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ON
PRESSURE RELIEVING SYSTEMS
FOR MARINE BULK
LIQUID CARGO CONTAINERS

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13. ABSTRACT

The Committee on Hazardous Materials were requested by the U.S. Coast Guard (now an agency of the U.S. Department of Transportation) to review the technical and engineering fundamentals which relate to safe cargo containment of dangerous cargos.

The Panel on Cargo Containment has compiled, reviewed, and analyzed factual data useful to the Coast Guard and to anyone interested in the problems related to a more complete understanding of cargo containment of vessels in marine transportation, with specific attention to control of over pressure during emergency conditions such as involvement in a fire.

After careful analyses of the formulae previously recommended for the sizing of the relief valves, the Panel has proposed a new formula for consideration by the Coast Guard, to more adequately reflect present knowledge and engineering practices, with the objective of encouraging additional attention to those details which make for a safer system.

Additional research on heat flux to cargo vessels during exposure to fire is recommended to refine and extend understanding of presently existing information.

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This report has been submitted in fulfillment of contract DOT-CG-15559 and is promulgated subject to the following qualifications:

Thi ntents of this report reflect the views of the Cargo Containment Panel of the Committee on Hazardous Materials, National Research Council, National Academy of Sciences, Washington, D.C. which is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policy of the Coast Guard. This report does not constitute a standard, specification or regulation.

J. R. Iversen

J. R. IVERSEN,
Captain, U.S. Coast Guard
Chief, Applied Technology Division
Office of Research and Development
U.S. Coast Guard Headquarters
Washington, D.C. 20590

CARGO CONTAINMENT PANEL REPORT ON PRESSURE RELIEVING SYSTEMS FOR MARINE BULK LIQUID CARGO CONTAINERS

A Report to the United States
Coast Guard

Prepared by The
Committee on Hazardous Materials

Advisory to the U. S. Coast Guard
Under Contract No. Tcg - 15559

Department of Transportation
Washington, D. C.

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The scientific study described in this report is part of a program undertaken under the aegis of the National Academy of Sciences - National Research Council with the express approval of the Governing Board of the NRC. Such approval indicated that the Board considered that the problem is of national significance; that elucidation and/or solution of the problem required scientific or technical competence, and that the resources of the NRC were particularly suitable to the conduct of the project. The institutional responsibility of the NRC was then discharged in the following manner:

Responsibility for all aspects of this report rests with the study panel and parent committee, to whom we express our sincere appreciation.

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FOREWORD

The Committee on Hazardous Materials was requested by the U. S. Coast Guard (now an agency of the U. S. Department of Transportation) to review the technical and engineering fundamentals which relate to safe cargo containment of dangerous cargos.

The Panel on Cargo Containment has compiled, reviewed, and analyzed factual data useful to the Coast Guard and to anyone interested in the problems related to a more complete understanding of cargo containment of vessels in marine transportation, with specific attention to control of overpressure during emergency conditions such as involvement in a fire.

After careful analyses of the formulae previously recommended for the sizing of the relief valves, the Panel has proposed a new formula for consideration by the Coast Guard, to more adequately reflect present knowledge and engineering practices, with the objective of encouraging additional attention to those details which make for a safer system.

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PREFACE

A general review of cargo containment, as it relates to overpressure encountered under emergency situations, has been prompted by recognition of the unique characteristics of systems involved in marine transport of bulk liquid hazardous cargos.

At the request of the Coast Guard, a panel was formed within the Committee on Hazardous Materials for the specific purpose to recommend, in view of existing knowledge, more nearly adequate pressure relieving systems, and to encourage design features which will decrease the inherent hazards.

Pressure vessels for liquid cargos have a pressure level at which they will fail, releasing their contents. The purpose of pressure-relieving systems is to prevent this pressure from being attained, thus preventing the rupture of the vessel and the release of the product. The safety of personnel, both those directly concerned with the vessel and those incident to the scene, is the primary consideration. Prevention of damage to property is a second important factor, since this protects both the vessel itself and the adjoining property that might be damaged by the rupture, and also conserves the product.

Excessive pressure in cargo vessels may develop through heat entering the vessel from the surroundings, generating vapor and

increasing the pressure. Heat may be transferred by ambient temperatures (for refrigerated vessels), or by fires (for vessels designed for ambient conditions). Overpressure may occur during filling or loading operations, or result from gases applied to provide discharge pressures. Insufficient ullage with temperature variations substantially in excess of normal operating conditions can also result in overpressure.

Pressure-relieving devices are intended to release only the quantity of product necessary to lower the pressure effectively to a predetermined safe value, without releasing an excessive quantity. This control is especially important in situations where the release of the product generates a hazard for personnel or property, because of its flammability or its toxicity. The following is a specific list of causes of overpressure:

1) Loss or deterioration of insulation from refrigerated tanks
2) Heat absorption from fire adjacent to the tank
3) Operating error, including pumping at excessive flow rate
4) Inoperability or failure of the relief valve
5) Restrictions or plugging of relief valve discharge concomitant with abnormal heat input to the vessel.

The pressure relief problem may be examined in significant detail by considering,

1) What is the purpose of relief valves and under what conditions should vapor be vented to the atmosphere?

2) What criteria should be used in sizing relief systems?

3) How should vapor relief be provided for non-pressurized cargos?

4) What treatment is extended to multi-range carriage of products?

and, by considering the following factors in providing answers to the above questions:

1. Mechanical Requirements

   a. Relieving capacities

   b. Maximum and minimum relief device settings

   c. Types of acceptable relief devices (valves, discs, fusible plugs), including materials of construction

   d. Location and number of relief devices

   e. Tank size and configuration

   f. Outage

   g. Vent diffusion

   h. Insulation

   i. Fire protection systems

   j. Test and maintenance

   k. Applicability to the various categories of cargos (i.e. cryogenic fluids, liquefied gases, compressed gases and volatile liquids).

2. Personnel Requirements

   a. Personnel should be instructed in 1) relief valve operation and maintenance and in 2) the specific hazards and precautions for the cargos carried.

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CARGO CONTAINMENT PANEL MEMBERS

Prof. D. L. Katz, University of Michigan

Chairman, Committee on Hazardous Materials, 1964 - Present

Panel Chairman, 1964 - 1966

Dr. Clyde McKinley, Air Products and Chemical Corp.

Panel Chairman, 1966 - Present

Howard H. Fawcett, Technical Secretary,

Committee on Hazardous Materials

Capt. R. J. Bosnak, United States Coast Guard

William H. Doyle, Factory Insurance Association

A. F. Dyer, Phillips Petroleum Company

Frank J. Heller, Phillips Petroleum Company

W. H. Lauderback, Texas Eastman Company

Dr. D. T. Neill, University of Oklahoma

Prof. C. M. Sliepcevich, University of Oklahoma

Dr. J. R. Welker, University of Oklahoma

Miles E. Woodworth, National Fire Protection Association

W. E. McConnaughey, United States Coast Guard

Liaison with Committee

The panel also gratefully acknowledges major contributions by:

Mr. Alan Schneider, Massachusetts Institute of Technology

Dr. M. F. Abd-El-Bary, Lehigh University

Prof. Ali M. Kiper, The George Washington University
Consultant to the Panel

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Dr. Leland W. T. Cummings, Consultant, Sun Oil Company
(Deceased Oct. 19, 1971)

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INTRODUCTION

Bulk transport containers for hazardous cargoes must include within the container system appropriate pressure relief devices. These must be capable of adequately venting sufficient cargo to prevent the pressure in the container from exceeding an acceptable maximum. Container rupture from overpressure, with attendant side-effects, is thus avoided.

Pressure relief devices are set to relieve fluids when the pressure reaches some intermediate pressure between normal operating pressure and a predetermined upper safe pressure. Close proximity to an external fire or other source of heat may cause a pressure rise in the container from expanding liquid or vapor generation from the liquid cargo. The metal in contact with the liquid cargo is cooled by the cargo as it boils, whereas the portion of the container in the vapor space is not cooled significantly by the boiling liquid. This unwetted metal rises in temperature when subjected to fire and if the fire continues will lose strength and may even eventually rupture, even though the relief system is maintaining the pressure at the normally acceptable maximum.[5] The time-temperature relationship for the temperature rise of the unwetted but fire-exposed portion of the cargo tank is calculable if the heat flux input is known. However, many fires do not heat the metal to the temperature of failure by

abating or being brought under control, by not totally involving the cargo tank, or as a result of water spray applied on the container to cool the vapor space. The safety valve prevents rupture of the vessel during heat exposure, and in addition, when the heat exposure is reduced, closes, and thus stops the flow of product which may have been contributing to the fire exposure.

A certain minimum vapor relief capacity is required for each container subjected to fire. Oversized valves will pop, close, wait for pressure to build up, and pop again. Undersized valves may result in sufficient pressure build-up that the container will rupture. For severe fires of long duration, the container may fail in the unwetted vapor space by weakening of the overheated metal, since such weakening lowers the strength of the vessel wall below the ordinary yield strength of the metal.

The severity of fires and the rate of heat transfer to containers to generate vapor depends upon several items: 1) fraction of container surface in contact with flame, 2) presence or absence of insulation on the tank, 3) the kind of fuel burning, 4) the geometry of the fuel source as compared to the vessel, 5) the thickness of the flame adjacent to the container wall, and 6) the availability of air to feed the flame and permit violent burning. Methods and recommendations for sizing relief valves to cope with all possible situations have historically been partly empirical and partly based on experimental data for heat transfer rates from fires to containers. Several formulae relate the total heat input to a container exposed to fire to that container's surface

area, with that area raised to an exponential power less than unity. This practice discounts the container area to account for the reduced fraction of the container likely to be engulfed in fire as the container size increases. Such a simple correlation between size and exposure to fire does not inherently reflect the elements of the hazard associated with the specific system, and may even obscure recognition of the intrinsic hazards.

For marine cargoes, the relative relationship between vessel and container size and shape, and the probable area exposed to fire can be considerably different than for the land based situation. The elements of the hazard will be in many respects the same but the relative significance of each element may well differ. Evaluation of the fire exposure hazard should involve examination of each element - local heat flux, the container environment factor, and the portion of the container exposed to fire - as it is related to the specific cargo container system.

This study suggests a view of heat transfer rate calculations to give credit for those items which both reduce the needed relief valve capacity and also ensure sufficient vapor relief when no special precautions are taken to confine a possible fire or to reduce its intensity.

Data indicate that free burning fires can transfer heat at rates which approximate 34,500 Btu/(hr)(ft^2), to bare containers under some conditions. For cylindrical tanks in barges this rate could apply for the portion of the container above the fuel burning from a pool in the bottom of the barge. Spills of fuel in a barge can be limited by

bulkhead dams; since a single source is probable for any fire, such dams can be significant in limiting the area of the cargo container subjected to fire.

Insulation can be very helpful in reducing heat transfer during fire exposure. Insulation of the upper portion of the cargo container, the portion for which it is probable that boiling protection will not exist, appears to offer a significant extra protection by reducing the likelihood of over-heating of the metal in that portion of the container.

CONCLUSIONS AND RECOMMENDATIONS

1. The following formula, described in detail beginning on page 27, is proposed for obtaining the heat transfer rate to marine bulk liquid cargo containers during exposure to fire. The heat absorption rate thus calculated may be used in sizing the relief system.

$$Q = qFEA \qquad [2]$$

where

- Q = rate of heat absorption by liquid cargo, Btu/hr
- q = heat flux from fire (per unit wetted area completely exposed to fire), Btu/(hr)(ft^2)
- F = environmental factor, dimensionless; accounts for the combined effects of difference in exterior environment conditions, such as insulation, water spraying, etc.
- E = fire exposure factor, dimensionless; the fraction of total wetted surface area which is exposed to fire
- A = total wetted surface area of the cargo container, ft^2

To most fully implement the above recommended formula for heat absorption the following conclusions and recommendations are made:

2. Large-scale fire tests (involving containers of the shape and size of those used or proposed for marine service) properly planned and carefully instrumented, are needed to resolve fundamental questions regarding heat transfer rates, metal failure, and relief valve operations.

3. Tests are needed to develop an improved correlation of radiant flux from fires as a function of the fuel burned. The limited data available show that the radiant flux varies from one fuel to another in a way apparently related to the specific fuel; a correlation which would permit predictions based on the molecular structure of specific fuels would be desirable.

4. More detailed study is needed, including performance testing, of vapor relief devices under conditions to be expected in marine service including:

   (i) when handling saturated liquid;

   (ii) when handling entrained liquid.

5. Further experimental characterization is needed of the entrainment to be expected from the liquid surface under conditions corresponding to those in actual pressure relieving.

6. Further study is needed of the rate of evaporation from burning pools.

7. A study should be instituted to develop, compare and prepare conclusions on the conflicting concepts of American versus European practices on relief in contrast to containment.

8. A study should be made of insulation efficiency, with particular attention to high integrity and thermal stability under fire exposures as well as weathering in the marine environment. The available information on this subject is neither precise nor comprehensive. (see Appendix 7)

PART THREE: DISCUSSION OF OVERPRESSURE PROBLEMS AND RELATED RELIEF SYSTEMS

Relief valves and attached systems are designed to relieve overpressure, thus minimizing the possible rupture of the container. Code of Federal Regulations (CFR)[27] requires that, where an additional hazard can be created by exposure of a pressure tank to fire or other unexpected sources of external heat, the combined relieving capacity of the pressure relieving devices shall be capable of preventing the pressure from rising more than 20 percent above the maximum allowable working pressure of the tank. In the same paragraph, the minimum rate of discharge which the pressure relief valve must be able to pass is given by the following formula:

$$(cfm)_a = 633{,}000 \frac{FA^{0.82}}{LC} \left[\frac{ZT}{M}\right]^{0.5} \qquad [1]$$

where

$(cfm)_a$ = Minimum required rate of discharge in cfm of air at standard conditions (60°F and 14.7 psia)*

F = Fire exposure factor

A = Total surface area of the cargo tank, ft^2

L = Latent heat of the material being vaporized at relieving conditions in Btu/lb.

C = Constant based on the relation of the specific heats (See Part VI)

Z = Compressibility factor of the gas at relieving conditions

T = Temperature of the gas at the relieving conditions, °R

M = Molecular weight of the cargo

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*In CFR (Ref. 27) minimum required rate of discharge is represented by Q, whereas in the present study Q = rate of heat absorption.

Equation [1] is based upon estimation of the rate of vapor generation due to exposure of a cargo tank to fire. If this vapor were not discharged, the container would be overpressured. Additional causes of excessive overpressure in a cargo tank have been specified in the Preface of the present study. Before considering problems associated with determining the required capacity of pressure relieving systems, four specific causes of overpressure will be discussed: overpressure caused by fire; by chemical reaction of cargo; by insulation loss; and by improper operation.

A. Overpressure Caused by Fire

Fire exposure represents the most critical factor when considering the requirements for relief of overpressure in marine cargo containers. The present study is concerned primarily with this aspect of the pressure relief problem. Design and evaluation of protection against fire requires a complete knowledge of marine cargo transport systems. Fire safety requirements influence design features. The designer of pressure relieving systems should consider the uncertain influences of

1) various cargo transport systems,
2) the variety and complexity of cargos, and,
3) the potentially unique and unplanned conditions caused by accident.

Appendix I contains some typical information descriptive of barge and ship transportation, and illustrates various types of

vessels on which relief valves are required. From the standpoint of fire exposure of the cargo, design features such as arrangement of cargo tanks with respect to surrounding walls, bulkhead locations, weather shields and other fire-limiting structural configurations are extremely important and should be considered in designing pressure relieving systems. This matter will be discussed in more detail in Part Four of this study. Most codes and regulations specify protection to meet the most severe hazards which may be encountered. Consequently, the relief requirement for cargo tanks are usually determined on the basis of the rate of heat absorption from a fire.

The requirement for relief of overpressure due to fire exposure is usually much greater than the relief required by overfilling, improper operation, and failure of control equipment. Although, from the standpoint of emergency relief, fire exposure is the major concern, the simultaneous occurrence of two or more unfavorable events should be considered by the designer. When such a probability exists, sound engineering judgment is required to arrive at a safe and economical relief rate.

