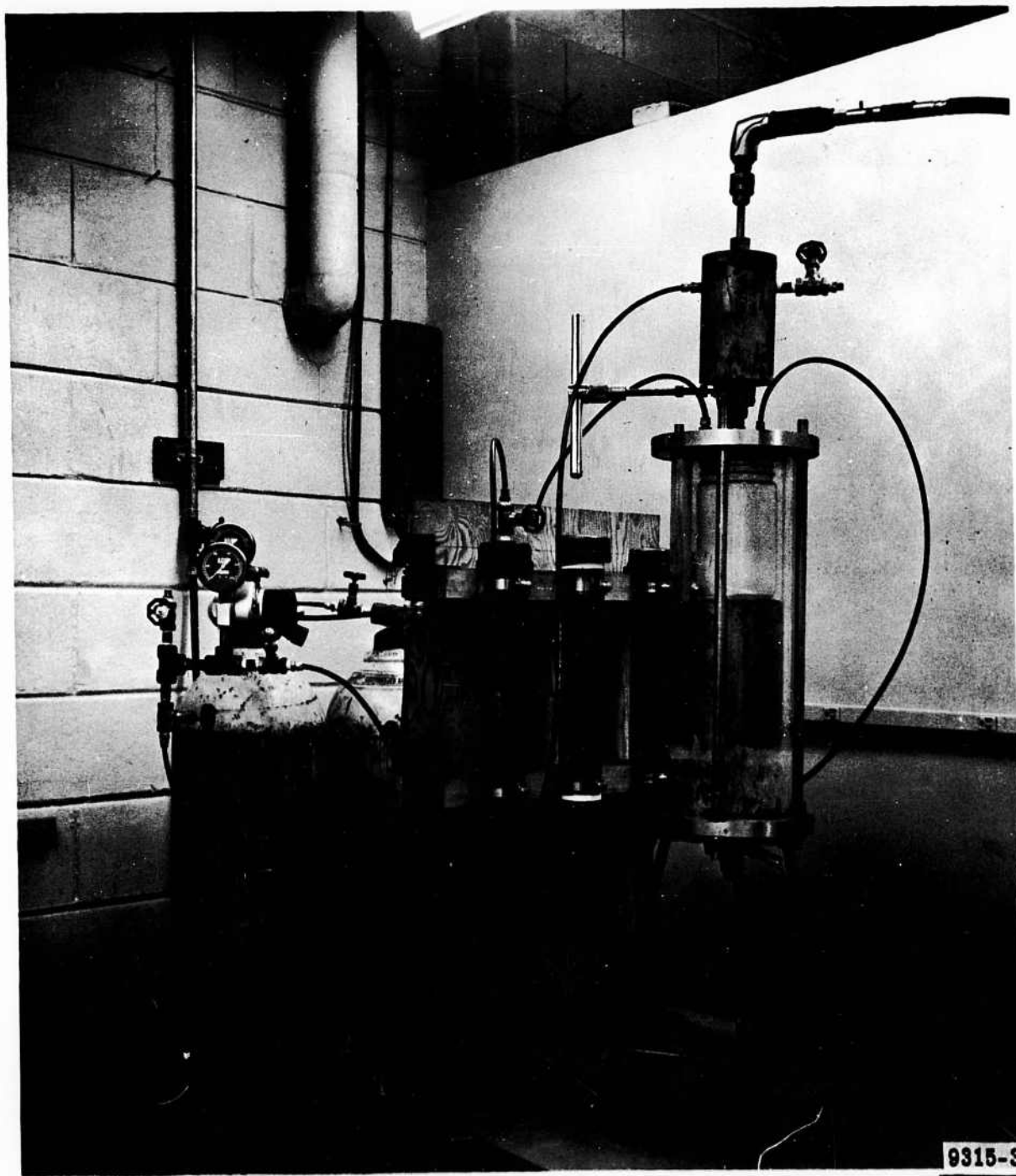
FIGURES

<u>Number</u>	<u>Description</u>
I	Laboratory Apparatus for Foaming Under Gas Pressure.
II	Effect of Pressure on Foam Density for Formulations T-7 through T-10.
III	Effect of Pressure on Foam Density for Formulations T-12 and T-13.
IV	Relationship of Water Content as a Function of Pressure to Obtain a Foam of Desired Density.
V	Effect of Water Absorption on Density of Foams Generated by Formulation T-10 and T-13 when Submerged in Water at One Atmosphere.
VI	Schematic of Laboratory Apparatus for Pressurized Continuous Feed Mixing.
VII	Schematic of Laboratory Apparatus for Batch Mixing.
VIII	Laboratory Apparatus for Foaming Under Pressurized Water.
IX	Reaction Chamber to Study Effects of Foam Dispersal Rising Within a Ship's Compartment.
X	Experimental Mixing Head. Cylindrical Body and Pin-Blade Paddle.
XI	Experimental Conical Mixing Head, Conical Body and a Modified Helicone* Paddle. *Trade Mark of Atlantic Research Corporation, Alex. Va.
XII	Sequence of Foam Flotation Events Taken From Motion Picture Film Showing a 600 ML Beaker Being Raised by Formulation T-8 at 66 psig (Test #25)
XIII	Sequence of Foam Dispersal Events Taken From High Speed Film (1000 PPS) during Test #25

APPENDIX 7.3 (continued)

FIGURES

<u>Number</u>	<u>Description</u>
XIV	Sequence of Foam Flotation Events Taken From Motion Picture Film Showing a 5-inch Diameter Acrylic Tube with a Wire Mesh Closure Being Raised by Formulation T-8 at Atmospheric Pressure (Test #27).
XV	Sequence of Foam Flotation Events Taken From Motion Picture Film Showing a 4-1/2-inch Diameter Wire Mesh (10 x 10) Basket Being Raised By Formulation T-8 at 66 psig (Test #23).
XVI	Preliminary Studies to Determine Water Absorption Rates at Atmospheric Pressure.
XVII	Effect of Pressure on Foam Density for Formulation XV-D and T-8 as Compared With Density Predicted by Boyles Law.



9315-3

Figure I. Laboratory Apparatus for Foaming Under Gas Pressure.