Special storage systems exist in which the requirement for relief of overpressure due to causes other than fire exposure is the major item. As one example, consider cargo tanks covered with substantial, fire-resistant insulation. In such systems an analysis may indicate that operational relief requirements outweigh that for fire exposure.

Another item which may cause overpressure and requires consideration is the possible occurrence of an uncontrolled chemical reaction within the cargo, thus increasing the rate of vaporization. This condition

would require a relief rate larger than that for the case of fire exposure only, and generally is not controlled by relief valve sizing. Such contingencies should require use of inhibitors, inert atmospheres and/or sufficient insulation to prevent overheating to the critical reaction temperature.

In order to get a reasonably complete picture of pressure relief requirements it is advantageous to identify different potential causes of overpressure in marine cargo tanks.

B. Overpressure Caused by Chemical Reaction of Cargo

Cargo vessels carrying organic materials which have the capacity of undergoing chemical reactions such as polymerization are subject to a peculiar hazard. A pressure rise may occur due to the internal reaction, which may not necessarily be associated with exposure to fire, but which will result in an emergency relief requirement. The problem of designing a safety relief device for such a system is difficult due to the unsteady state nature of the evaporation process. Temperature, composition, rate of polymerization, vapor pressure, and rate of evaporation are all changing with time.

An investigation of several ethylene oxide tank car derailments, involving explosions, resulted in the conclusion that the initial fires heated the tank cars sufficiently to initiate polymerization. Even after the fires were extinguished and the cars

cooled, the contents remained hot due to the tank insulation. Polymerization slowly builds up heat and pressure. Ethylene oxide, once heated and then cooled, may continue to polymerize, overpressure the container, and rupture. The Dunreith, Indiana, derailment and fire case history is an example of the interaction between the two sources of overpressure, i. e., chemical reaction and fire exposure.

Behavior of a monomer cargo during rapid polymerization and pressure relief considerations associated with polymerization process are discussed in Appendix 9.

C. Overpressure Caused by Insulation Loss

The Coast Guard regulations are concerned with the efficacy of insulation in two ways: first, how the insulation affects the design pressure of the tank when insulation is used to protect ambient temperature cargos or refrigerated cargos, and second, how the insulation affects the rate of vapor generation during fire exposure. "Where cargo tanks, in which the cargo is transported at or near ambient temperature, are lagged with an insulation material of a thickness to provide a thermal conductance of not more than 0.075 Btu per square foot per degree Fahrenheit differential in temperature per hour, the tanks shall be designed for a pressure of not less than the vapor pressure of the gas at 105°F. The insulation material shall conform to the requirements 46 CFR 38.05-20.[22] The design shall also be based on the minimum internal

pressure (maximum vacuum) plus the maximum external static head to which the tank may be subjected."[21] Where used, tank insulation shall satisfy the specified requirements for combustibility, installation, and arrangements.[22] This section of the regulations is concerned with protecting the cargo system against the hazards caused by loss of insulation effectiveness due to ageing, fire, water damage, mechanical damage, and deterioration of a vapor barrier. Such insulation effectiveness loss might be important with cryogenic cargos even without exposure to fire, due to increased heat input causing excessive vapor generation.

The value of insulation during a fire and the problems related to its use will be discussed in Part Four of this report, (Insulation, its value during a fire). The problem of cargo tank insulation has many interrelated features.[7] The insulation system should be evaluated under both normal operational and fire conditions. This evaluation would assist in the identification of the conditions which are controlling in establishing relief requirements.

Some tanks designed for normal liquid cargos at ambient vapor pressure have insulation installed and supplementary refrigerating equipment provided aboard the vessel in order to accommodate transfer from or to cryogenic storage systems ashore. In normal

operation with normal liquid cargos, the insulation is of little concern. Consequently, the insulation requirements for such tanks in normal operations should be studied under fire conditions only.

In the case of tanks designed for normal operation at less than the vapor pressure of the cargo at ambient temperature, i. e., refrigerated or semi-refrigerated tanks, the containment of the cargo is dependent upon the integrity of the insulation. For example, if the effectiveness or quantity of insulation is allowed to deteriorate, the recompression capacity on the vessel will eventually become overloaded, the cargo pressure will rise, and cargo will be periodically released by the relief valve to the surroundings. This violates the premise that under normal conditions cargo will not be released to the surroundings.

It is required that the insulation should not, under normal operating conditions, lose its effectiveness and should, in case of fire, before it deteriorates, allow adequate time for the efforts to control the fire. Considering the safety of refrigerated cargos, questions might arise in regard to specifying the insulation materials which would be effective at low temperatures and yet can withstand high temperatures without failure. This two-fold requirement is not always realized in practice without excessive financial burden. An insulation system, for instance, may be considered safe for protection against fire; however, if the insulation does not perform in the normal operation as intended, and cargo is released to the atmosphere, this will soon become an economic burden on the

owner, and the insulation must be replaced.

An additional consideration in the safety related and normal operational requirement for insulation performance is the need for periodic inspection. Presently, the only requirement for periodic inspection is that, if deemed necessary by the marine inspector, sufficient insulation shall be removed from insulated tanks at least once in each eight calendar years to permit spot external examination of the tanks and insulation.[25] No guidelines presently exist for the evaluation of insulation in service. The insulation problem will be discussed further in Part Four.

D. Overpressure Caused by Improper Operation

Equipment failure and human error, alone or in combination, can contribute to overpressure in a liquid cargo tank. The simplest case is overpressure caused by overfilling of the cargo tank.

Coast Guard regulations[23] specify that refrigerated and semi-refrigerated tanks shall be filled so an outage of at least 2 per cent of the volume of the tank exists when the tank contents are at a temperature yielding a vapor pressure of the cargo corresponding to the safety relief valve setting. In other words, the regulations are intended to ensure that cargo vapor, not liquid, is released from the relief valve, and that the tank at no time is 100 per cent liquid filled.

With non-refrigerated tanks and cargos, the regulation specifies the maximum permissible filling densities in terms of cargo, specific gravity values and the tank volumes, for both unlagged and lagged tanks. The "filling density" is defined as the per cent ratio of the weight of the liquefied gas in the tank to the weight of water the tank will hold at 60°F. In the case of non-refrigerated cargos, the relief valve capacity should be specified as to vapor or liquid relief. Considering for the moment a cargo having a specific gravity of 0.63, it may properly be filled, so that the tank will have an outage of 4.8 per cent. If the relief valve setting is high, the tank may become completely liquid filled through warming of the tank contents. Pentane has a specific gravity of about 0.63 at 60°F; it has a cubical expansion coefficient of about 0.0009 cc/cc per degree F. Thus the 4.8 per cent outage of 60°F is reduced to 0.0 per cent outage when the tank contents are warmed to 113°F, at which temperature the vapor pressure of pentane is 20 psia. Pentane would start to be vented at the relatively low temperature of 113°F; at that temperature the outage would become zero and the pressure would rise rapidly upon further increase in cargo temperature. The venting of flammable liquids could increase the fire potential by ignition. The outage design consideration for non-refrigerated tanks should give

specific considerations to such factors as: vapor pressure, volumetric expansion coefficient, flammability limits, and the acceptability of, or prohibition of, venting liquid instead of vapor to relieve pressure.

Overpressure could also be created in cases where high capacity pumps are used in transferring the cargo from one tank to another or where the filling stream is from equipment operating at a much higher pressure through a flow control valve.

Malfunction of control valves might cause serious overpressure; such controls should be dependable in order to achieve successful operation. Pressure relief for pipe lines and accessory equipment should not be neglected nor absurdly overdone. Prevention of overpressure during transfilling operations requires good system design and careful operation if justifiable safety protection is to result.

The opposite of overpressure, namely, vacuum collapse, is another real operating hazard which occurs when the pumps emptying a tank are capable of a greater rate of displacement than the rate at which air or inerting gases can enter the tank. The system should be analyzed in terms of the complete cycle of operations to insure that the operating requirements do not produce transient conditions which exceed expected or planned design criteria for pressures and vacuums. Other possible causes of overpressure or underpressure can

generally be determined by a careful study of the cargo transport system. As a result of the analysis, the relief capacity required for such systems can be predicted for practically all operational difficulties.

PART FOUR: ESTIMATION OF NEEDED RELIEF CAPACITY IN PRESSURE RELIEVING SYSTEM VENTING VAPOR

In order to estimate or design an adequate pressure relieving system, two separate but interrelated factors must be considered: (1) estimating the volume of vapor or gas which may be anticipated, and (2) sizing the valve and related discharge vents.

A. Previously Developed Formulae

Previous studies which have evolved or developed criteria for relief capacity have had the objective of specifying what capacity the system must accommodate to prevent excessive pressures. Fundamental approaches have considered data based on heat transfer into the vessel from a fire, translated into the capacity of the system.

Recognition of the fire hazard as the most critical threat to the cargo and the personnel safety requires the utilization of adequate preventive and also protective means against fire. The importance of fire preventive design features, and the standardized operational procedures (both routine and emergency) cannot be overemphasized. However, it is recognized that fire hazards may exist, even with non-flammable cargos. Consequently, a complete understanding of the fire characteristics is needed in order to determine the pressure relieving capacity of the safety system. Estimation of this capacity, in turn, necessitates prediction of the amount of heat absorbed by

a cargo tank which is exposed to an open fire. The heat absorbed is affected by size and design features of the cargo system and by environmental factors, particularly insulation.

A comprehensive review of the formulae that have been used over the years for calculation of pressure relief capacity is given in Appendix 2. Some of these formulae relate the area of the tank to the rate of heat transferred into the tank or the equivalent amount of vapor generated. Several of these discount the tank area by means of an exponent which may vary from 2/3 to unity. It is interesting that one formula uses two different exponents depending on the tank size.[37] Other methods relate valve size to a variety of situations including maximum pressure allowed. For ease of comparison, these historically used formulae are listed in Appendix 2, each formula being presented separately in some detail. To facilitate the comparison, where possible, an "Equivalent Equation" is determined for each formula which results from converting the original equation into a form which sets a rate of heat input, in Btu/hr, equal to a constant times the container area raised to a power. The area used in the equivalent equation is that considered significant in the original equation and does not necessarily equal the total tank area.

Critical consideration of the information given in Appendix 2 indicates that further experimental data and improved theoretical studies are needed for a more accurate estimation of the heat absorbed by a cargo tank exposed to fire. It is recognized that there is no substitute for well organized and carefully performed fire tests. However, the theoretically-based methods for predicting heat absorption from

fires may be improved by reexamination of the available experimental data.

As an example, although it is generally recognized that the heat absorbed is in some way proportional to the surface area of the tank, there is no agreement among different formulae as to which surface area is to be used; total tank area, or wetted surface area. ("wetted area" is that area of the tank which is in contact with liquid cargo). And, in addition, when the wetted area is used it is more proper to relate the actual heat flux values (Btu per unit area per unit time) to the part of the wetted area which is actually exposed to fire rather than the total wetted area. A number of formulae make use of constants which are determined by dividing the experimentally measured total heat input either by total tank area or by the total wetted area. Since, in general, neither the tank nor the wetted area is completely exposed to fire these computed values do not represent the real heat fluxes; they are average values which vary considerably with the tank size and the flame-tank configuration.

It would appear that this method of correlation of the experimental data may result in equations with a rather limited range of applicability. Considering the special design features of the marine cargo systems, it would appear to be inadequate to express the portion of the tank surface exposed to the fire by using a factor which is equal to the total container area raised to a power.

In a marine cargo transport system the tank surface area exposed to fire may be limited by tank supports, transverse and longitudinal

bulkheads and other structures. As a result, significant protection against fire is provided along the length of the cargo tank by such structures which isolate the exposure from a possible fire. Consequently, a factor based on the total tank area for representing the area exposed to fire is unrealistic. Similarly, the use of an average heat flux obtained from open fire tests, without any surrounding walls, is inadequate for marine cargo tanks. These problems will be discussed further in Part Four, Section B-1b, of this report.

Considering the main objectives of the present study, it is appropriate to predict the heat flow into the cargo by using the fundamental heat transfer equation rather than an empirical equation obtained from limited experimental data. This prediction would permit one to take into account, in an orderly manner, the following typical items related to the heat transfer problem:

1) The local heat flux from a fire to the cargo tank--effects of fuel type, fire characteristics and environment on the heat flux.
2) Portion of the cargo tank surface exposed to the fire--influence of special design features used to limit the exposed area.
3) Effect of the nonwetted tank area on the safety hazard. ("nonwetted" is the area of the tank in the vapor space)

4) Evaluation of the possibility of liquid entrainment and/or two-phase flow through the relief valve and determination if such flow adversely affects the capacity of the valve; and consideration of the possibility that the relief valve will be exposed to liquid rather than vapor during its relieving operation.

Each of these items involves a number of variables. These variables and their influence on the preventative measures against fire hazard will be discussed in the following sections.

B. Recommended New Formula

The most critical cause of overpressure in a liquid cargo tank is excessive heat flow from a possible fire. Therefore, a realistic prediction of the amount of heat absorbed by the cargo exposed to fire is very important. In the case of thermally unstable cargos, total heat absorbed by liquid should also include the heat of reaction caused by the chemical process within the cargo unless the cargo is effectively inhibited against such reaction.

1. Rate of Heat Transfer From Fire To The Cargo Container

Estimation of the rate and amount of heat transfer to a liquid cargo container during fire exposure requires knowledge of both

the heat flux from the fire and the portion of the container surface exposed to the fire. The suitable sizing of a pressure relieving system depends a great deal upon correct estimation of these two quantities.

It is recognized that the arrangement of adjacent wall compartmentation, shrouds, protective covers, and insulation significantly affects the area of a cargo container exposed to fire as well as the heat flux to the container from that fire. It would appear that very significant control over the container area having a probability of becoming involved in a fire may be exercised through strategic location of bulkheads and protective covering. Further, such restrictive surroundings could materially lower the flame temperature through reducing its thickness and access of air to the fuel. Such flame temperature reductions would substantially lower the heat flux to the containers, especially as a large fraction of the heat flux will be induced by means of radiation.

It is evident that maximum attention should be given to the design features which would keep a cargo container from being fully involved in a possible fire. Accordingly, credit should be allowed for these safety-contributing design features in heat transfer calculations.

The fundamental equation used in calculating the amount of heat absorbed by a liquid cargo container exposed to fire can be expressed as:

$$Q = qFEA \qquad [2]$$

where

Q = rate of heat absorption by the liquid cargo, Btu/hr

q = heat flux from fire (per unit wetted area completely exposed to fire), Btu/(hr)(ft^2)

F = environmental factor, dimensionless, accounts for the combined effects of the exterior environment conditions.

E = fire exposure factor, dimensionless; the fraction of total wetted surface area which is exposed to fire

A = total wetted surface area of the cargo container, ft^2

Equation [2] allows credits or corrections for the effects of different situations through suitable selections of the exposure factor E and the environmental factor F. The product EA represents the fraction of the total wetted area A which is in actual contact with the fire. The fire exposure factor E, therefore, accounts for items which keep the tank from being fully involved in the fire, such as the bulkheads placed along the length of the cargo container in such a way as to isolate sections of that container.

The factor F includes the combined effect of different environmental conditions on the amount of heat absorbed; such as the effect of insulation. The heat flux q varies with the kind of fuel burning and depends on the heat transfer characteristics, such as the geometry of the fuel source as compared to container, the thickness of the flame opposite the container wall, etc., and also on the configuration of the reradiating surfaces. Parameters involved in Equation [2] will be studied in more detail below.

a. Structural configuration

It is recognized that maximum effort should be applied to keeping the liquid cargo container from being fully involved in the fire. Hence, credit should be given for special structural configurations which will limit the area of the container exposed through confinement of the fire. This credit is accounted for, as it has been seen, through the use of the fire exposure factor E.

The previously used formulae as summarized in Appendix 2 often use an exponent for the container surface area to account for the container expected to be engulfed in the fire as the container size increases. For increasingly larger tank sizes, the probability of full envelopment by fire is acknowledged to be less than for smaller tanks. The fraction of the total wetted surface which is exposed to fire is described in Eq. [2] by the exposure factor, E. The formulae of Appendix 2

have in many cases estimated the fraction of the vessel area exposed by relating an exponential function of the area to the total heat flux. Such a relationship could have been described in terms of the fire exposure factor, E, of Eq. [2] as:

$$E = \frac{A_e}{A} = \left(\frac{a}{A}\right)^m \quad \text{with} \quad a = 1 \text{ ft}^2 \qquad [3]$$

where, in accordance with definition of the fire exposure factor, A_e and A are the portion of the wetted surface area which is exposed to fire and the total wetted surface area, respectively. The dimensional constant $a = 1 \text{ ft}^2$, is used in Eq. [3] in order to make E dimensionless; a and A are given in the same system of units both in ft^2. The exponent m, in Eq. [3] varies from 0 to 1 depending on the tank size.