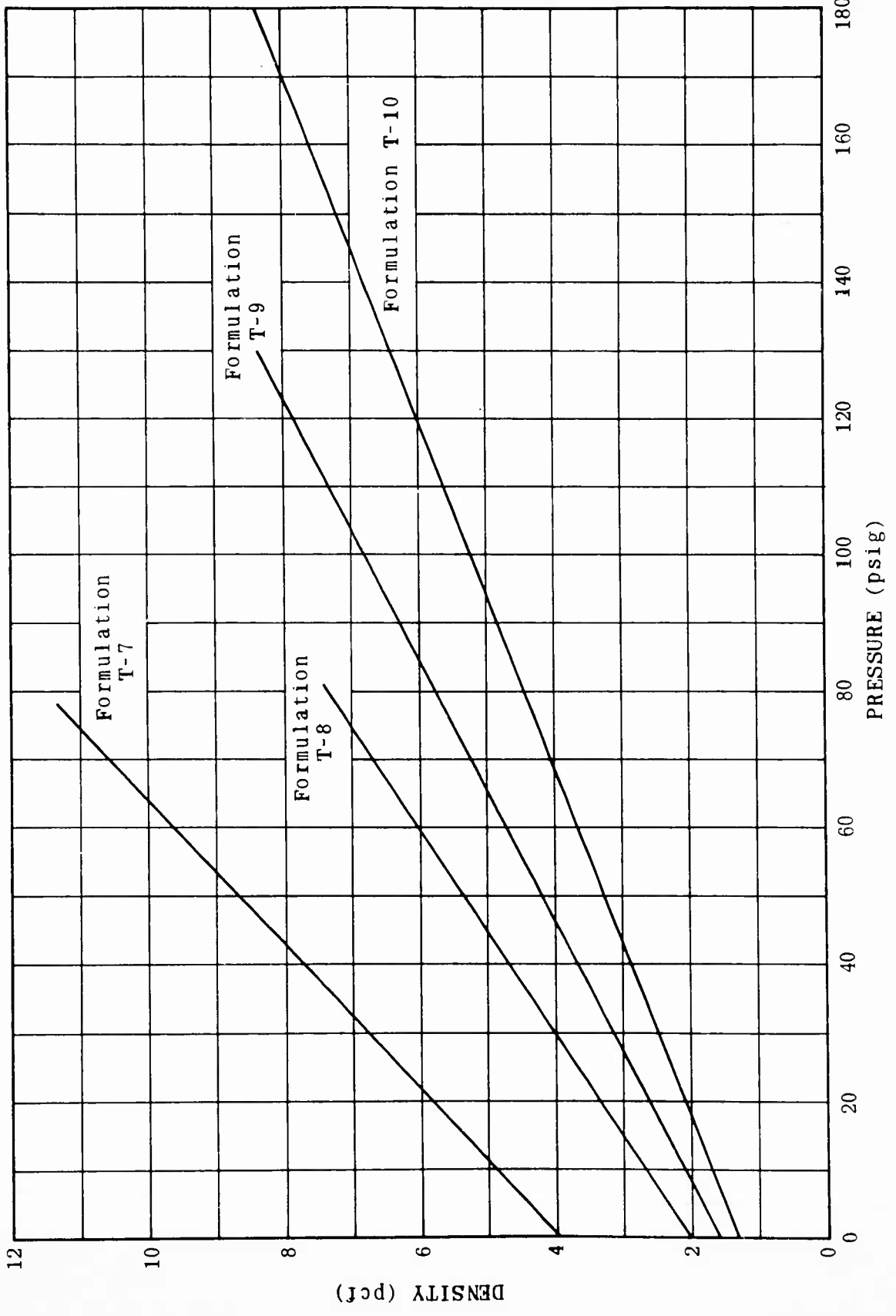


Figure II. Effect of Pressure on Foam Density for Formulations T-7 Through T-10.

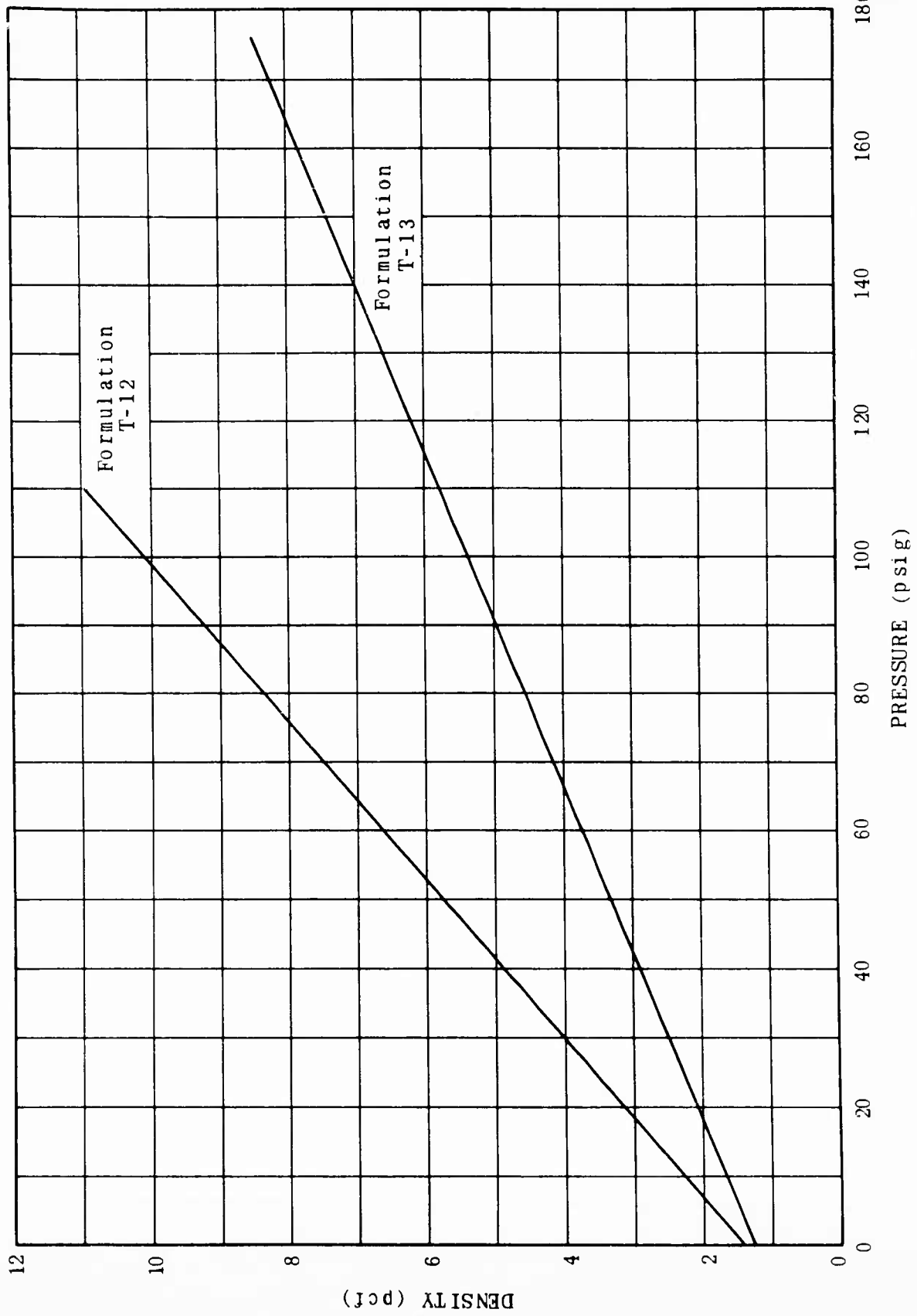


Figure III. Effect of Pressure on Foam Density for Formulations T-12 and T-13.