Considering the characteristics of marine liquid cargo containers, Eq. [3] has very limited use, since this equation does not include the effects of supporting structure or other specially introduced features which may serve to confine the fire. Therefore, for such cargo containers, the actual fractional tank area exposed to fire is almost always less than that determined by using a general relation in the form of Eq. [3]. It has been seen in Part Four, Section A, that, even with the simplest tank configurations, it is not possible

to correlate the results of fire tests by assigning a single constant value to exponent m in Eq. [3]. Therefore, for the cases where measures are taken to limit a possible fire, it is more realistic to compute the exposure factor by considering the configuration of the cargo container with respect to the probable surrounding fire. By making some rather plausible simplifying assumptions, it is possible to determine the exposure factor in terms of geometrical configuration of the cargo container with respect to its surrounding boundaries. The computed value of E is then substituted directly in Eq. [2].

The following example illustrates the differences between the exposure factor values E_1 and E_2 determined by using the direct method suggested above and the conventional method which makes use of Eq. [3].

In a cargo barge, the tank surface area exposed to fire is assumed to be limited due to the effect of the transverse frames which serve to confine a spill to a local area, and therefore confine the fuel for a potential fire, and presumably the fire itself.[10] It is also assumed that the total wetted area is almost equal to the total container surface area. It is reasonable to assume that any one of the transverse bulkheads might be breached due to collision and thus be ineffective. With a transverse frame spacing "S", the effective length of fire in case of a

breached bulkhead becomes "2S". For a fire involving a tank of cylindrical configuration the surface area $2\pi DS$ is assumed to be subjected to the full heat flux from the fire, D being the tank diameter. It should be noted that this assumption reduces the exposure factor E to a parameter which depends purely on the geometry. In the majority of cases, the supposition is plausible, thus simplifying the problem considerably. However, if the existing experience, conditions and requirements do not justify this assumption, it is more convenient to apply a correction to the environmental factor F rather than using a more complicated procedure to predict E. Such considerations lead to the need for applying two factors E and F, rather than only one. As a general statement it can be said that for a given design, E is fixed, whereas q and F, in Equation [2], depend on varying environmental and operating conditions.

Considering again the example, the fractional area exposed to fire becomes

$$E_1 A = \left[\frac{2S}{L}\right] A \qquad [4]$$

where L = length of tank

and the fire exposure factor

$$E_1 = \frac{2S}{L} \qquad [5]$$

On the other hand, referring to present U. S. Coast Guard regulations,[27] the fire exposed area is given as

$$E_2 = \left(\frac{a}{A}\right)^{0.18}, \text{ with } a = 1 \text{ ft}^2 \qquad [6]$$

and

$$E_2 A = \left(\frac{a}{A}\right)^{0.18} A = A^{0.82} \text{ ft}^2 \qquad [7]$$

It should be noted that in the Coast Guard regulations, although F is called the fire exposure factor, it is equivalent to the environmental factor F defined in Eq. [2]. It is seen from Eq. [7] that the exposure Factor E_2 is already included in $A^{0.82}$. For a simple comparison of results of the two methods used, it is convenient to rewrite Equations [5] and [6] in the following forms:

$$\overline{E}_1 = E_1\left(\frac{A}{a}\right)^{0.18} = \frac{2S}{L} A^{0.18} \qquad [8]$$

$$\overline{E}_2 = E_2\left(\frac{A}{a}\right)^{0.18} = 1 \quad \text{(dimensionless)} \qquad [9]$$

Obviously $\overline{E}_1/\overline{E}_2 = E_1/E_2$

Values of $\overline{E}_1$ and $\overline{E}_2$ are plotted in Figure 1 versus the total wetted area A. This figure covers approximately the following properties:

L = tank length from 100 ft. to 300 ft.

E = tank diameter from 10 ft. to 25 ft.

S = frame spacing from 5 ft. to 9 ft.

For example, for a 300 foot long tank of 25 foot diameter, A is about 23,500 sq. ft. If the frame spacing is 9 feet, then 2S/L - 0.06. Then from Figure 1, one obtains

$$\overline{E}_1 = 0.36 \quad , \quad \overline{E}_2 = 1$$

Therefore, the effective surface area exposed to fire obtained from the formula of the Coast Guard regulations would be approximately three times the effective area obtained if only frame spacing is considered to limit fire exposure. A general statement of results would show that the fractional tank area exposed to fire under the

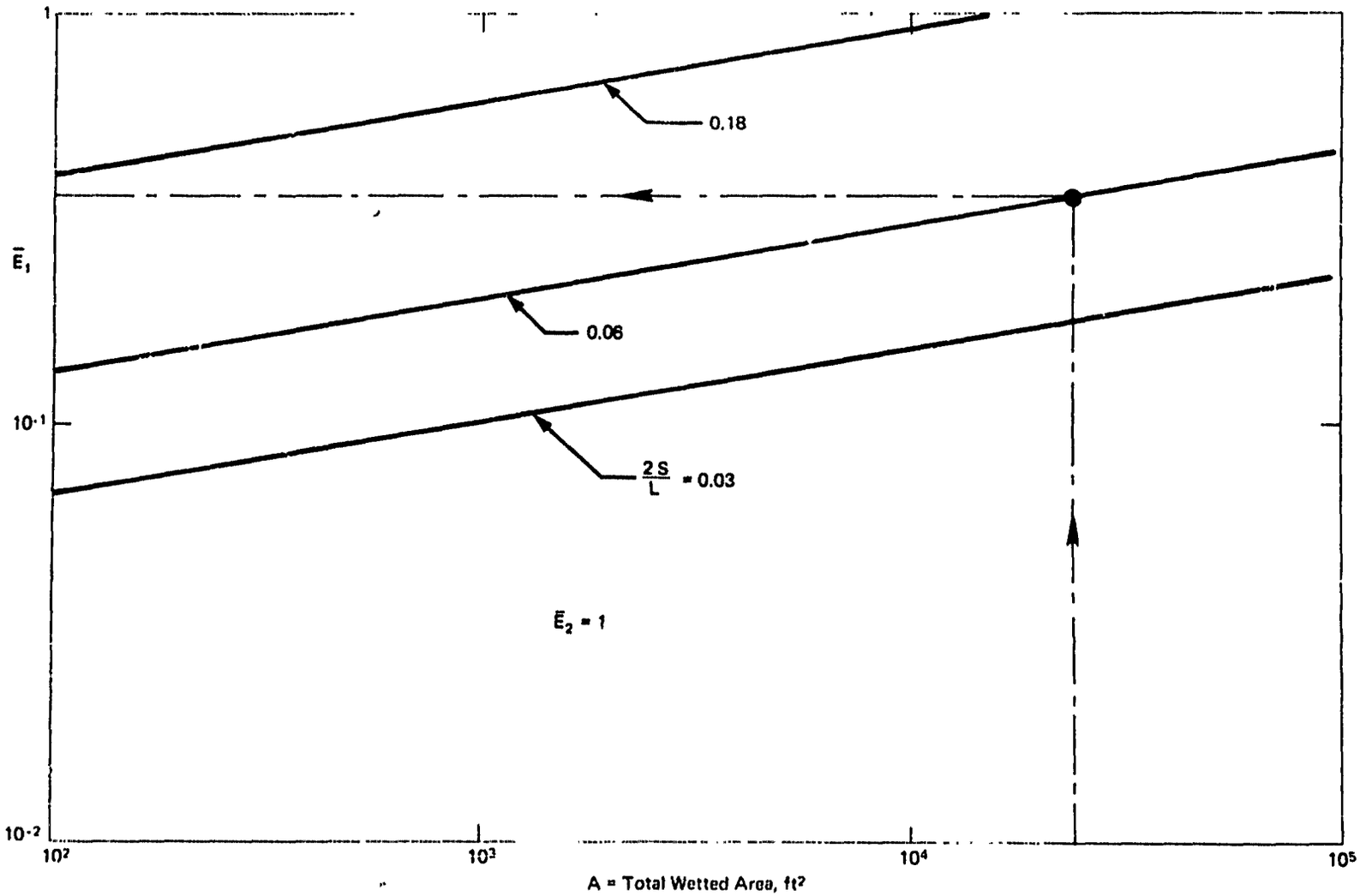


FIGURE 1

EFFECT OF THE FRAME SPACING ON THE FIRE EXPOSURE FACTOR.

frame spacing limitation is always less, for the same tank, than the area predicted by Equation [7], if only practical values of diameters are considered.

In the calculation of heat transfer from fire to a cargo tank, special consideration should be given to the design features used to limit the portion of the tank surface directly exposed to the fire, such as: bulkheads, weather shields, etc. This precaution would serve to reduce substantially the effective safety device sizing requirement. The exposed surface area can be determined in terms of the fire exposure factor E which depends upon the geometrical configuration of the cargo tank with respect to its surrounding boundaries. Therefore E can be determined by considering the system geometry only. Additional effects of the special design features on the flame characteristics would probably cause further reduction in the safety device sizing requirement. These effects can be incorporated into either the environmental factor F or the heat flux q in equation [2].

Consideration should be given, as much as possible, to provide drainage away from the tank so that pools of fuel cannot accumulate. Suitable baffle walls which separate spills from the tank may be of great value by delaying, in case of a fire, the direct contact between the tank and the flame. The importance of carefully arranged design features in improving fire safety cannot be overemphasized.

b. Heat flux from fire to the cargo container

One major problem in calculation of the total heat absorbe

HEAT ABSORPTION RATES IN FIRE TESTS

Fuel	Source	Wetted Area (A) Ft ^{2}	Q/A in Btu per hr per ft ^{2}	Q
Naphtha	Std. Oil of California	26	16,000	416,000
	Std. Oil of California	105	32,000	3,370,000
Gasoline	Underwriters Lab. (flat plate)	24	32,500	780,000
Gasoline	Rubber Reserve Test No. 17	400	23,200	9,280,000
Gasoline	Rubber Reserve Test No. 17	400	21,000	8,400,000
Gasoline	Rubber Reserve Test No. 17	9	30,400	274,000
Kerosene	API Project Test No. 1	6.13	15,700	95,800
Kerosene	API Project Test No. 2	6.13	16,800	102,500
Butane	48-ft Butane Sphere	4363	5,400	23,560,000
Wood-Kerosene	Fetterly	57.8	23,300	1,350,000
Gasoline	Aluminum Co. of America	15	(20,100 (29,500	(302,000 (442,000
"Chemical Wastes"	Lauderback	162	33,400	5,410,000
"Chemical Wastes"	Lauderback	100	32,100	3,210,000
Hydrocarbons (May have been Propane)	Duggan, Gilmour and Fisher Test #1	242	25,900	6,270,000**
"	" Test #2	242	17,300	4,186,000**
"	" Test #3	242	18,700	4,522,000**
"	" Test #4	176	12,800	2,225,000
Kerosene	Union Carbide (FRL-62) Test A	1,480	28,800	42,600,000
JP-4	Bader (Sandia) measurements by a heat meter	-	(35,960 (47,540	-

References can be found on pages 100 - 110
**Water flowing over tank

Table 1

SUMMARY OF FIRE EXPOSURE TESTS

Authority:	Underwriters' Laboratory	Duggan Gilmour & Fisher Test #1	Duggan Gilmour & Fisher Test #4	Rubber Reserve Test #17	Rubber Reserve Test #17	Rubber Reserve Test #17	API Project Test #1	API Project Test #2	Standard Oil of California
Type of Exposure	Water Flowing over Plate	Water Flowing Over Tank	Water Heated in Tank	Heating Water in Tank	Generating Steam in Tank	Water Flowing inside 3/4" Std. pipe	Heating Water in Tank	Heating Water in Tank	Heating Water in Tank
Fuel	Gasoline	Propane Gas	Propane Gas	Gasoline	Gasoline	Gasoline	Kerosene	Kerosene	Naphtha
Heat Flux to Wetted Surface Btu/hr/ft^2 $\frac{Q}{A}$	32,500	25,900	12,630	23,200	21,000	30,400	15,700	16,800	32,000
Observed Fire Exposure % Wetted Surface	100	100	75	60 to 70	60 to 70	80 to 90	46	46	100
Temp. Receiving Surface, °F	76	136	120	300	-	-	300 (approx.)	320 (approx.)	70 to 212
Heat Flux to Exposed Wetted Surface Btu/hr/ft^2 (C)	32,500	25,900	16,850	35,700	32,300	35,800	34,200	36,500	32,000
Total Surface, ft^2	24	242	242	568	568	9.0	16.2	16.2	206
Wetted Surface, ft^2	24	242	176	400	400	9.0	6.13	6.13	105
Nominal Vessel Capacity, Bbl.	-	72	72	119	119	-	0.88	0.88	33

References can be found on pages 100 - 110

Table II

by a liquid cargo exposed to fire is the assignment of a correct value to the heat flux q in Equation [2]. Predictions of q have usually been made either by use of total heat transfer rates measured during fire tests, or by the use of measured or calculated average flame temperatures to calculate the heat transfer rates. However, in the light of present knowledge, it is recognized that the conventional methods used in the past in analysis of radiant heat transfer from flames are not adequate for understanding the significant details of the heat transfer process. Simultaneous occurrence of heat release and heat transfer in a fire makes it difficult to calculate the heat flux from flames by using an average flame temperature. Improvement in the heat transfer calculations requires consideration of the local varients and of the parameters which affect the heat transfer process, such as temperature distribution in the flame.

Experimental data on heat transfer from fire to liquid cargo tanks have been summarized in Table I, page 37. It is noted that the Q/A value in this table is the average heat flux based on the entire wetted surface area although, in general, this area is only partially exposed to the fire. Therefore, the Q/A value in Table I, is not equal to the heat flux q since, from Equation [2] one obtains

$$\frac{Q}{A} = qFE \qquad [10]$$

assuming that F = 1 for bare tanks in open fire tests, then

$$q = \frac{Q}{EA} \qquad [11]$$

Since E, in general, is less than 1.0, the heat flux q for experiments should be greater than Q/A values reported in Table I both being equal for small tanks where E = 1. Consequently, smaller Q/A values in this table do not necessarily mean small values of the heat flux q.

Table II, page 38 gives a more meaningful presentation of the experimental data. It is rather significant to observe that the heat flux q to the exposed wetted surface does not vary too much for most of the experiments listed in Table II, whereas the average flux based on the total wetted surface area varies rather substantially. The reason for this variation in the average heat flux Q/A can be understood by referring to Eq. [1] where it is seen that the average heat flux is dependent on the exposure and environmental factors. Evidently, presentation of the experimental heat flux data on the basis of the wetted surface area completely exposed to fire is much more informative. However, for the great majority of experimental data, this is not possible since some relevant information required for this purpose was not reported in these experiments and because the experiments were designed to maximize the heat input and not test the probable flame envelopment. One cannot help but emphasize the need for more completely documented detailed experiments; the data presently available, although they are extremely important, offer the design engineer only a modest help.

Table I, shows that the experimental average heat flux values varied, with the exception of one case, from approximately 13,000 to 47,000 But/(hr)(ft^2). For the latter value, E is found to be a unity.[6] Therefore, the highest experimental value reported for the heat flux

is about 47,000 Btu/(hr)(ft^2). It should be noted that local heat flux rates from 83,000 to 90,000 Btu/(hr)(ft^2) were reported in references 4 and 29, for air-methane flames impinging on flat surfaces and for free-burning liquid hydrocarbon fires, respectively.

Upon analysis, it may be found that (see Part VI-A) a heat flux of q = 34,500 Btu/(hr)(ft^2) is inherent in Eq. [1] which is used presently in the U. S. Coast Guard regulations. In this formula, however, heat flux is given per unit area of the total cargo tank surface, adding a margin of safety if the local flux is no more than 34,500.

It is recognized that heat flux q varies with the fuel and depends upon many variables; such as, geometry and the radiation characteristics of the flame, configuration of reradiating surfaces, and gas-air ratios (combustion efficiency). It is difficult and expensive to carry out large-scale fire tests where the effects of these variables on the heat flux can be investigated in a combined way. As important is the fact that there exists a lack of basic information which is required in applying the fire test results to cases where conditions are not identical to those of the tests. Therefore, until this information and further representative fire test results are made available, the problem of predicting the heat flux can be approached rationally only through the adjustment of the experimental data to fit, as closely as possible, the design conditions and by applying the analytical heat transfer calculation methods and engineering judgment based upon actual experiences. Not one of the conventional radiation calculation methods provides by itself more than a rough estimate of

the radiant heat transfer rates from flames. The several techniques for calculating the radiant heat transfer from fires consist of the use of an average flame temperature and some modified form of the Stefan-Boltzmann Law. This method, of course, over-simplifies the problem by eliminating the need for the knowledge of the flame configuration and the temperature distribution within the flame. Without this information, however, it is very difficult to predict the average flame temperature and the form of the modified heat transfer equation. Even small inaccuracies in the predicted average flame temperature may result in large differences between the actual radiant flux and the flux computed by using the Stefan-Boltzmann equation. This does not imply, however, that theoretical calculations are useless for the present problem. On the contrary, they help the design engineer make the best use of the available fire tests data for his specific design problem by providing him with the general guidelines toward final solution.

Theoretical heat flux calculations in Appendix 5 are given in the spirit of the foregoing discussion, illustrating the steps involved in the performance of heat transfer calculations by conventional procedures. In order to perform a heat transfer analysis satisfactorily, it would be necessary to have detailed information on the thermal radiation from flame, as well as rather involved computer solutions.

For a given set of conditions, it is convenient to predict the heat flux q with reference to a properly defined standard heat flux such as q_o. By definition, q_o will be the heat flux for a reference fuel under well-defined reference conditions. These conditions should include, as much as possible, all the parameters relevant to the heat transfer from flames to the cargo tank. The reference conditions and the reference flux q_o should be chosen by critically reviewing all the experimental fire tests data available. Once q_o has been determined, the actual heat flux q, under conditions different from the reference, will be predicted by applying corrections to q_o. In this correction procedure the guidelines provided by the theoretical calculations would be indispensable.

To summarize: It seems to be very convenient to determine the heat flux q as follows:

(i) Define a reference heat flux q_o by using the available experimental fire tests data. As more accurate data becomes available, q_o can be redefined.

(ii) For the conditions of a given problem, apply a number of corrections to q_o and obtain the heat flux q.

As a first and good approximation q_c = 34,500 Btu/(hr)(ft^2) can be selected as the reference heat flux. Referring to Table II, this value seems to represent approximately the heat flux q for the majority of experiments performed with different fuels, under different conditions. Therefore,

it would be convenient to use either 34,500 Btu/(hr)(ft^2) or a modified value close to it as the reference heat flux q_o. However, the reported heat fluxes for some fire tests are substantially different from 34,500 Btu/(hr)(ft^2). For this reason, this reference flux would not serve its full purpose unless the overall fuel characteristics and the test conditions associated with it have been clearly specified.

Prediction of the heat flux q, starting with the reference flux q_o, requires a complete understanding of the energy transfer mechanism and the effects of different parameters on the heat transfer rate from fire to the tank surface. The following discussion is concerned with this aspect of the problem:

c. Convection versus radiation

Appendix 5 discusses contributions of convection and radiant heat transfer to the total heat flux from fires. The literature cited does not contain much information on convection heat transfer coefficients inside buoyant diffusion flames. However, it is believed that these coefficients should be higher than those predicted by correlations based on moderate temperature differences and nonreacting systems. The effective convection heat transfer coefficient for a fire should exceed 2 Btu/(hr)(ft^2) °F.[61].

Welker and Sliepcevich[81] have recently reported an experiemental convective heat transfer coefficient of about 5 Btu/(hr)(ft^2) (°F) for JP-4 fires. These data are further discussed in Appendix 5.

Maximum heat fluxes between optically thick flames from single burners and cold (200-300°F) target surfaces are given, for different fuels, in Table III, Appendix 5. It is seen that contribution to the total flux through convection is far from being negligible. For the six fuels listed, the convective portion of the total heat flux varied from 15% for benzene to 58% for a methanol flame. In determining the heat flux, both the radiative and convective heat transfer modes should be considered.

d. Effect of the fuel type on the heat flux from fire

Fuel type has effects on both modes of heat transfer, since it influences the flame temperature distribution and the radiation characteristics of the flame. The radiant contribution, in general, varies more with the type of fuel than does the convective portion as seen in Table III. Major steps of the calculations t predict the radiant heat flux from flames are given in Appendix 5.

Heat transfer rates in Table III, Appendix 5, are given for specific experimental conditions. Therefore, values from this table or from similar tables cannot directly be used for design calculations. This information, however, may be used for predicting approximately the heat from an arbitrary fuel at reference conditions. As an example, assume that the reference heat flux q_o for hexane is chosen, from Table III, as 29,500 Btu/(hr)(ft^2). Of course, unless the reference conditions are identical to those in this table q_o would not exactly equal the value 29,500. Assume, however, that q_o for hexane is already known. In determining the total heat flux for JP-4, for instance, it is necessary to multiply q_o for hexane by

30,700/29,500 in order to obtain the standard heat flux for JP-4 under reference conditions. This correction approximately accounts for the effect of fuel type on the heat flux. If the existing conditions are different from reference conditions, additional corrections would be required. Recognizing the limitation of this type of correction procedure, in the face of scarcity of experimental data, it nevertheless, can be taken as a starting point. Corrections, modifications, and reasoning should be performed with full recognition of the validity of the experimental data.

e. Effect of the burning rates of liquid fuels on the heat flux from fire.

Heat flux from a fire to a cargo tank is related to the burning rate of the fuel i.e., the rate at which the fuel is added to the fire (as through evaporation). The general problem of burning rates of liquid fuels has been discussed in Appendix 6. Generally speaking, an increase in the burning rate will cause an increase in the heat flux. Because of this direct relation, information concerning burning rates may be useful in predicting the heat flux.

For engineering purposes, the maximum or steady state burning rate (steady state evaporation from pool of liquid fuel exposed to fire) is usually more meaningful because it defines an upper limit. The problem of predicting the burning rates of large fires still remains to be solved. For this reason until experimental measurements on larger steady state pool fires can be made, the predictions similar

to that given in Table III, Appendix 5, will have to suffice. The results presented in this table are all based on experimental data, but none of the data can be considered ideal for making predictions.

With reference to the fuel type, Tables III, Appendix 5, and IV, Appendix 6, suggest a somewhat consistent relationship between the variations in the heat flux and the burning rates. This relationship, however, by itself will not aid the heat flux predictions to any marked degree unless contributions of the other parameters have also been considered.

2. Additional Considerations

a. Effect of the geometrical configuration on the heat flux

Position of the cargo tank with respect to surrounding surfaces should have noticeable influence on the heat flux q by affecting the flame characteristics and the heat transfer process.

Configuration with respect to the surroundings influences the heat flux q by affecting the following items:

(i) Accessibility of air and the stoichiometric balance

(ii) Reradiation from surrounding surfaces

There exist no large scale fire test data which can be used for predicting variations in the heat flux caused by the changes in the two items above. Change in the stoichiometric balance should significantly affect heat transfer characteristics of the flame. Temperature distribution in the flame and the relative roles of convection, and radiation

would be influenced by the degree of accessibility of air. Surrounding surfaces tend to increase the heat flux q by reradiating the radiant energy coming from the flame back toward the cargo tank unless the flame is optically thick.

It is evident that the overall effect of the geometrical configuration on the heat flux q is to be determined by the combined effects of items (i) and (ii). For instance, if a cargo tank is completely surrounded by other surfaces, the reradiation contribution to q would be maximum. However, because of the complete confinement, a fuel-rich mixture with soot formation and incomplete combustion may lead to lower flame temperature, thus reducing the direct heat transfer to the cargo tank. The net change in the heat flux q, therefore, can be either an increase or a decrease, depending on the interplay of the two effects considered.

It needs no argument that further research work, theoretical and experimental, is needed to understand the effect of the geometrical configuration on the heat transfer rates from flames to a cargo tank. However, since there is no standard cargo configuration, a correct answer to this problem will depend largely on engineering judgment, even when better information has become available.

Referring back to Eq. [2], the environmental factor F in this equation is concerned with the degree of limitation of the heat flow to the tank surface. This limitation can be accomplished by various methods, such as insulation and radiation shields. For bare vessels with no limitation of the heat input from flames, the value assigned

to F is 1.0. Use of any measure to limit the heat absorbed by the liquid cargo makes the value of F less than 1.0. Various methods of limiting heat input from fire may be considered:

b. Insulation, its value during a fire

In case of a fire, insulation on a liquid cargo tank serves a twofold purpose:

(i) It reduces greatly the heat flow to the liquid cargo, thus reducing the amount of vapor generated inside the tank; and,

(ii) It also reduces the temperature rise of the unwetted metal surface of the cargo tank.

The present Coast Guard regulations[27] are concerned with the effect of insulation on the rate of vapor generation during fire exposure. It is stated that the factor F may be taken as 0.5 for pressure vessel type tanks insulated with approved fireproofing material. This credit in the regulations recognizes the important effect of insulation in fire by allowing a reduction in the vapor flow capacity of the safety relief system to half of that for an uninsulated tank. On the other hand, the regulation does not require the use of insulation as a measure of fire safety. It is not a simple matter to introduce a set of rules which would tell the design engineer when and where the use of insulation is warranted or is absolutely necessary. This problem has a number of special features which should be considered rather carefully.

The insulation effectiveness in reducing the heat transfer from fire to a liquid cargo tank has been studied in Appendix 7. This study shows that the insulation, as expected, is very effective in reducing the heat flow to a liquid cargo. The final decision concerning the use of insulation should be made after considering the following:

General evaluation of merit of insulation: Application of insulation to a cargo system which is already in service would improve the safety considerably. However, if the vapor flow capacity of the safety relief system has been computed by giving full credit to the effect of insulation, then it clearly is important from the effectiveness of the relief system that the insulation maintain quality during normal use and during fire exposures. As an extreme case, for instance, if insulation deteriorates rapidly during a fire, it would leave the cargo tanks with a safety relief system of underdesigned capacity. Such a system, of course, would not be as safe as a system with no insulation but equipped with a full capacity vapor relief safety device.

Sample calculations in Appendix 7 show that the temperature of the exposed insulation surface approaches the flame temperature, and, that the better the thermal insulation, the closer the approach becomes. Unfortunately, maximum permissible temperatures for most of the insulation materials are lower than that which would be attained due to fire exposure. Surface temperatures higher than the safe maximum value could result in deterioration of the insulation

material. It is evident that predictions of the surface temperatures and stability characteristics of the insulation at these temperature levels are of utmost importance. Otherwise, design of a pressure relief system, with the assumption that the insulation remains effective at all times during fire exposure, could be dangerous, since failure of the insulation material could cause excessive vapor generation with the result that the safety relief system would be too small to relieve the vapor generated.

Need for insulation in vulnerable areas: Insulation, or an equivalent protective measure, is especially desirable for fire-safety in especially vulnerable parts of the system.

Discussion presented in Appendix 7 indicates that exposure of the unwetted surface of a liquid cargo tank to fire could cause a metal temperature high enough to reduce the strength below the safe limit, thus leading to the metal failure by bulging. The time needed to heat the unwetted surface of a cargo tank to a certain temperature, and also the time it takes for rupture after attaining that temperature, are given in Figures 12 and 13 of Appendix 7. Predictions from these figures show that, under fire conditions which are not rare, the unwetted surface of a liquid cargo tank has a high probability of failure within a few minutes unless it is protected by insulation, water sprays and/or by other means. Therefore, protection of the unwetted surface, by insulation, for instance, may be desirable as protection against a possible fire hazard.

The overheating of the unwetted portion of the container wall is particularly critical if it is subjected to an impinging flame; in this event, wall failure can occur very rapidly. An intense impinging flame may result in local heat flux values so high that the wall will fail even below the liquid level of the cargo. If film boiling occurs, the wall is no longer protected by the high heat transfer coefficients of the nucleate boiling regime. For the metal to be protected during nucleate boiling, the heat flux should be below the maximum value for the nucleate boiling. This matter is considered in Appendix 8. The probability of this type failure depends on many factors, including cargo container configuration, predicted fire thermal characteristics, insulation effectiveness and degree of container filling.

If the chance of failure of the tank below the liquid level is not negligible, then it may be necessary to insulate that portion of the tank as well as the unwetted surface. Although the problem concerning protection by utilizing insulation has a large number of parameters, technically speaking, it is not very difficult to decide whether or not the insulation is required for a given cargo tank system.

It is recognized that insulation should be very effective both in reducing the heat flow to the liquid cargo and also in reducing the probability of metal failure during a possible fire. This protection exists however, only if an insulation maintains its structural integrity for sufficient time to allow the fire fighting personnel to bring in other equipment to control the fire.

Calculations in Appendix 7 show that the temperature of the exposed insulation surface approaches that of the surrounding flame temperature. This surface temperature increase occurs within seconds or a few minutes following exposure to the fire. In addition to the ability to withstand high temperatures, other factors should also be considered in the selection of insulation, such as moisture resistance, cost, resistance to attack by chemicals, ageing, flammability, and settling (of powder).

In order to protect the insulation from deteriorating at high temperatures, heat shields, sheet steel covers and fireproof surface finish or covering might be useful and, therefore, should be considered. The design engineer needs information about the high temperature insulation materials and their stability features under fire fighting conditions. Without this information, he cannot predict how the insulation would function under the actual fire conditions.

It should be recognized that an ineffective insulation may impair the fire safety both by not really improving it and also encouraging, by its presence, the relaxations in the requirements of other safety measures.

A comparison between the heat transfer rate of completely insulated tanks and the heat transfer rate of an uninsulated tank of equal area has been performed in Appendix 7. The ratio of heat transfer rates is denoted by r. For this case r is equal to the environmental factor F due to presence of the insulation. It has been mentioned that the present Coast Guard regulations allow a single value, F = 0.5, for

cargo tanks insulated with approved fireproofing material. In view of the foregoing remarks concerning the insulation effectiveness, one cannot fail to appreciate the caution exercised in the Coast Guard regulations which has been emphasized by the use of the phrase "approved fire-proofing material".

Referring to Table VI of Appendix 7 for 100 percent insulated tanks, the value of environmental factor F varies from 0.023 to 0.176 under specified conditions. Effects of the flame temperature and the mean thermal conductivity of insulation on factor F are seen in Tables V, VII and Figures 9, 10 and 11 of Appendix 7. Values of F obtained for 90 to 100 percent insulated tanks are in general agreement with API RP520 recommendations. In this regard F = 0.5 allowed in Coast Guard regulations might be somewhat conservative. However, it should be noted that the regulation does not mention 100 percent insulation coverage. Therefore, as an average value, F = 0.5 is adequate. This value corresponds to about 60 to 70 percent insulation coverage, depending on the flame temperature and the thermal conductivity. If the insulation cover is more than, say 70 percent, factor F can be determined by using the method used in Appendix 7. This F value, of course, would be less than 0.5 under conditions comparable to those used in the Appendix.

Fire test results reported in ref. 68 indicate that the failure of the liquid filled bottom drain line on the test tank within a matter of a few minutes is an item which should be given serious consideration in the designing of piping arrangements and in the protection of such piping from fire exposure.

Role of water spray protection: It is recognized that the application of water to a container exposed to fire definitely decreases the heat input to the contents of the container and also prevents the excessive increase of metal temperature. In this matter, however, marine liquid cargo transport systems are apparently at a disadvantage compared to land storage systems. This is mainly due to the very compact and crowded nature of the marine systems which also restricts the fire fighting efforts.

Although an automatic water spray system might be used, its proper installation within the cargo system would be a problem and its performance effectiveness and reliability would be questionable. It is recommended that capacity of the safety relief system should be determined on the basis of the assumption that in case of a fire, the water spray and supply system of a marine cargo transport would be totally inoperative. The system should assume fire-fighting water is not available.