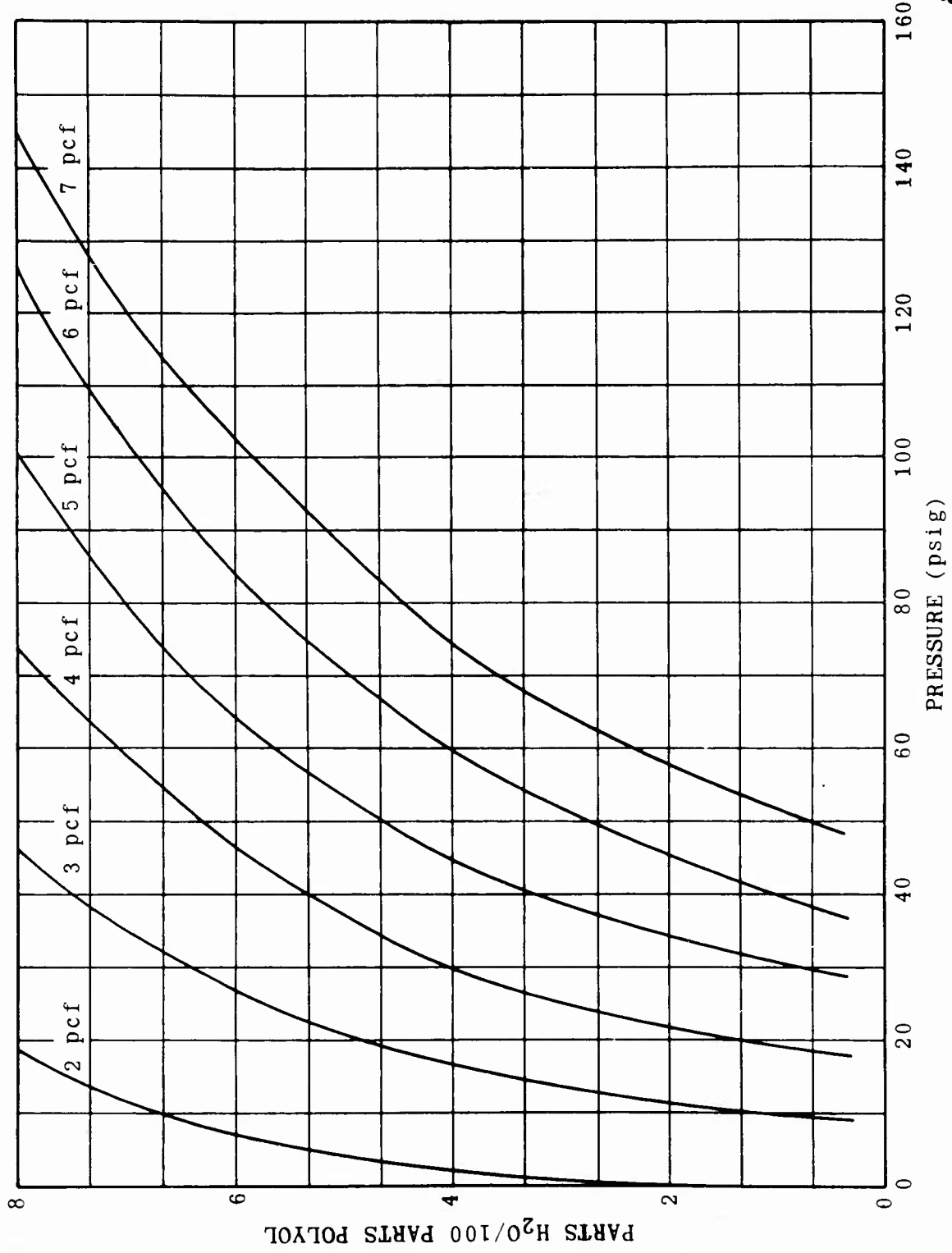
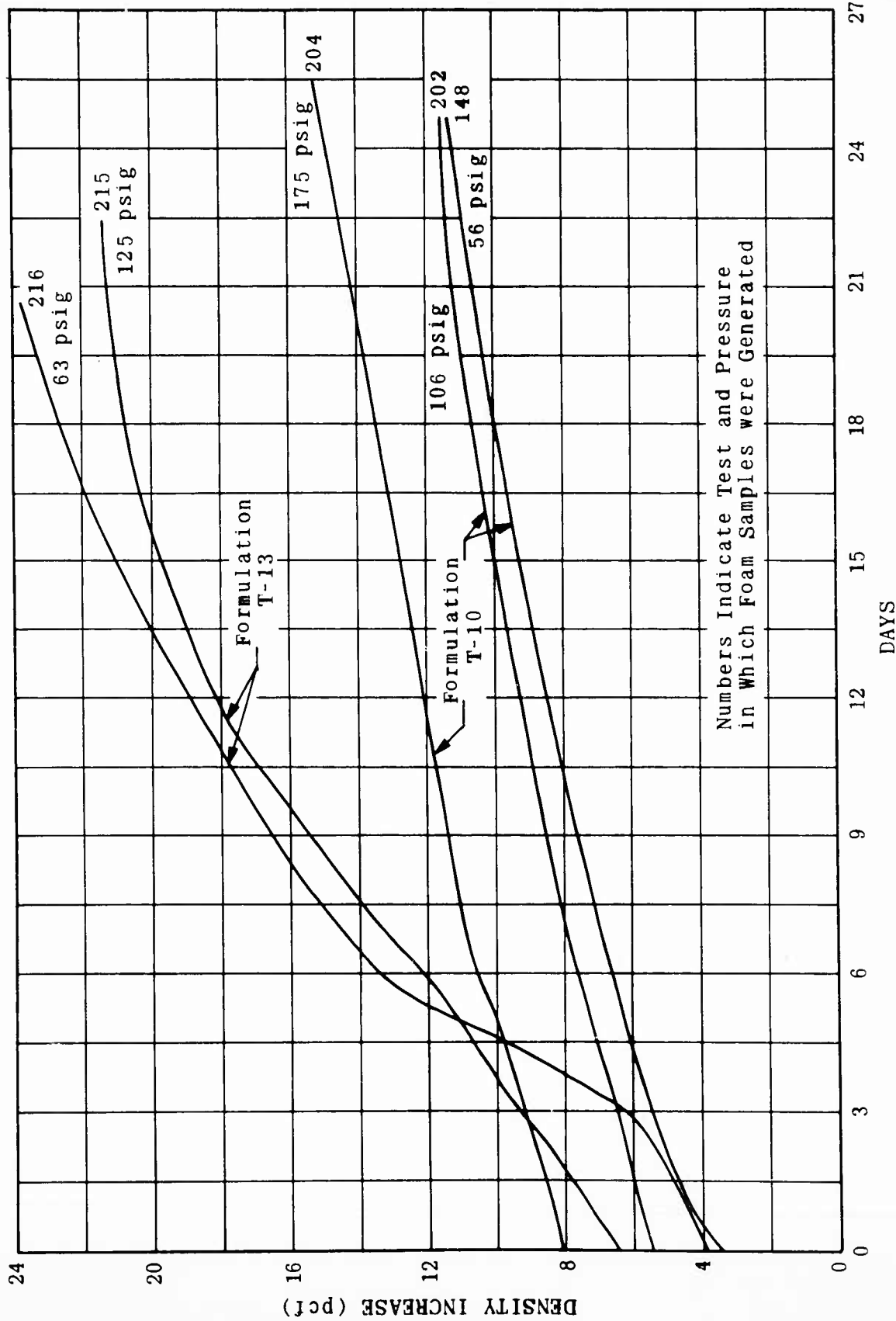
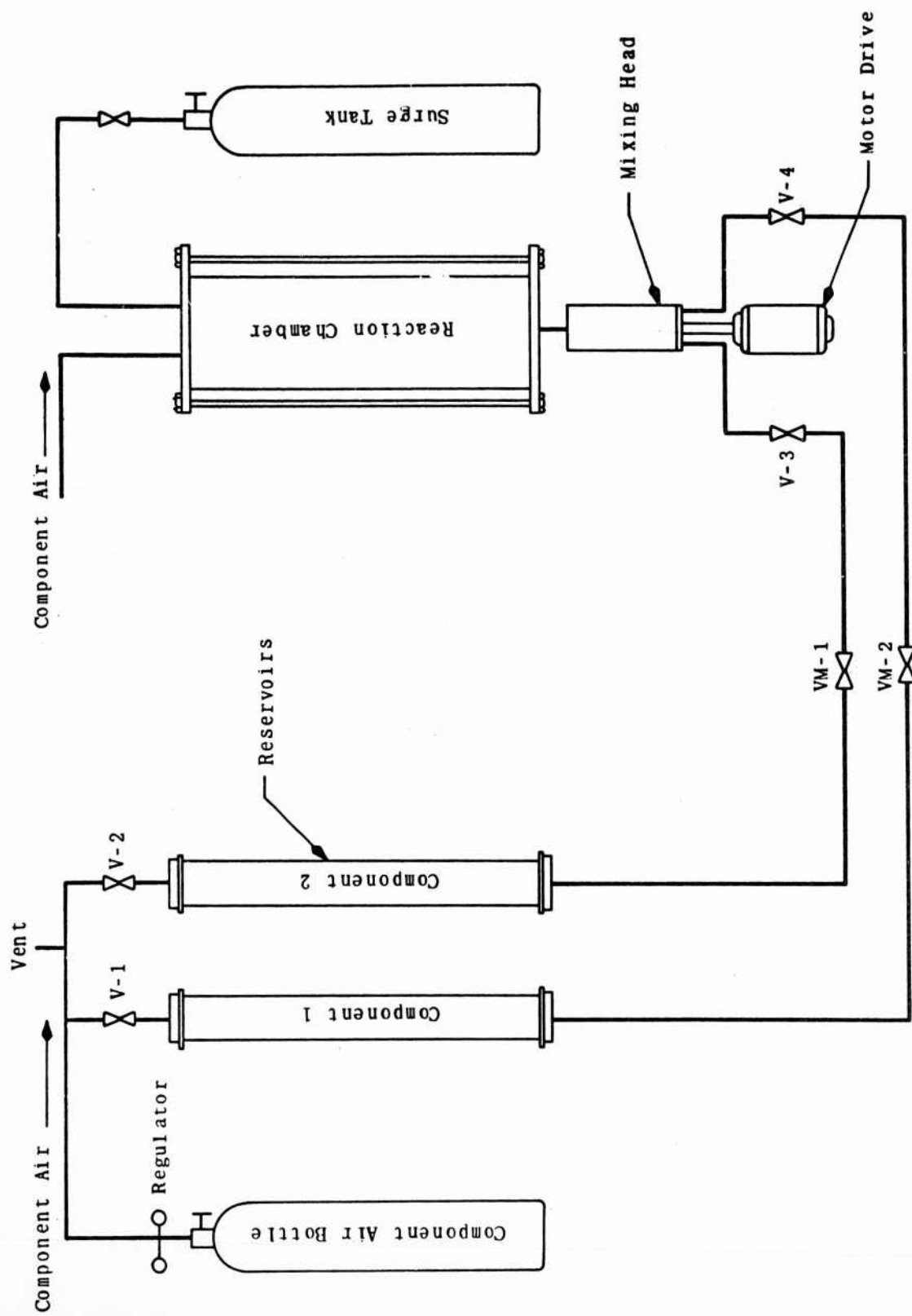


Figure IV. Relationship of Water Content as a Function of Pressure to Obtain a Foam of Desired Density.



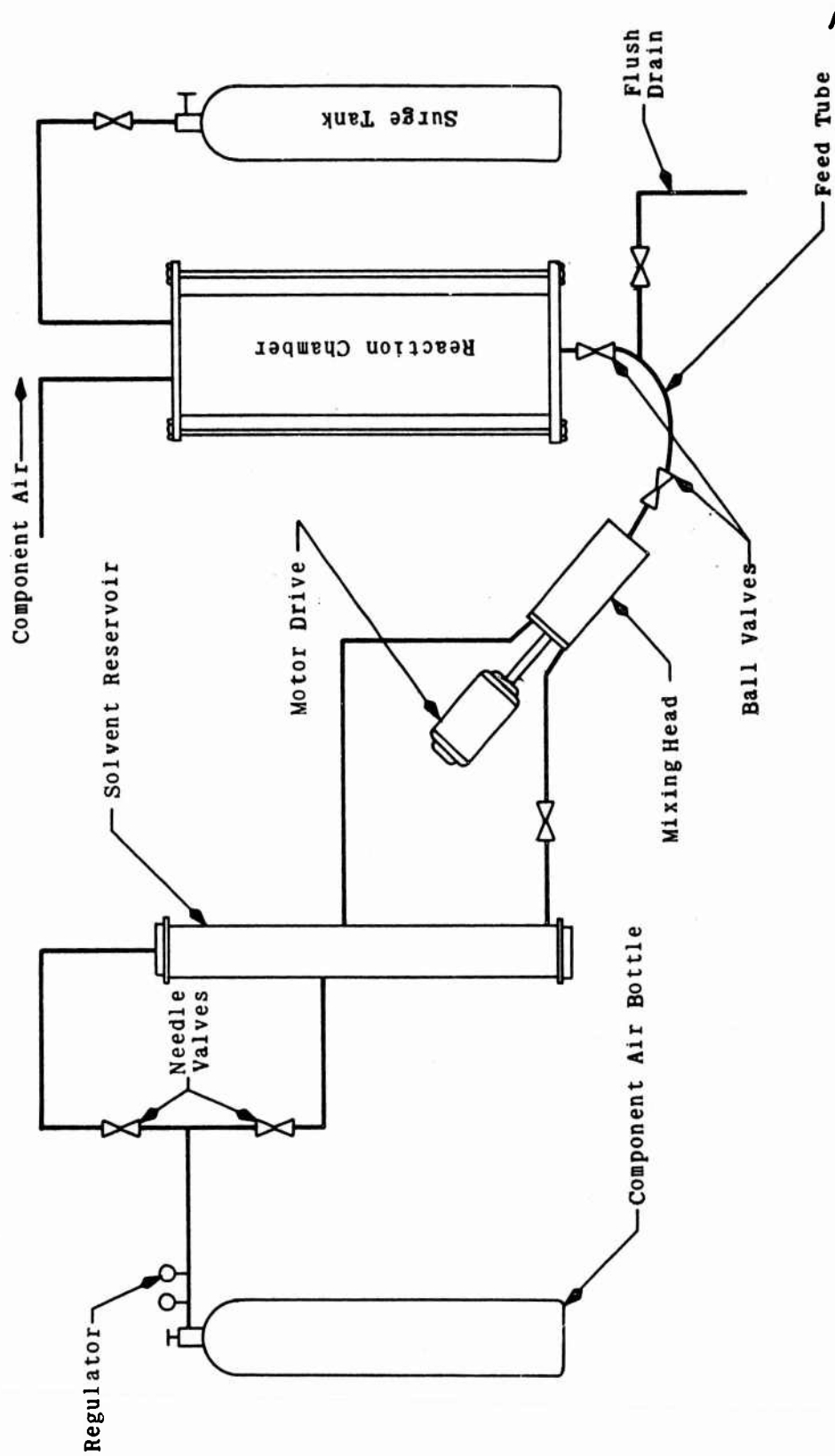
Numbers Indicate Test and Pressure
in Which Foam Samples were Generated

Figure V. Effect of Water Absorption on Density of Foams Generated by Formulations T-10 and T-13 When Submerged in Water at One Atmosphere.



2260

Figure VI. Schematic of Laboratory Apparatus for Pressurized Continuous Feed Mixing.



2269

Figure VII. Schematic of Laboratory Apparatus for Batch Mixing.