The National Fire Protection Association Flammable and Combustible Liquid Code[41] specifies that the required vapor flow rate for a pressure relief valve may be multiplied by the factor of 0.3 for an uninsulated tank which has an approved water spray system, and where both an approved insulation and an approved

water spray are utilized, the factor is 0.15. In contrast, the American Petroleum Institute, RP520 [65] recommends no reduction in the environmental factor due to water application, considering it unreliable. Nevertheless, RP520 does emphasize the importance of providing water to the outside of a tank exposed to fire to keep the metal temperature below a safe limit.

Coast Guard regulations allow no credit for water spray systems. Considering the special characteristics of the marine liquid cargo systems, and also the adverse effects of the water spraying on the insulation, no credit is given for water spray when calculating vapor flow rate. However, the protection of especially vulnerable uninsulated surfaces with water spray should be considered without any credit to the environmental factor F. Consequently, the vapor relief valve sizing would not be affected by the presence or absence of water spray protection. It must be re-emphasized that fire protection means, such as insulation, are used solely for providing ample time until the fire fighting equipment can be operated in order to control and extinquish the fire. Therefore, it is obvious that improvements in the fire prevention and protection measures should never lead to any relaxation in strict fire fighting regulations.

c. Multi-range carriage of products

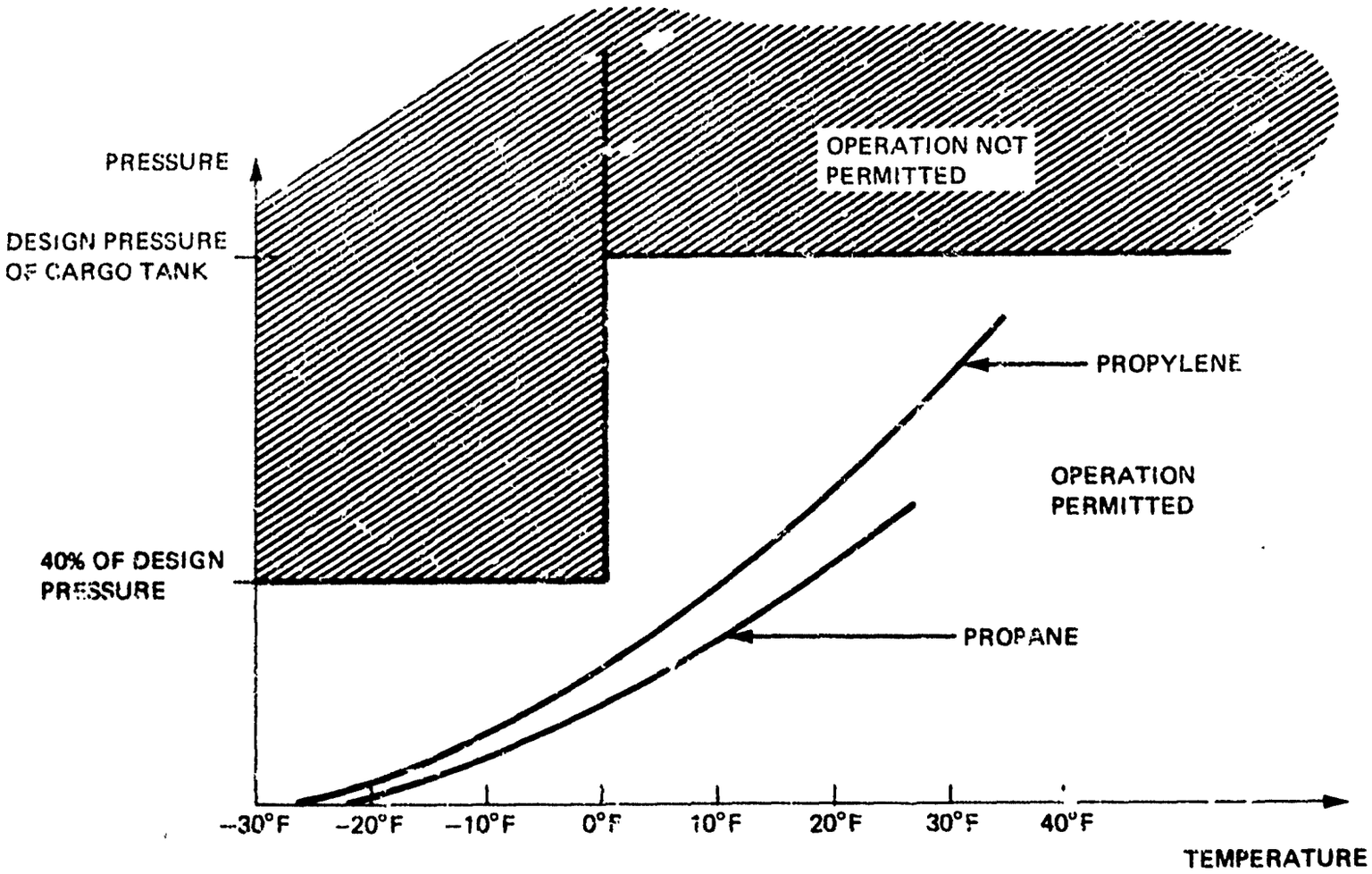
A carrier of bulk liquid cargo may wish to use a certain cargo transport system in a variety of services. This raises the question

of the proper setting of relief valves. The allowable working stress may vary depending upon the actual service temperature of the cargo.

For service temperatures below 0°F, Coast Guard regulations require that cargo tanks be stress-relieved. Since thermal stress-relief is often not possible due to the large size of the tanks under certain limitations, Class II-L (pressure 250 psia or less, temperature below 0°F) pressure tanks may be mechanically stress-relieved. Since mechanical stress relief has little or no beneficial metallurgic effects, the maximum allowable working pressure (MAWP) of mechanically stress-relieved pressure vessels has been limited to 40 per cent of the pressure which would be allowed if the tank were thermally stress-relieved. This limitation on pressure has the effect of restricting the operating range of pressure and temperature of the tank as shown in Fig. 2.

This limitation presents no problem when the tank is intended to operate with the cargo temperature always below 0°F; the safety valves are set at 40 per cent of the design pressure or lower and the tank is filled so that 2 per cent outage remains at a pressure corresponding to the relief valve setting. (Operators tend to set their valves as close as possible to the working pressure in order to minimize outage required.)

However, problems arise when the operator wants the option of being able to carry cargo in either the fully-refrigerated or semi-



Allowable Operating Range of Mechanically Stress-Relieved Low Temperature Tanks.
(where experimental stress analysis is not done)

FIGURE 2

refrigerated condition. This means that the tank will operate both above 0°F where its MAWP may be its design pressure, or below 0°F where its MAWP is limited to 40% of the design pressure.

To accomodate this dual role, consideration must be given to the settings of the relief valve or valves.

Some thought has been given to requiring only one relief valve set at the full design pressure of the tank. This reasoning is based on the assumption that the tank will not see high pressure (above 40% of design) while at low temperature due to the shape of the equilibrium pressure-temperature curve for the cargo. This solution has two drawbacks:

(i) There is the possibility that the cargo pressure deviates significantly from the equilibrium pressure-temperature relation, especially during loading.

(ii) When the difference between operating pressure and relieving pressure is large, the outage required at operating pressure becomes economically unacceptable to the owner if a requirement is imposed for a fixed outage at relieving conditions.

The other alternative at present is to have two relief valves per tank with one valve set at high pressure and the other at low and arranged so that one valve is connected to the tank at all times. This has the drawback of relying on the operator to have the proper valve connected at the proper time and having the tank filled to the proper outage.

Section 54.15-5 of CFR Title 46, requires that all pressure vessels, irrespective of size or pressure, shall be provided with protective devices (pressure-relief devices) in accordance with the requirements of UG-125 through UG-134 of the ASME Code, Ref. 63, except as modified in

46 CFR 54.15. Safety relief valves used in liquefied compressed gas service shall meet requirements of 46 CFR 162.017 or 162.018 Subchapter Q (Specifications), as appropriate.

When a cargo transport system is used for multi-range carriage of products, it is compulsory that requirements imposed by Division I of Section VIII of the ASME Code, as limited, modified, or replaced by specific Coast Guard requirements are met for each cargo and for the operation conditions to be utilized for this cargo. Considering only the pressure relieving systems, the following items should be checked in order to insure that requirements of the Coast Guard regulations are satisfied.

Minimum relief capacity. When the storage pressure and temperature conditions for a given cargo are to be changed or a different cargo is to be transported, the existing pressure relieving system should be capable of providing the required minimum relief capacity under the new service conditions. This capacity is given by Eq. [1]. Therefore, flow rate through the pressure relieving system should be determined for the new conditions and compared with the minimum relief capacity. If the flow rate is smaller than the minimum capacity, either a large size valve or a supplemental valve would be needed for providing the additional flow capacity. If the existing valve is too large for the new service conditions, adverse effects of an over-sized valve on the operation, such as valve chattering, should be considered before a final decision is made.

Materials. With the changed cargo conditions, materials of the pressure relieving device should be suitable for the chemical characteristics of the new cargo and for the changed pressure and temperature ranges and other pertinent service conditions.

Pressure setting. For liquefied compressed gas applications, relief valves are of either the internal or external spring-loaded type, suitable for the intended service. When changed operating conditions require a new pressure setting, the Code specifies the re-set may not be more than 10 per cent above or below the pressure for which the valve is marked.

Change of valve spring. A new spring will be needed for pressures outside the re-set range given in the above paragraph. Code specifications require the valve adjusted to the new service conditions and re-marked by the manufacturer or his authorized representative.

Rupture disks. Paragraph UG-127 of the ASME Code and Sec. 54.15-13 of CFR Title 46 outline the specifications for use of rupture disks. Relief area, the bursting pressure at a specified temperature, and material of the rupture disks should be checked against the changed condtions of operations. If the Code requirements are not met under the new conditions, new rupture disks should be installed.

Presure-indicating gauges. If used, gauges shall be graduated to not less than 1.2 times the pressure at which the relieving device is set to function. Therefore, when service conditions are changed, a replacement of the pressure gauges may be necessary.

Other Adjustments. With the multi-range carriage of products, other changes in the pressure relieving system may be required. The requirements may be determined by referring to the current Coast Guard regulations concerning pressure relief devices.

PART FIVE: ESTIMATION OF NEEDED RELIEF CAPACITY IN PRESSURE RELIEVING SYSTEMS VENTING LIQUID OR LIQUID-VAPOR MIXTURES

A. Vapor Relief Versus Liquid Relief

Calculation of the effective discharge area of a pressure relief valve for a liquid container exposed to fire is based on the rate of vapor generation caused by the heat absorbed from fire. The rated capacity of the relief device should be greater than the rate of vapor generation. Otherwise, the pressure will build up, and it may reach a level which is unsafe for the cargo container.

When assumption of adiabatic and reversible flow may be made, the capacity of the relief valves for gas and vapor relief can be calculated by using the ASME Code formula, i.e., Eq. [3-1], Appendix 3.

It is equally important for the marine transport cargo containers, to predict the expected performance of the pressure relief systems under flow conditions that differ from design conditions. An approach to this prediction is to answer, to the extent possible, the following two questions:

i. Are there pressure relieving conditions where it is possible to relieve liquid to the surroundings rather than vapor? What would be the performance of the pressure relief valve under these conditions?

ii. Is the possibility of two-phase flow and entrained liquid through a relief valve significant during a fire, and would such two-phase flow affect adversely the capacity of the valve?

Due to the lack of literature on the prediction of valve performance with respect to the application of various fluids, answers to the foregoing questions can be only qualitative. In the majority of cases, however, this might be sufficient in order to reach a sound engineering decision concerning this matter. Now, these questions will be discussed briefly in a qualitative manner.

The simplest case where liquid might be relieved through the relief valve is that of a cargo container overfilled during the pumping operation. Although the means of warning against overfilling and means of shutting down the pump automatically are usually provided, the capacity of the relief device, nevertheless, should be at least equal to the maximum liquid pump-in rate.

Next, consider the case where the cargo container is disoriented, as in the case with a container which is tilted (Fig. 3) so that the line to the safety relief valve is below the liquid line inside the container. If the container is exposed to a fire the vapor generated accumulates in the space above the liquid line, the pressure increases and as a result the liquid will be relieved through valve A. It is possible that a relief valve in contact with liquid will relieve enough liquid within an acceptable time period to reintroduce the relief valve to communication with the vapor space before the vessel experiences overpressure difficulties. If this does not occur, and the valve continues to relieve liquid, the question of adequacy arises. (Here it is assumed that the container has only one relief valve, located as shown in Fig. 3) Now the question is whether the relief of liquid during a fire would provide adequate protection and how such relief would compare with the normal relief of vapor.

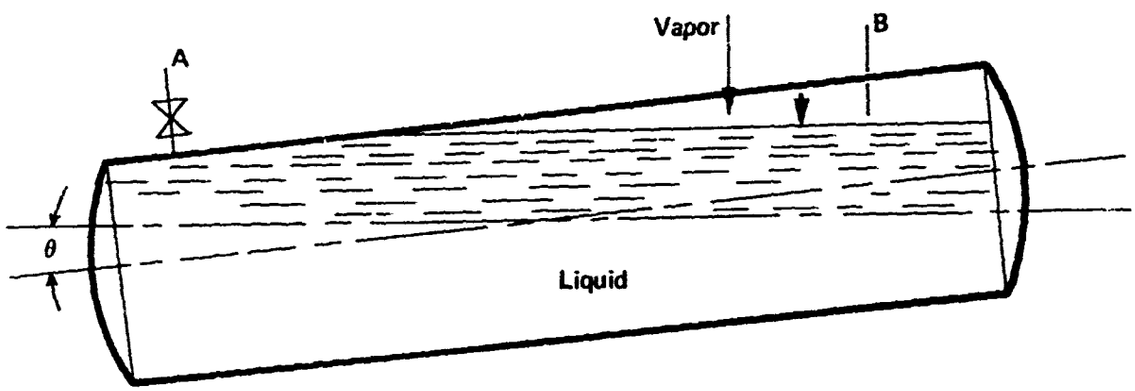


FIGURE 3

CARGO CONTAINER DISORIENTED IN THE LONGITUDINAL DIRECTION

As a rule, the pressure relief valves located in the liquid zone on tanks that may be exposed to fire conditions should have the flow capacity to pass a volume of liquid equivalent to the volume of vapor generated at the relief pressure. The rate of vapor formation of liquid during fire exposure can be determined from the rate of heat absorbed by the liquid cargo

$$\dot{M}_g = \frac{Q}{h_{fg}} \quad \text{lb/hr.} \qquad [12]$$

where

Q = Heat absorbed by the cargo, Btu/hr.

h_{fg} = Latent heat of vapor formation, Btu/lb.

Assuming that the cargo is a saturated liquid and $v_g \gg v_f$ the volume rate of vapor formation is given by

$$\dot{V}_g = \dot{M}_g \cdot v_g \qquad [13]$$

Since the liquid volume flow rate through the relief valve should be equal to the volume rate of vapor formation

$$\dot{V}_f = \dot{V}_g \qquad [14]$$

or

$$\dot{M}_f \cdot v_f = \dot{M}_g \cdot v_g \qquad [15]$$

Therefore,

$$\dot{M}_f = \frac{v_g}{v_f} \dot{M}_g \qquad [16]$$

In the derivation:

$\mathring{V}_g$ = Volume rate of vapor formation, cu.ft/hr.

$\mathring{V}_f$ = Volume rate of liquid flow through the relief valve, cu.ft/hr.

$\mathring{M}_g$ = Mass flow rate of vapor formation, lb/hr.

$\mathring{M}_f$ = Mass flow rate of liquid through the valve, lb/hr.

v_f, v_g = Specific volumes of liquid and vapor at the relief pressure, cu.ft/lb.