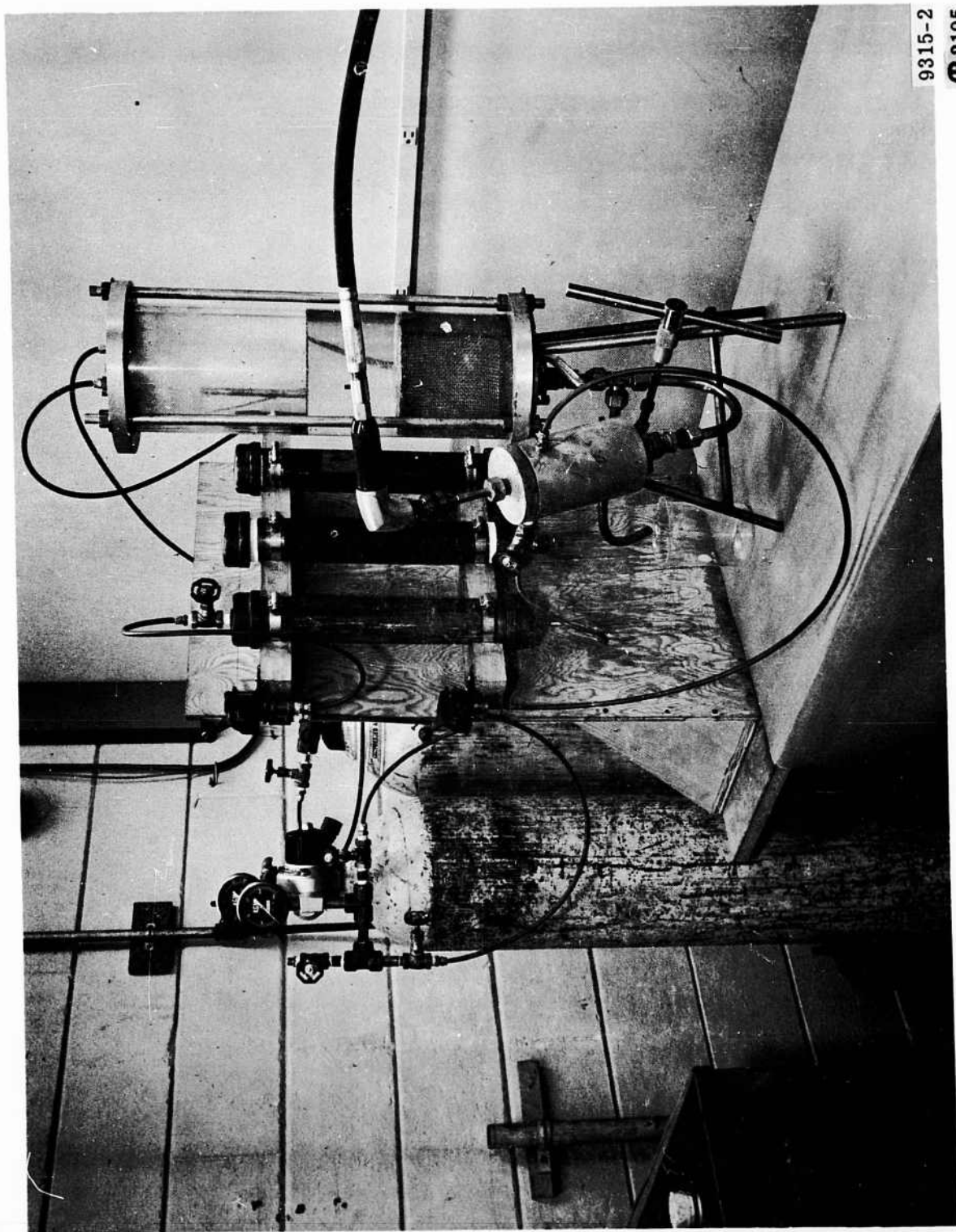


Figure VIII. Laboratory Apparatus for Foaming Under Pressurized Water.

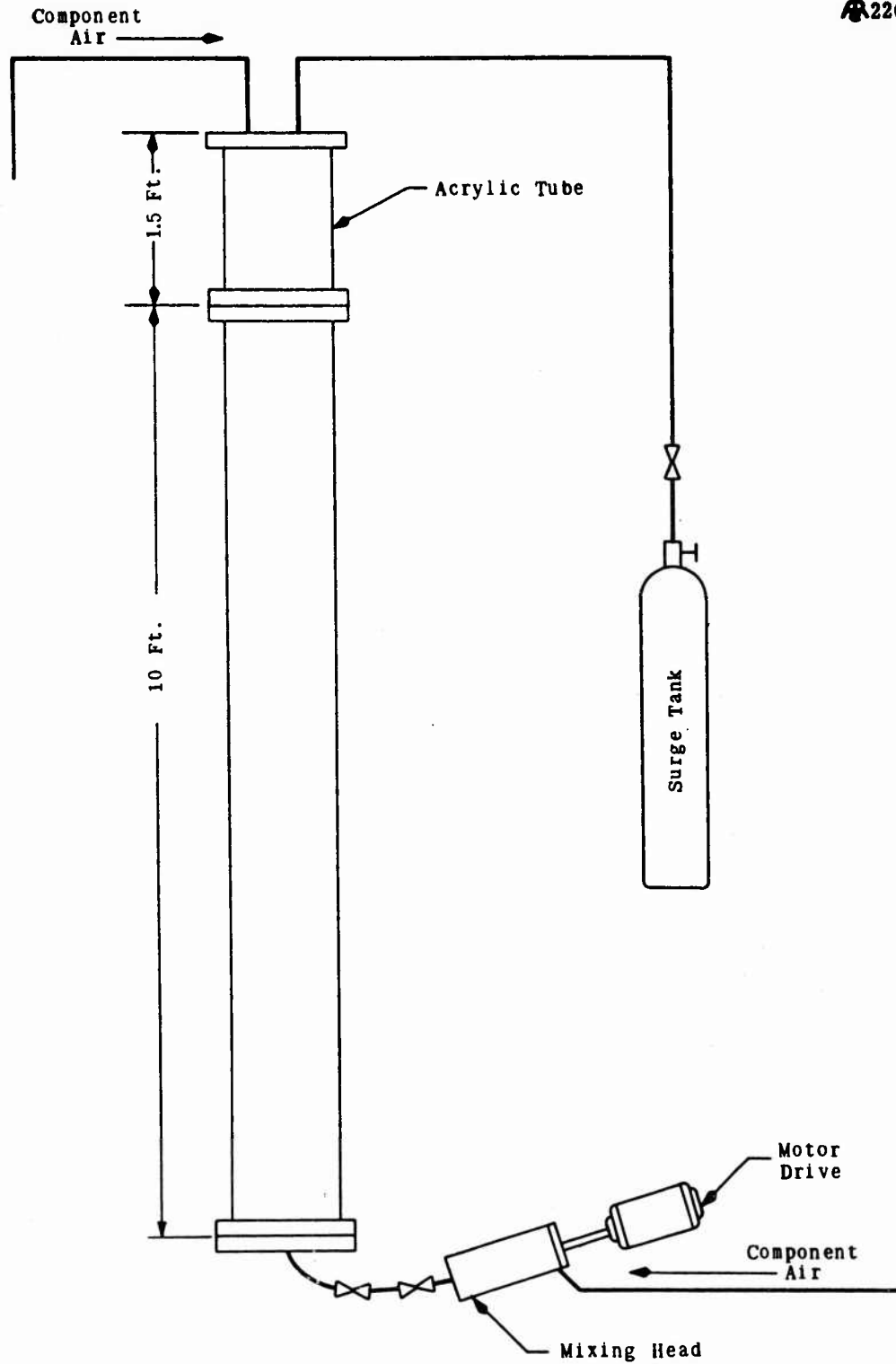
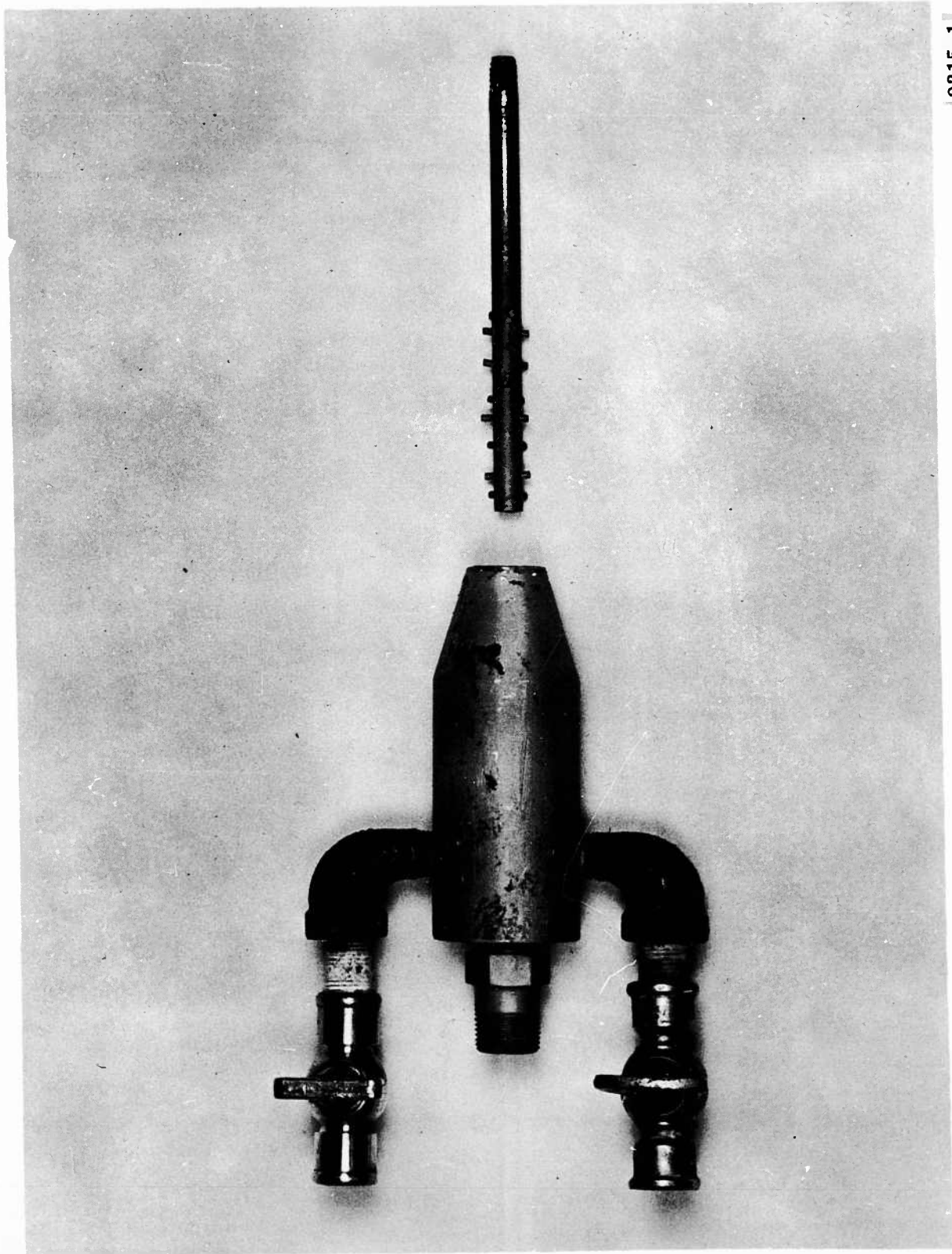