In Eq. [16] $\mathring{M}_g$ is the vapor mass flow rate through the pressure relief valve when the valve is located in the vapor zone. In other words, with vapor relief, minimum capacity of the relief valve would be $\mathring{V}_g$. With liquid relief, the relief valve should be designed to pass a volume rate of liquid equivalent to the volume rate of vapor generated at the relief pressure. Under this condition the liquid mass flow rate required is given by Eq. [16]. Therefore, with liquid relief, v_g/v_f times more mass of liquid must be discharged than vapor, if pressure is to remain constant. Now the question is whether a relief valve designed to discharge a given volume flow rate of vapor can pass equal volume rate of liquid under similar tank and discharge pressures. The answer involves the consideration of flashing characteristics of saturated liquids. With saturated liquids, when the pressure is reduced through the relief valve, flashing is anticipated. Buxton[17] observed that when saturated water passed through an orifice the pressure drop was so rapid that the water passed through the restriction and did not flash until some distance

further downstream from the orifice. However, when the saturated water passed through a nozzle, flashing occurred.

When no flashing is anticipated liquid and vapor velocities for isentropic flows can be determined as

$$V_f = [2g_c (P_o - P) v_\ell]^{1/2} \quad \text{(liquid)} \qquad [17a]$$

$$V_g = \left[\frac{2g_c (P_o - P) v_g}{1 - \frac{1}{4} (V_g/c_o)^2}\right]^{1/2} \quad \text{(vapor)} \qquad [17b]$$

where

g_c = 32.2 (lbm - ft)/(lbf - sec^2), gravitational constant

P_o = Inlet pressure, psfa

P = Exit pressure, psfa

c_o = Sonic speed at inlet conditions, ft/sec. v_ℓ and v_g are at P_o and saturation temperature.

For a given pressure difference $(P_o - P)$, since $v_\ell \ll v_g$, the liquid velocity V_f is considerably smaller than the vapor velocity V_g. Assuming that liquid and vapor discharge coefficients are about equal, it is evident from Eqs. [17] that liquid volume flow rate through a relief valve is less than the vapor flow rate. Hence, the relief valve designed to pass the required volume of vapor will not discharge the correct volume with liquid relief. Liquid volume flow rate will be less at least by a factor of $(v_g/v_\ell)^{1/2}$ than required. For saturated propane at 138°F, for instance, $v_g/v_\ell = 8.9$; i.e., liquid volume flow rate is at least three times less than required, although the liquid mass flow rate is about three times the vapor mass flow rate.

When the pressure reduction is gradual as the saturated liquid proceeds through the relief valve, flashing occurs. The degree of flashing through the valve can be determined by assuming adiabatic and reversible (i.e. isentropic) flow conditions. The flow rate is determined by using the steady flow, steady state energy equation

$$V_2^2 - V_1^2 = 2Jg_c\ (h_1 - h_2) = 2g_c\int_2^1 vdp \qquad [18a]$$

in this equation

V_2 = Velocity in the valve nozzle, ft/sec.

V_1 = Velocity upstream of the nozzle, ft/sec.

h_1 = Enthalpy of the fluid upstream of the nozzle, Btu/lb.

h_2 = Enthalpy of the fluid in the nozzle, Btu/lb.

J = 778 ft-lbf/Btu (foot pound force per Btu)

Velocity V_1 is very small compared to V_2, hence it can be neglected. To find V_2, it is necessary to evaluate $\int vdp$ graphically between pressures p_2 and p_1. Specific volume v can be plotted in terms of pressure by using

$$v = v_f + x\ (v_g - v_f) \qquad [18b]$$

$$x = \frac{s_1 - s_f}{s_g - s_f} \qquad [18c]$$

where the subscripts f and g denote saturated liquid and vapor at pressure p which changes from p_1 to p_2.

x = Quality of the liquid - vapor mixture

s = Entropy, Btu/(lb)(°R)

s_1 = Entropy of the fluid upstream of the nozzle (constant along the nozzle)

By using Eqs. [18] maximum mass flow rate through the relief valve can be determined.

Let us take again, as an example, saturated liquid propane at 138°F (pressure 301.4 psia) discharged to the atmosphere. For isentropic flow with flashing the maximum mass velocity (mass flow rate per unit flow area) is determined as 2270 lb/(sec)(ft^2); see Ref. 73. If the flowing fluid is saturated propane vapor, the maximum mass velocity becomes 1210 lb/(sec)(ft^2). Hence, with flashing liquid propane the increase of mass flow rate over the flow rate of saturated propane vapor is given by

$$\mathring{M}_f/\mathring{M}_g = \frac{2270}{1210} = 1.86$$

The relief valve, according to Eq. [16], must pass

$$\mathring{M}_f/\mathring{M}_g = v_g/v_f = 8.9$$

Therefore, under given conditions, liquid relief capacity of the valve would be 8.9/1.86 = 4.76 times less than the required capacity.

In conclusion, a relief valve designed for the vapor flow rate $\mathring{M}_g$ would not be able, under usual conditions, to handle safely the liquid flow rate $\mathring{M}_f$ given by Eq. [16]. Furthermore, Sec. 54.15-25 of CFR 46 requires that the relief valves should be placed so that a number of valves sufficient to provide the required relieving capacity would always be in communication with the cargo vapor phase. Thus, if conditions similar to that shown in Fig. 3 can happen, a design decision should be made in regard to the number, capacity, and location of the relief valves to be utilized. Use of a single valve may be objectionable, since the valve would be oversized under conditions where only vapor is relieved from the cargo container. Therefore, the simplest solution is to use

two relief valves at locations A and B, each with a vapor relief capacity of $\mathring{M}_g$. This would insure the relief of $\mathring{M}_g$ through either of the valves which is open to the vapor space. Since in this case both valves would operate, it would be possible to assign to each valve equal capacities which would be smaller than $\mathring{M}_g$. This smaller capacity can be determined by assuming that vapor flows through one of the two identical valves, whereas the saturated liquid flows through the other valve. Total volume flow rate of the two valves should be at least equal to the volume rate of vapor generated at the relief pressure, i.e.,

$$\mathring{M}_g v_g = \mathring{m}_g v_g + \mathring{m}_f v_f \qquad [19]$$

where

$\mathring{m}_g$ = Vapor flow rate through one of the valves, lb/sec.

$\mathring{m}_f$ = Saturated liquid flow rate through the other valve, lb/sec.

$\mathring{M}_g$ = The total rate of vapor formation due to fire exposure, lb/sec.

If each valve can handle a saturated liquid flow rate which is n times greater than the rate of vapor flow it can handle, one can write

$$\dot{m}_f = n\,\dot{m}_g \qquad [20]$$

Buxton[17] notes that there is no direct correlation to capacity when any valve is subjected to a variety of fluids, but correlation is dependent on the particular valve design. For this reason theoretical predictions based on isentropic flow conditions have only qualitative value. Consequently, due to the lack of literature on the prediction of valve performance with respect to the application of various fluids, the value of n in Eq. [20] should be determined experimentally. When n is known, design capacity of each of the two valves is obtained from the last two equations

$$\dot{m}_g = \frac{\dot{M}_g}{1 + n\,v_f/v_g} \qquad [21]$$

When $n = \frac{v_g}{v_f}$, vapor flow capacity of each valve becomes half of the total rate of vapor formation.

It should be noted that the foregoing argument is very general. The final decision on this matter would be influenced by other factors, such as the tank geometry and size, the amount of liquid cargo, ullage, etc.

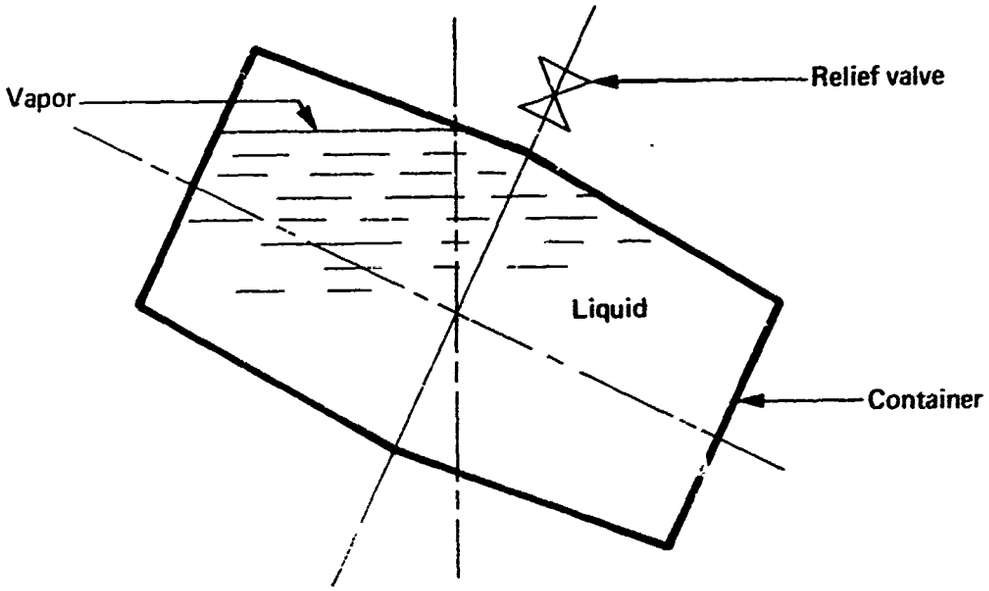


FIGURE 4

CARGO CONTAINER DISORIENTED IN THE TRANSVERSE DIRECTION

Another possibility which should be considered is the disorientation of the cargo container in the transverse direction. This condition also may bring inlet of the relief valve below the liquid line as shown in Fig. 4. This possibility seems to depend largely on the container geometry. It is expected that the cylindrical containers will be less liable to this problem compared to geometries similar to that in Fig. 4. The same argument will be applicable in this case.

If the pressures close to the critical values are expected, then assumption $v_g \gg v_f$ is no longer true. In this case, Eq. [12] should include the change in mass of vapor in the cargo container due to the change in volume of the vapor space.

B. Performance of Relief Valves if Handling Two-Phase Flow

In a liquid cargo container some entrained liquid could enter into the relief valves when the heat transfer rate from fire is high. If the amount of entrained liquid is not small, the relief valve not only must handle the vapor generated but also must carry the entrained liquid. Further, the entrained saturated liquid could flash vaporize as it flows through the relief nozzle. Very little information is available in the literature on this matter.

The amount of entrained liquid depends on the size distribution of liquid droplets and the vapor velocity. When this velocity exceeds the limiting velocity for a given size of droplet, then the droplet will be carried by the vapor flow. The limiting velocity of a liquid droplet can be obtained approximately by balancing the form drag and the buoyancy forces acting on the droplet

$$\frac{CA\rho_v U_v^2}{2g_c} = V\left[\rho_\ell - \rho_v\right]\frac{g}{g_c} \qquad [22]$$

where

C = dimensionless drag coefficient

A = projected area of droplet in direction of motion, ft.^{2}

V = volume of droplet, ft.^{3}

U_v = relative velocity between droplet and vapor, fps

$\rho_v \rho_\ell$ = vapor and liquid densities lb/ft.^{3}

g = gravitational acceleration, fps^2

g_c = gravitational constant

For a spherical liquid droplet Eq. [22] becomes

$$G = C^1\left[\rho_v\left(\rho_\ell - \rho_v\right)\right]^{1/2} \qquad [23]$$

where

$$C^1 = \left[\frac{4}{3}\frac{gd}{C}\right]^{1/2} \text{ fps} \qquad [24]$$

$G = \rho_v U_v$ = mass vapor velocity, lb/sec,ft.^{2}

d = droplet diameter, ft.

Referring to Eqs. [23] and [24], for a given vapor velocity U_v, liquid droplets with diameters equal to d or smaller will be carried over by the vapor flow. The parameter C^1 can be used as a measure of the droplet size carried by the vapor flow. Drag coefficient C is a function of the droplet Reynolds number.

Little is known regarding C^1 due to lack of information on the size distribution of liquid droplets in a given flow situation. Therefore, the amount of liquid entrainment should be determined experimentally. For a given vapor velocity C^1 is determined from Eq. [23], and then the experimentally determined entrainment values are usually plotted with respect to C^1. The liquid entrainment is expressed as pounds vapor per pound of liquid which is called "the decontamination factor". An average vapor velocity can be determined by using the rate of vapor generation and by considering the geometry of the vapor space in the cargo container.

As an example, consider the case of saturated propane at 140°F. Assume that the average vapor velocity in the container vapor region has been determined as 0.5 fps. Densities of the vapor and the liquid are 3.13 lb/cu.ft and 27 lb/cu.ft., respectively. By using Eq. [23], one obtains C^1 = 0.18 fps. For liquid cargo containers the experimental data on decontamination factor is not available. However, for the purpose of estimating the order of magnitude of the liquid entrainment the data reported for evaporators could be utilized. Referring to Fig. 11-31 of The Chemical Engineer's Handbook,[62] decontamination factor is determined approximately as 100 for C^1 = 0.18.

Therefore, with an average vapor velocity equal to 0.5 fps each 100 pounds of propane vapor would carry over one pound of liquid propane. This amount of liquid entrainment would not require any special consideration in design calculation of the pressure relief valve. However, in this example the average vapor velocity has been purposely chosen very

low in order to use the experimental data.[64] Especially if the vapor space in the cargo container is very small, the vapor velocity could be unusually high, thus causing considerable liquid entrainment.[53]

Evidently experimental and analytical investigations are needed concerning the liquid entrainment in cargo containers. This information is not available at the present time. When it is available the amount of liquid entrainment can be estimated. Then the allowance in the relief valve size can be made in order to handle the entrained liquid. The analysis utilized for relief valves handling liquid flow can be applied to the case with liquid entrainment. The possibility of flashing of entrained liquid could be taken into account without causing too much complication.

PART SIX: PRESSURE RELIEF VALVE SIZING

A. Vapor Flow Calculations

Practical merit of a relief device formula is dependent largely on the accuracy of the assumptions made. In vapor flow calculations relief devices are commonly compared to nozzles or orifice restirctions and this introduces some variations between theoretical and actual flows. When assumptions of adiabatic and reversible flow may be made, the flow capacity of a nozzle may be computed by two methods. The first method assumes that the fluid follows the ideal gas law which compressed gases do not. This assumption results in formulae for determining the flow capacity similar to the ASME Code formula.[63]

The deviation from the ideal gas law becomes greater as the actual gas or vapor approaches saturation conditions. Consequently, the second method does not assume ideal gases but utilizes the thermodynamic properites of the actual fluid. This method, illustrated in Sylvander and Katz[73] requires a graphical solution for the relationship of nozzle area, valve efficiency, fluid pressure and flow rate.

The ASME Code formula is occasionally corrected for deviations from the ideal gas laws, thus eliminating the need for graphical solution These corrections are applied to the isentropic expansion coefficient which is equal to the ratio of specific heats for an ideal gas. For further information on the second method consult the cited references.