Figure IX. Reaction Chamber to Study Effects of Foam Dispersal Rising Within a Ships Compartment.



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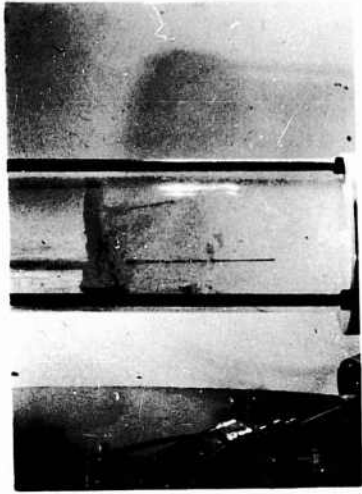
Figure X. Experimental Mixing Head. Cylindrical
Body and Pin-Blade Paddle.



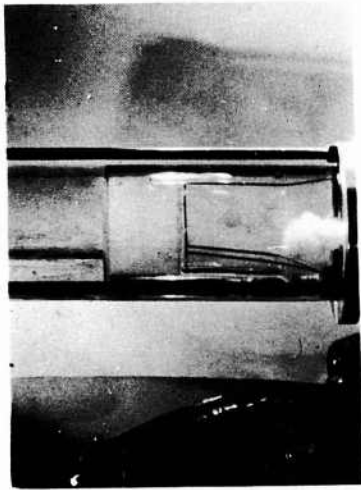
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Figure XI. Experimental Conical Mixing Head. Conical Body
and a Modified Helicone* Paddle.

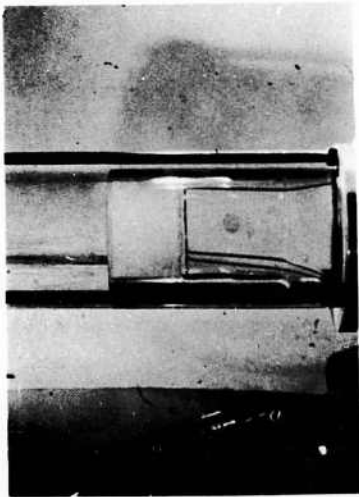
*Trademark of Atlantic Research Corporation, Alexandria, Va.



C



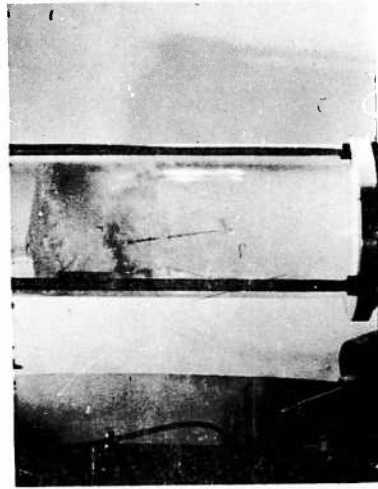
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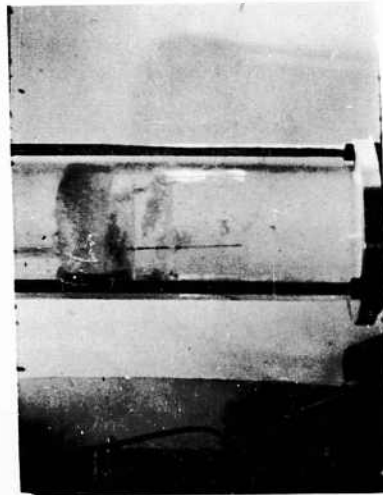
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F



E



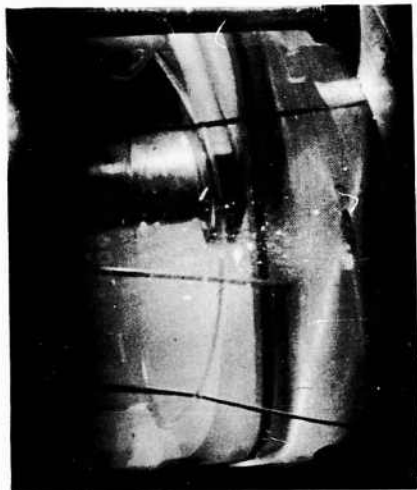
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2236

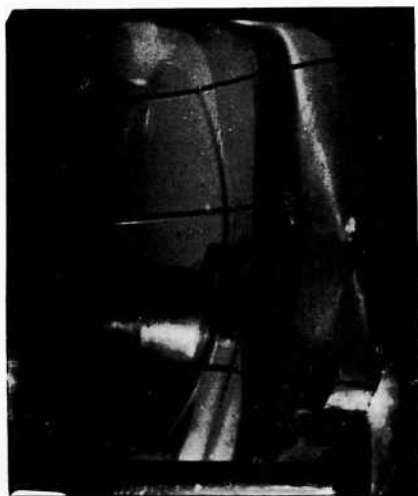
Figure XII. Sequence of Foam Flotation Events Taken from Motion Picture Film Showing 600 ml Beaker Being Raised by Formulation T-8 at 66 psig During Test Number 25.



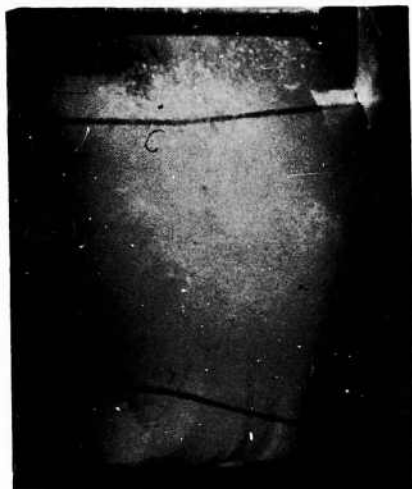
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B



A



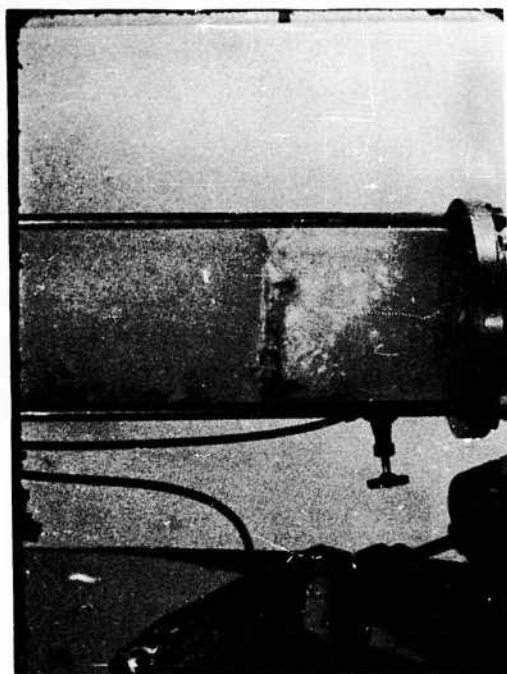
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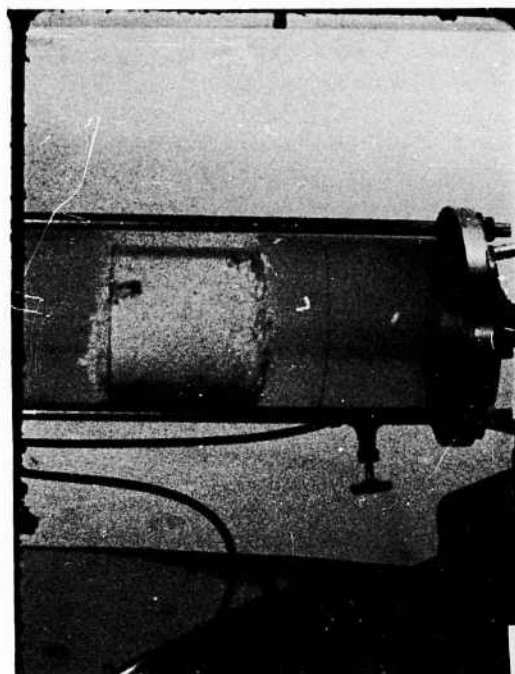
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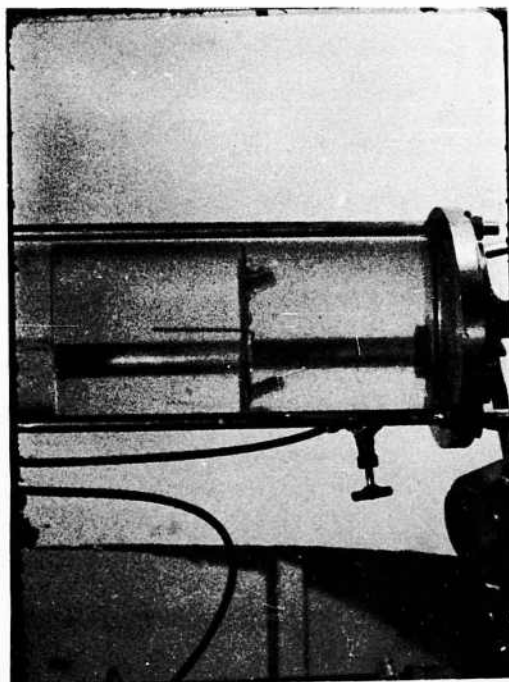
Figure XIII. Sequence of Foam Dispersal Events Taken from High Speed Film (1000 pps) During Test Number 25.



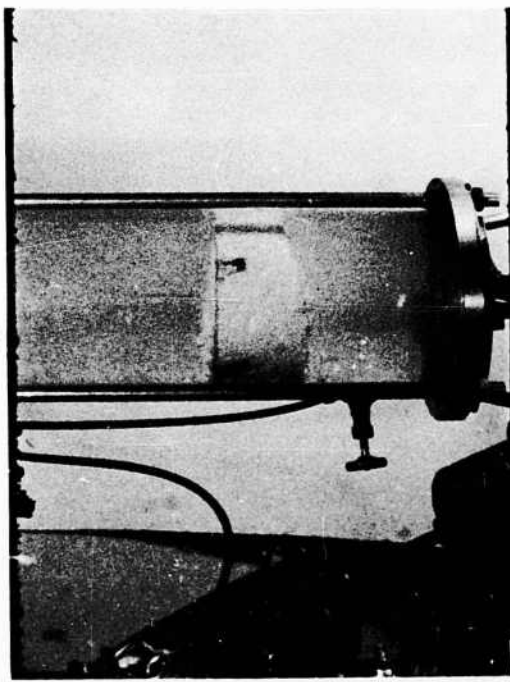
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D

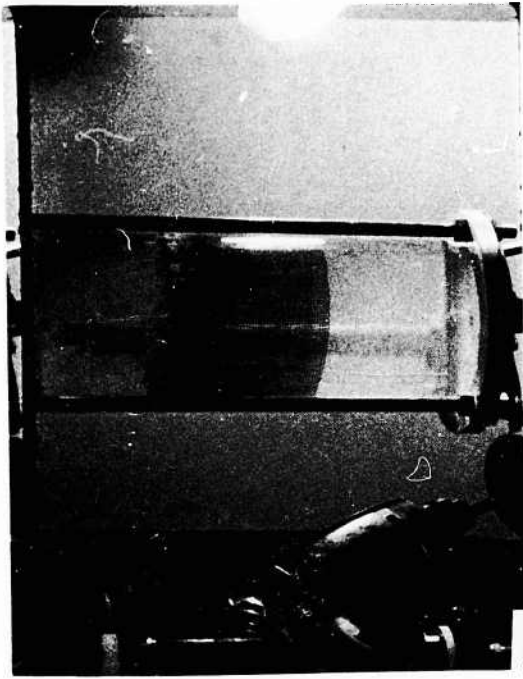


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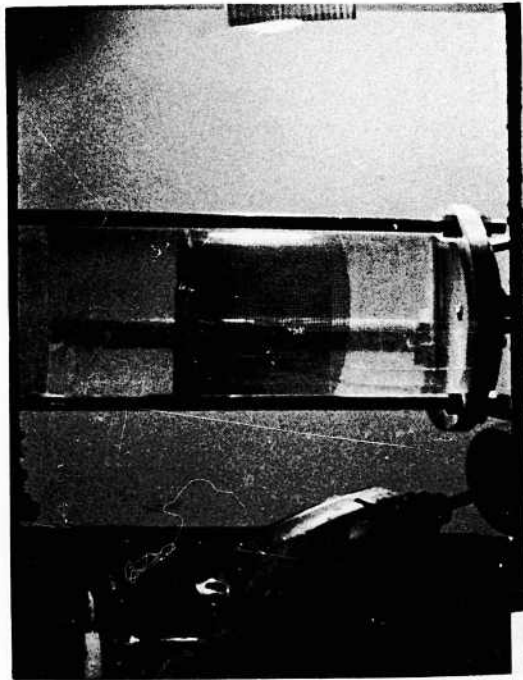


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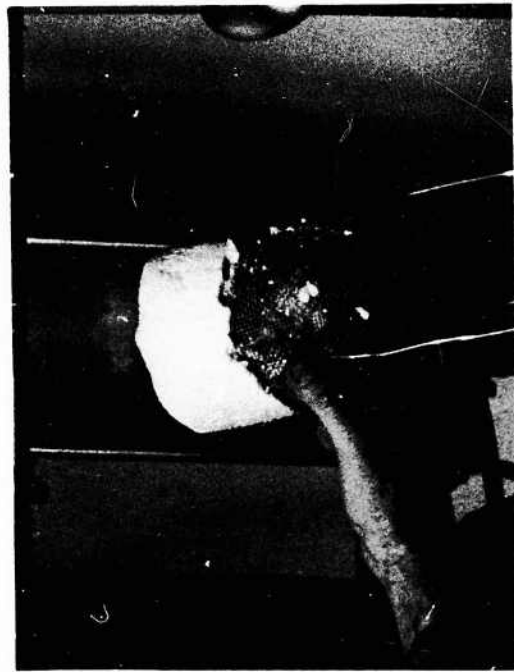
Figure XIV. Sequence of Foam Flotation Events Taken from Motion Picture Showing a Five Inch Diameter Acrylic Tube With a Wire Mesh Closure Being Raised by Formulation T-8 at Atmospheric Pressure During Test Number 27. **AR 2237**



A



B



C

Figure XV. Sequence of Foam Flotation. Events Taken from Motion Picture Showing a 4-1/2 Inch Diameter Wire Mesh (10 x 10) Basket Being Raised by Formulation T-8 at 66 psig During Test Number 23.