Starting with the ASME Code formula, discharge capacity of a pressure relief valve in equivalent air flow rate at standard conditions (60°F and 14.7 psia) has been determined, in Appendix 3, Eq. [3-10], as

$$(cfm)_a = 18.34 \frac{Q}{LC} \left[\frac{ZT}{M}\right]^{1/2} \qquad [25]$$

In this equation

$(cfm)_a$ = equivalent air flow rate, minimum required rate of discharge in cfm of air at standard conditions (60°F, 14.7 psia)

Q = rate of heat absorption by the liquid cargo, given by Eq. [2], Btu/hr

L = latent heat of the liquid being vaporized, Btu/lb

C = constant (with dimension) for gas or vapor which is a function of the specific heats ratio, $k = c_p/c_v$

Z = compressibility factor of the gas evaluated at the relieving conditions, dimensionless

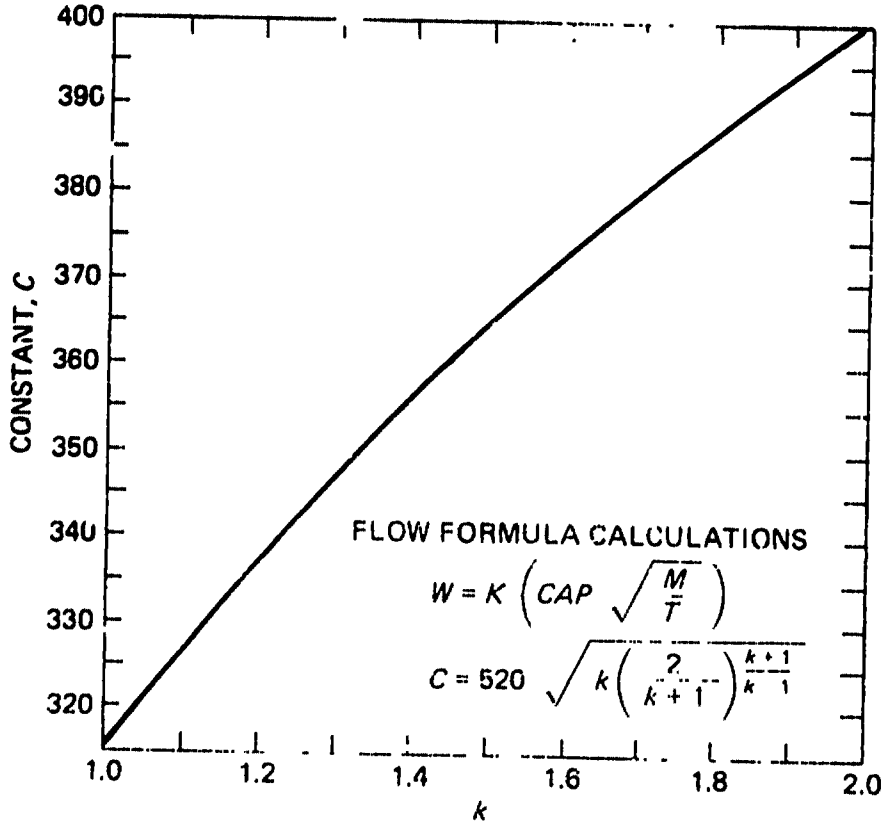
T = temperature of the gas at the relieving conditions, °R

M = molecular weight of the gas, lbm/lbmole

When Eq. [2] is substituted, Eq. [25] becomes

$$(cfm)_a = 18.34 \frac{GFHA}{LC} \left[\frac{ZT}{M}\right]^{1/2} \qquad [26]$$

The minimum air equivalent discharge rate which the pressure relief valve must be able to pass is determined from Eq. [26]. Values of C for different k are given in Fig.5.



k	Constant C	k	Constant C	k	Constant C
1.00	315	1.26	343	1.52	366
1.02	318	1.28	345	1.54	368
1.04	320	1.30	347	1.56	369
1.06	322	1.32	349	1.58	371
1.08	324	1.34	351	1.60	372
1.10	327	1.36	352	1.62	374
1.12	329	1.38	354	1.64	376
1.14	331	1.40	356	1.66	377
1.16	333	1.42	358	1.68	379
1.18	335	1.44	359	1.70	380
1.20	337	1.46	361	2.00	400
1.22	339	1.48	363	2.20	412
1.24	341	1.50	364		

FIGURE 5

CONSTANT C FOR GAS OR VAPOR RELATED TO RATIO OF SPECIFIC HEATS ($K = C_p/C_v$)

Source: Figure UA230, ASME Boiler & Pressure Vessel Code, Section VIII, Unfired Pressure Vessels

If instead of Eq. [2] $Q = 34{,}500\ FA^{0.82}$ is used, Eq. [26] becomes

$$(cfm)_a = 633{,}000\ \frac{FA^{0.82}}{LC}\left[\frac{ZT}{M}\right]^{1/2} \qquad [27]$$

This is the formula* of the Code of Federal Regulations;[27] see also formulae 16 to 21 in Appendix 2. Evidently Eq. [26] is more comprehensive compared to Eq. [27]. Therefore, in sizing pressure relief valves for liquid cargo containers this equation is recommended as the starting point.

It should be emphasized that in Eqs. [25-27] critical flow (maximum mass flow rate per unit area) is assumed to occur. Pressure ratio under this condition is given by

$$\frac{P_{cr}}{P_1} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} \qquad [28]$$

where

P_1 = upstream pressure, psia

P_{cr} = pressure in the nozzle or orifice throat at the maximum flow, psia

Let p_2 = downstream pressure (possibly atmospheric pressure), psia

If $P_2/P_1 < p_{cr}/p_1$, the flow rate is always at the maximum value. However, when p_2/p_1 is greater than the critical pressure ratio, flow rate is smaller than its maximum value. Under this condition, $(cfm)_a$ can no longer be computed by using Eqs. [25-27]. This case may arise in calculating the area of relief devices for low pressure equipment, where for an atmospheric discharge, the upstream pressure is less than approxi-

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* In CFR (Ref. 27) minimum required rate of discharge is represented by Q, whereas in the present study Q = rate of heat absorption.

mately 30 psia or for systems where back-pressures are high. The present study is not concerned with such systems. For further information on this matter refer to references 2 and 75.

Eq. [25] breaks down near the critical point of the mixture, where L approaches zero. For this reason where values of L are less than 50 Btu/lb this equation should not be used.[86]

It is important to recognize that p_1 is the set pressure multiplied by 1.10 or 1.20 (depending on the permissible overpressure) plus the atmospheric pressure.

Actual discharge area of the pressure relief valve can now be determined from Eqs. [3-7] and [3-9] of Appendix 3 as

$$A = \frac{0.714\ (cfm)_a}{Kp_1\ v_o} \qquad [29]$$

where, p_1 = upstream pressure, psia

A = actual discharge area, orifice or the nozzle throat area, in.^{2}

K = coefficient of discharge, dimensionless

v_o = 13.1 cu.ft./lb. specific volume of dry air at 60°F and 14.7 psia

Discharge coefficient for a given relief valve will be determined by tests conducted in accordance with the ASME Code[63]. For specific information concerning the discharge coefficients, manufacturers' literature should be consulted.[19]

As has been mentioned earlier, if the actual gas can not be treated as ideal gas, the foregoing formulae can still be utilized provided that a proper average isentropic expansion coefficient is used instead of the ratio of specific heats k. This method, however, should be employed after very careful consideration of expansion behavior of the fluid.

A comparison of the pressure relief valve discharge area calculations by using different methods, has been previously presented.[73]

In conclusion, it is seen that with vapor flow the discharge area of a pressure relief valve can be determined by using Eqs.[26 and 29] if the ratio of the exit pressure to the upstream pressure is smaller than the critical value given by Eq.[28].

In using these equations it is important to be sure that the given design conditions do not invalidate any of the assumptions utilized in the derivation of these equations.

B. Calculations for Systems Venting Liquid or Liquid-Vapor Mixtures

The following discussion is related to the problem which has already been discussed in Part Five of this study.

Under the pressure relieving conditions where liquid discharge as well as vapor discharge to the surroundings is expected, the relief valve size can be calculated by using the method and formulae of the preceding section. In this case, however, design vapor capacity

is given by Eq. [21]. This equation assumes that two identical valves are being used for pressure relieving purposes. When pressure exceeds the permissible value, both valves will discharge simultaneously; vapor flowing through one of these valves and the saturated liquid flowing through the other valve.

It is evident that flow characteristics of a relief valve will be different for a vapor than for a saturated liquid. Therefore, characteristic flow parameters present in the flow formulae depend on the type of fluid handled by the relief valve. Considering a relief valve which may discharge either vapor or saturated liquid to the surrounds, the overall liquid flow characteristics of the valve are expressed in terms of its vapor flow characteristics by using the parameter n in Eq. [21]. In view of the lack of theoretical work on this problem, for a particular valve, n should be determined experimentally.

It should be repeated here that the discussion presented in Part Five treats the problem in a very simplified form, neglecting a number of parameters which influence performance of the relief valve when it discharges a saturated liquid.

Considering the possibility of the liquid entrainment through the relief system, the central problem is the prediction of the amount of liquid carried by flowing vapor. Discussion presented in Part Five has indicated the need for experimental and analytical investigations concerning liquid entrainment in

cargo containers. When this information is available relief valve flow calculations can be performed by using the methods published in literature, for instance, those in references 30 and 35.

PART SEVEN: Relief Vent Location and Vent System Design

A. Injection Into Air

When substances are released under pressure, the nozzle or discharge of the relief system should be so engineered that the gases and vapors are dissipated to harmless concentrations as rapidly as possible. This is especially important in the case of substances of high flammable and/or toxic nature. The possibility of a "cloud" should be recognized, especially in atmospheric conditions of inversion with nominal winds. Bridges, lock areas, and low-flying aircraft (such as helicopters) would be vulnerable to such "clouds". If a "cloud" should form and then ignite, it may produce a fire-ball with serious effects, or, in the case of toxic materials, might drift into the pilot house, crew quarters, or dockside habited areas.[16]

Another consideration in the design of nozzles or discharge piping systems is to avoid any possible flame impingement of the discharging gas or vapors on other pipes, tanks, or related equipment. Flame impingement on an unwetted tank surface may result in metal failure. (This was an important factor in the Warren LPG Fire and Explosion in Newark, N. J. in 1951)[79]

Emergency exposure limits have not yet been developed for the public (these are under study by the NRC Committee on Toxicology

and others). The purpose of emergency relief is to prevent, or at least minimize, the probability of catastrophic container failure, which would release large amounts of cargo in a short time. Emergency venting is recognized as essential, even though it introduces other risks.

B. Injection Into Water

At first glance, the possibility of piping the discharged material into water, to avoid or minimize release to the air, may appear attractive. However, unless the circumstances are unusual, and the product possess unique characteristics, water injection is not recommended. With few exceptions, the water solubility of common cargos is not sufficient for fast solubility. The additional equipment needed to "bubble" or otherwise bring the discharge vapors or gas into sufficiently intimate contact with the water to insure solubility, would be major equipment. This equipment would require continuous maintenance to prevent obstruction by ice, mud, debris and other foreign bodies. Back-pressure would be exerted on the pressure relief system, as well. In addition, some chemical cargos would hydrolyze to products which would corrode the hull and land-related equipment. As an additional matter, the contribution to water pollution should be studied in the context of Public Law 91-224, which prohibits the discharge of oil and other hazardous materials into navigable waterways, and with reference to other legal and ecological restraints.

C. Burning

Procedures for igniting waste gases by passing them through a "flare stack" could be incorporated into the discharge system, but such burning has limitations and restrictions in marine use.

The pressures and flow-rates of a large relief valve system discharging flammable vapors or gases under emergency conditions would approximate a "flame thrower" if ignited. While this might not be hazardous in free air on open seas, if the vessel were in the vicinity of a bridge, aircraft, or a congested harbor with other vessels near, serious complications could result. In addition, a burning release would complicate the approach of vessels carrying emergency personnel who were deployed to cope with the original emergency, and would divert attention from the major problem of overpressure. The possibility of flash-back into the venting container, is remote, but should be considered.

D. Special Consideration for Poisonous and Toxic Materials

When especially toxic substances are carried, release of even small amounts may lead to serious consequences. Hydrogen cyanide, hydrogen sulfide, and carbon monoxide are examples of substances whose release requires special considerations. In the case of HCN, tank car and truck operations have been carried out for several years with an excellent safety record. Standard operating procedures for emergency personnel involved in spills of this liquefied gas specify ignition, to conver the gas into combustion products

which are less toxic than the HCN itself. The same consideration could apply to hydrogen sulfide, whose toxicity by inhalation is of the same order. Carbon monoxide is not normally considered as having the same potential hazard as HCN and H_2S, but liquefied carbon monoxide as a cargo demands great respect. Of the three, pure carbon monoxide offers a unique hazard in that it presents no warning odor. The warning odor of HCN and H_2S are very unreliable deterrents to excessive inhalation.

Phosgene, chlorine, hydrogen sulfide and several other "toxic" gases have considerable volume in commerce. Small cylinders of these gases are equipped with a temperature-activated fusible disc to release the whole contents in case of excessive temperature. European practice does not include provisions for release, but attempts to have complete containment up to the point of complete rupture of the container.

This panel has not addressed itself to the relative merits of the two philosophies. Relatively complete and comparable experience data from either U. S. or Europe has not been available to us, and we defer judgement on the matter of venting versus containment to ultimate failure until such data can be studied in detail. It is suggested that this problem of venting versus containment should be considered if comparable experience and data can be developed At present no such study is planned or underway, on either side of the Atlantic, to the best of our knowledge.

PART EIGHT: INSPECTION, TESTING AND MAINTENANCE

General regulations concerning periodic tests and inspection of liquefied flammable gas cargo containers and the related equipment are described in 46 CFR 38.25.[24] This subpart specifies procedures for both internal and external examination of unlagged cargo containers and the visible parts of lagged containers. It also describes inspection requirements for the insulation along with the hydrostatic or pneumatic tests which could be performed any time the marine inspector considers such tests necessary to determine the condition of the cargo container. Pneumatic testing shall be in accordance with 46 CFR Subchapter F, Marine Engineering.

The cargo container pressure relief valves shall be designed, constructed and flow tested for capacity in conformance with 46 CFR 162.018, Subchapter Q (Specifications).[28] Relief valves and relief valve discs shall be inspected in accordance with section 38.25.0 of the same code.

Other codes such as ASME, API, NBFU, etc. may also contain advisory provisions and recommendations which are not included in Coast Guard Regulations. Reference to these provisions and recommendations should be encouraged.

PART NINE: SAFETY CHECK LIST FOR EVALUATION OF TERMINALS AND RELATED FACILITIES

I. Terminal

A. Site

1. Is terminal well situated with regard to topography and adequate drainage?
2. Will the climate materially affect operations? (Earthquake, floods, fog, hurricane, lightning, smog, snow, tornadoes, excessive heat, and very low temperatures)
3. Will toxic fumes from fire, explosion or other accidents affect the surrounding community?
4. Are major highways, airports or congested areas located near the site? Is there unusual risk from low-flying aircraft during cargo venting? Can emergency equipment get through traffic at all times?
5. Are utilities dependable? (Water, gas, electricity, compressed air, etc.)
6. Does the community provide adequate fire fighting personnel and equipment? Is emergency personnel well trained in ship emergencies and in the specific hazards of hazardous cargos?
7. Does the community provide adequate ambulance, hospital and police protection? Do plant or local nurses and physicians understand the specific medical treatment for exposure to hazardous cargos and related substances likely to be encountered?

8. Can air, river, landfill, and sewage systems be used for waste disposal without violating local or federal ordinances or the health and welfare of the surrounding community? (see P.L. 91-224)
9. Do nearby facilities present fire explosion or toxic hazards?
10. Are sources of toxic and/or flammable vapors in close proximity?

B. Layout

1. Is the terminal area enclosed by adequate fences and gates?
2. Is there a "safe" distance from the boundary to the nearest terminal unit?
3. Are process areas separated from utilities, storage, office, and laboratory areas?
4. Do all buildings conform to the National Building Code? To local Code?
5. Are foundations and subsoil adequate for all loadings?
6. Are structural (steel) members and supports insulated so as to be fire resistive?
7. Have fire spread factors such as openings in floors, walls, elevator shafts, air conditioning and ventilation ducts been minimized?
8. Are hazardous process areas separated by fire walls?
9. Are buildings exposed to explosion hazards vented for relief according to standards?
10. Are all buildings properly ventilated to limit exposure of personnel to toxic substances and to reduce hazard from flammable substances?

11. Are there sufficient and clearly marked exits, stairwells, or escape chutes in all buildings?
12. Do electrical installations conform to the National Electrical Code? (Especially Article 500?)
13. Are drainage facilities in buildings adequate? Where do they ultimately discharge?
14. Are chemical reactions possible in the drains - for example, acids plus cyanides or sulfides?
15. Are hazardous units separated from all critical areas such as control room or process computer installations?
16. Does spacing of equipment consider the nature of the product, the quantity, the operating conditions, the sensitivity of the equipment, the need to combat fires, and the concentration of valuables?
17. Are loading areas on the periphery of the terminal and away from sources of ignition?
18. Are administrative buildings and warehouses on the periphery of the plant?
19. Are storage tanks away from the periphery; not too closely spaced, and diked or buried? Are they plainly marked as to contents?
20. Are waste disposal systems downwind from concentrations of personnel?
21. Are there adequate roadways for vehicles to enter and exit in the event of an emergency?

22. Does terminal have ship-shore communications? Is there a language problem?

23. Is cargo handling equipment (such as booms, chicksan connections, lines, pipes, and hoses) in good condition and ready for use?

II. VESSELS

A. Anchorages - Moorings and Docks

1. Are moorings and docks firm, secure, uncluttered, and well-lighted for night operations?

2. Is communication (telephone, intercom, radio, or other) available? Is emergency equipment (protective clothing, self-contained breathing apparatus) at hand?