AR 2235

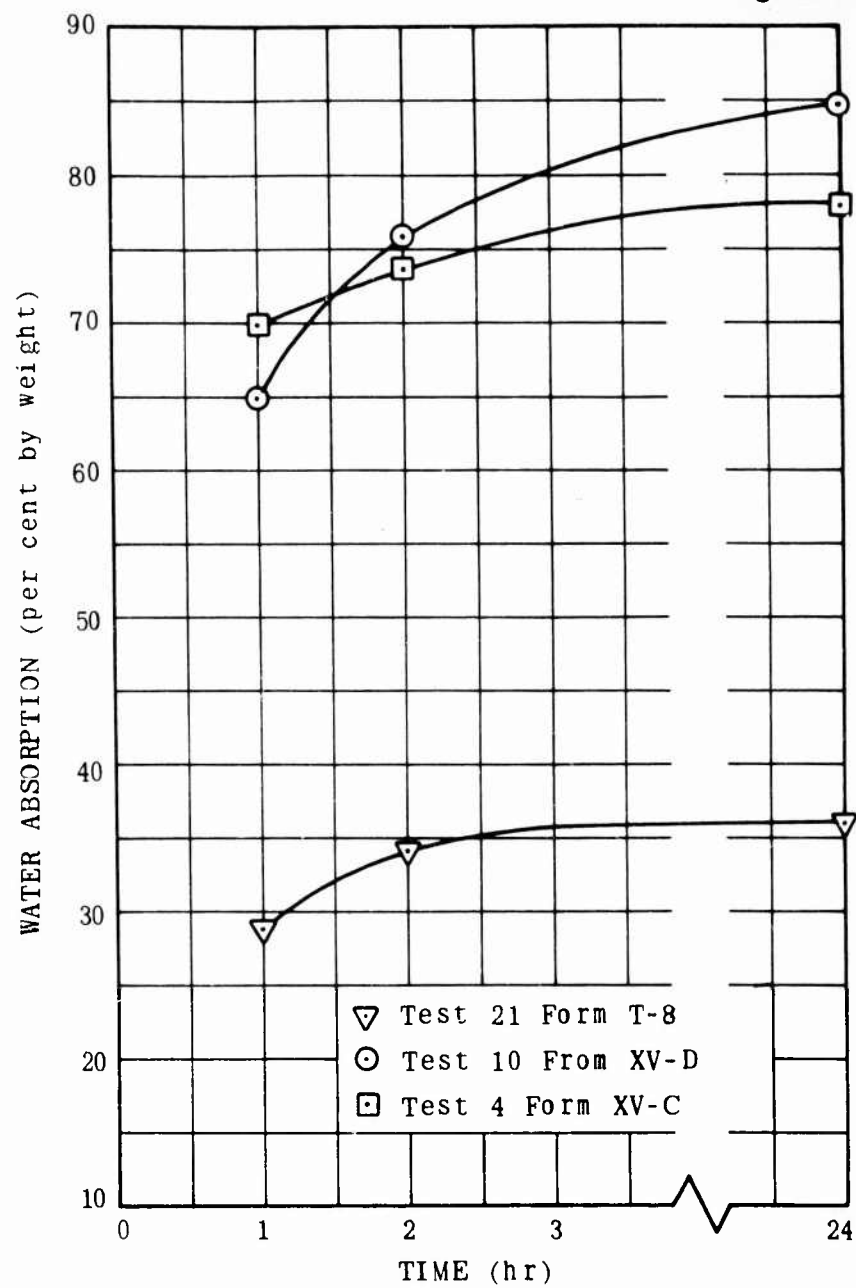


Figure XVI. Preliminary Studies to Determine Water Absorption Rates at Atmospheric Pressure.

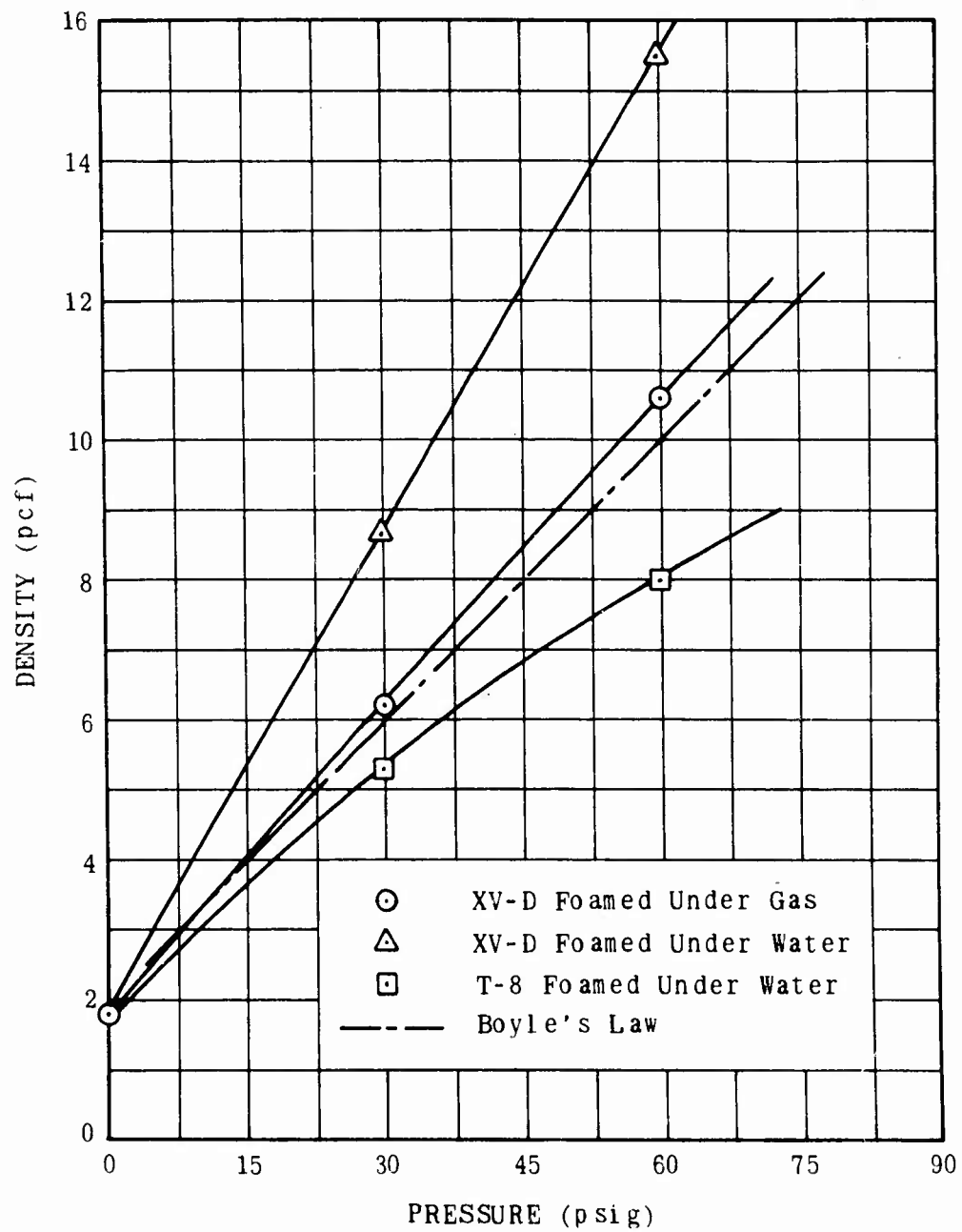


Figure XVII. Effect of Pressure on Foam Density for Formulations XV-D and T-8 as Compared With Density Predicted by Boyle's Law.

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