3. Will cargo vented from relief valves during anchorage or while in dock create exceptional hazard for low-flying aircraft or bridges? (see Section 7, p. 86)

4. Are international fittings provided for fire-fighting water connections?

B. Layout

1. Are tanks both on vessels and shoreside, properly designed, operated, and vented for the cargo handled?

2. Are cargo transfer controls and emergency shut-offs, such as valves, pump switches, and quick closing valves properly located and plainly identified? Do they actually work?

3. Are product alarms operable and capable of being checked?

III. CARGO TRANSPORTED

1. Have the quantities of cargo transported in all stages of handling, transport, and storage and in all physical states been considered in relation to the hazards of fire, explosion, toxicity, pollution and corrosion?
2. Have the pertinent physical properties of each cargo been determined? Melting point, boiling point, vapor pressure, particle size, etc? (See Appendix 4, Typical Physical and Chemical Properties Suggested for Evaluation of Pressure Relief Requirements)
3. Have the chemical properties of each cargo been classified? (Especially chemical reactivity with other products)
4. Have the hazards of the cargo been classified? Have highly hazardous materials been identified and their location in the plant determined?
5. Is the cargo toxic? Have Threshold Limit Values and Acute Short-Term Limits been established?
6. Have the stability hazards of the cargo been determined? (Reactivity, spontaneous combustion, decomposition of elevated temperatures, self-polymerization)
7. Is the material corrosive? (Skin, metal, plastics, and other materials of construction?)
8. Have the effects of impurities been taken into account as related to fire and explosion, toxicity, corrosivity, and stability of the product?

9. Are overpressure protection devices adequate as to sizes and construction?

10. Have the overpressure protective devices been properly set and sealed? By whom? When?

11. Have the potential hazards of all cargos and products involved been evaluated?

12. Are precautionary measures taken to guard against accidental release of flammable or toxic liquids, gases, or combustible dusts?

13. Are unstable chemicals handled in a way to minimize exposure to heat, pressure, shock, or friction?

14. Are the facilities properly designed, instrumented, and controlled to minimize losses?

15. Have all heat transfer operations been properly evaluated for hazards?

16. Have all transport operations been checked for operator safety?

17. Are chemical cargos packaged, labeled and transported in accordance with current regulations?

18. Are waste disposal and air pollution problems handled in accordance with current regulations?

IV. VESSEL AND TERMINAL PERSONNEL

1. Has an adequate "Station Operating Procedure" manual been prepared and understood in detail by all personnel? Is it reviewed periodically and reviewed when process changes are made? Is a copy at hand?

2. Are adequate personnel job training programs instituted? Do they cover both supervisory and operating personnel?
3. Have adequate start-up and shut-down programs been initiated?
4. Do the vessels and terminal operations include a "permit" system for hazardous jobs? Is it enforced?
5. Are marine chemists or other qualified technical personnel available to monitor or check-out work in confined spaces, gas-freeing or inerting, and related entry procedures?
6. Are personnel trained to recognize potential equipment or facilities malfunctions?
7. Are employees trained to handle emergency situations? Is there an organized and trained emergency squad or brigade on 24 hour coverage? Is cooperation with public and private fire departments encouraged? (Mutual-aid, Coast Guard response, and other local emergency coordinators)
8. Are operators trained in the utilization as well as limitations of protective equipment? (Face, head, eye, and respiratory protection). Is full suit available if needed?
9. Are communications between vessel and terminal adequate? Are they actually checked by operation periodically?
10. Are emergency procedures understood and all situations covered?
11. Do personnel actually use emergency equipment without hesitation?

12. Are facilities for control of spills adequate? On all shifts?

13. Are spills promptly reported to both on-site and off-site authorities? Are procedures for reporting plainly displayed and understood by all personnel?

PART TEN: APPENDICES

1. Information Descriptive of Barge and Ship Transport
2. Formulae for Calculation of Vapor Flow Capacity in Pressure Relieving Systems
3. Formulae for Sizing Pressure Relief Valves
4. Typical Physical and Chemical Properties
5. Heat Transfer to Cargo Containers When Walls Are Subjected to Fire
6. Rate of Burning of Fuel for a Free Liquid
7. Evaluation of Insulation Effectiveness
8. Boiling Conditions in Liquid Cargo Containers Exposed to Fire
9. Behavior of a Monomer Cargo During Rapid Polymerization and Pressure Relief

APPENDIX I: INFORMATION DESCRIPTIVE OF BARGE AND SHIP TRANSPORTATION

Illustrations of Various Type Vessels on Which Relief Valves are Required

Section A - General Information on Types

Section B - Independent Tank Barge

Section C - Integral Tank Barges

Section D - Tank Ships

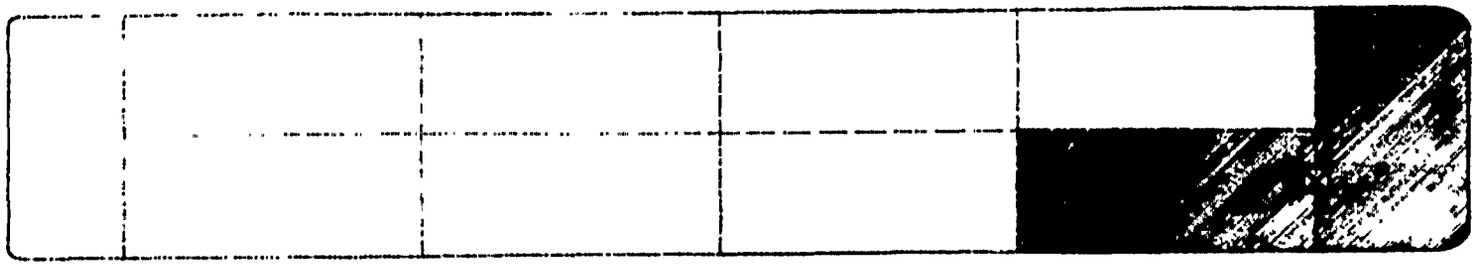
Section A - General Information on Types of Barges and Ships

1a Definition of barge hull types

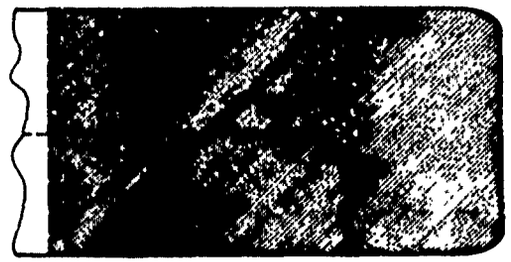
2a Illustration of stability differences between types 1 & 2

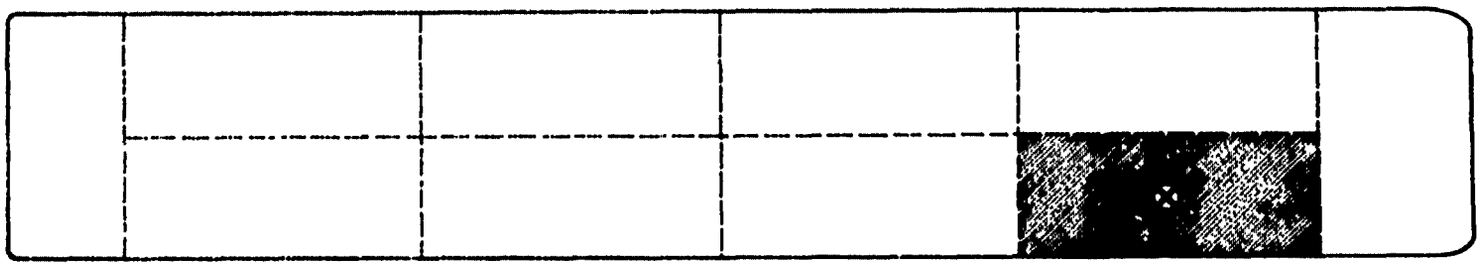
3a Illustration showing structural differences between types 1, 2, & 3

DESIGN FEATURE \ BARGE CLASSIFICATION AND TYPICAL CARGOES	MAXIMUM PREVENTIVE MEASURES	SUBSTANTIAL PREVENTIVE MEASURES	MODERATE PREVENTIVE MEASURES
	TYPE I	TYPE II	TYPE III
	CHLORINE, LIQUID OXYGEN, LIQUID HYDROGEN, MOLTEN PHOSPHORUS, ETHYLENE OXIDE	LIQUEFIED PETROLEUM GASES, ANHYDROUS AMMONIA	HYDROCHLORIC ACID, SULFURIC ACID, SODIUM HYDROXIDE
BOW RAKE	SUITABLE FOR DESIGN SPEED OF TOW		
OPEN HOPPER COAMINGS	36 INCH FWD---24 INCH MIDLENGTH---18 INCH AFT		
BREAKWATER	36 INCHES HIGH		
SUBDIVISION STABILITY	REMAIN AFLOAT AND UPRIGHT WITH HOPPER FLOODED TO DECK HEIGHT		REMAIN AFLOAT AND UPRIGHT UNDER OPERATING CONDITIONS
	REMAIN AFLOAT AND UPRIGHT AFTER HOLING IN WAY OF TRANSVERSE BULKHEAD	REMAIN AFLOAT AND UPRIGHT AFTER HOLING NOT IN WAY OF TRANSVERSE BULKHEAD	NO DAMAGED STABILITY REQUIREMENT
HULL STRUCTURE	CLASSIFICATION SOCIETY STANDARD		
	ADDITIONAL STRENGTH BASED ON GROUNDING STUDY		NO ADDITIONAL REQUIREMENT
CARGO TANK COLLISION PROTECTION	INDEPENDENT 1.5g LONGITUDINAL COLLISION CHOCK		INDEPENDENT 1.0g LONGITUDINAL COLLISION CHOCK
	25 FEET FROM HEADLOG 4 FEET FROM SIDE	25 FEET FROM HEADLOG 3 FEET FROM SIDE	NO DISTANCE FROM HEADLOG SPECIFIED-2 FEET FROM SIDE EXISTING REGULATIONS
INDEPENDENT CARGO TANK STRENGTH	SUFFICIENT TO WITHSTAND LOADING DUE TO BARGE GROUNDING HULL DEFLECTION		SUFFICIENT TO WITHSTAND LOADING DUE TO STILLWATER BARGE HULL DEFLECTION

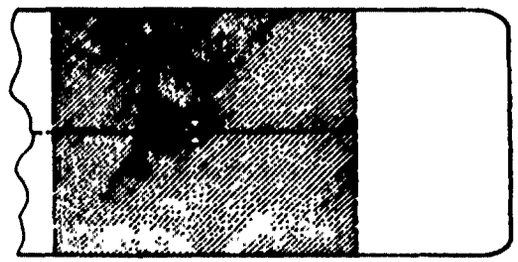


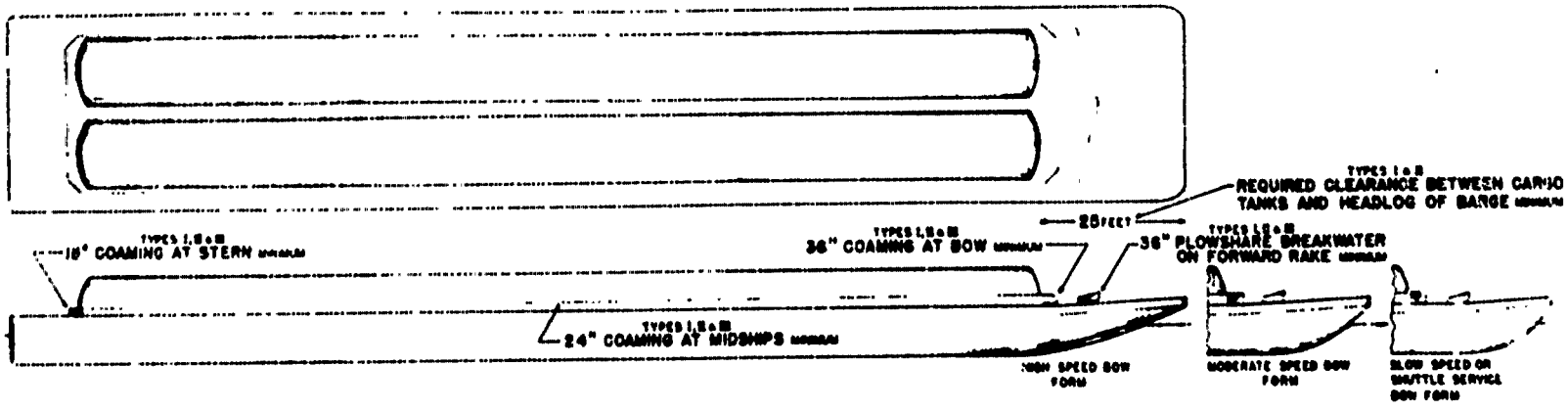
TYPE I BARGE - MUST RETAIN POSITIVE BUOYANCY & STABILITY AFTER BEING HOLED IN WAY OF TRANSVERSE WATERTIGHT BULKHEAD

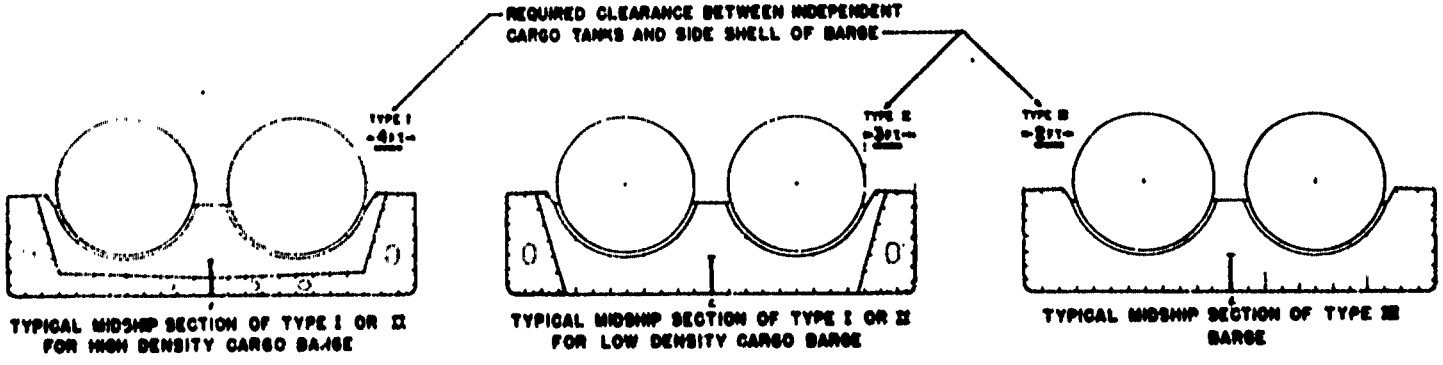




TYPE II BARGE - MUST RETAIN POSITIVE BUOYANCY & STABILITY AFTER BEING HOLED ANYWHERE EXCEPT IN WAY OF A TRANSVERSE WATER-TIGHT BULKHEAD







TYPICAL MIDSHIP SECTION OF TYPE I OR II FOR HIGH DENSITY CARGO BARGE

TYPICAL MIDSHIP SECTION OF TYPE I OR II FOR LOW DENSITY CARGO BARGE

TYPICAL MIDSHIP SECTION OF TYPE III BARGE

Section B - Independent Tank Barge

1b Aerial view of a refrigerated LPG & NH_3 Type 1 barge

2b Cross-section of refrigerated LPG & NH_3 barge

3b Installing foam glass insulation on barge similar to 2b

4b Aerial view of compressed NH_3 & LPG barge

5b Cross-section & profile of compressed NH_3 & LPG modified type 2 barge (uninsulated)

6b Three views of an older NH_3 - LPG barge built before hull type requirements

7b Cross-section of an older NH_3 - LPG compressed barge

8b Aerial view of one of the original refrigerated NH_3 - LPG carriers

9b Aerial view of chlorine tank barge

10b View of tank saddle on chlorine tank

11b View of cargo piping on Cl_2 barge

12b View of independent tank barge in acid service

13b View of cargo piping on acid barge

14b View showing insualtion and relief valves installed on refrigerated LPG & NH_3 barge

15b Independent tank barge certificated to carry carbon disulfide

16b Independent tank barge - carries molten sulfur

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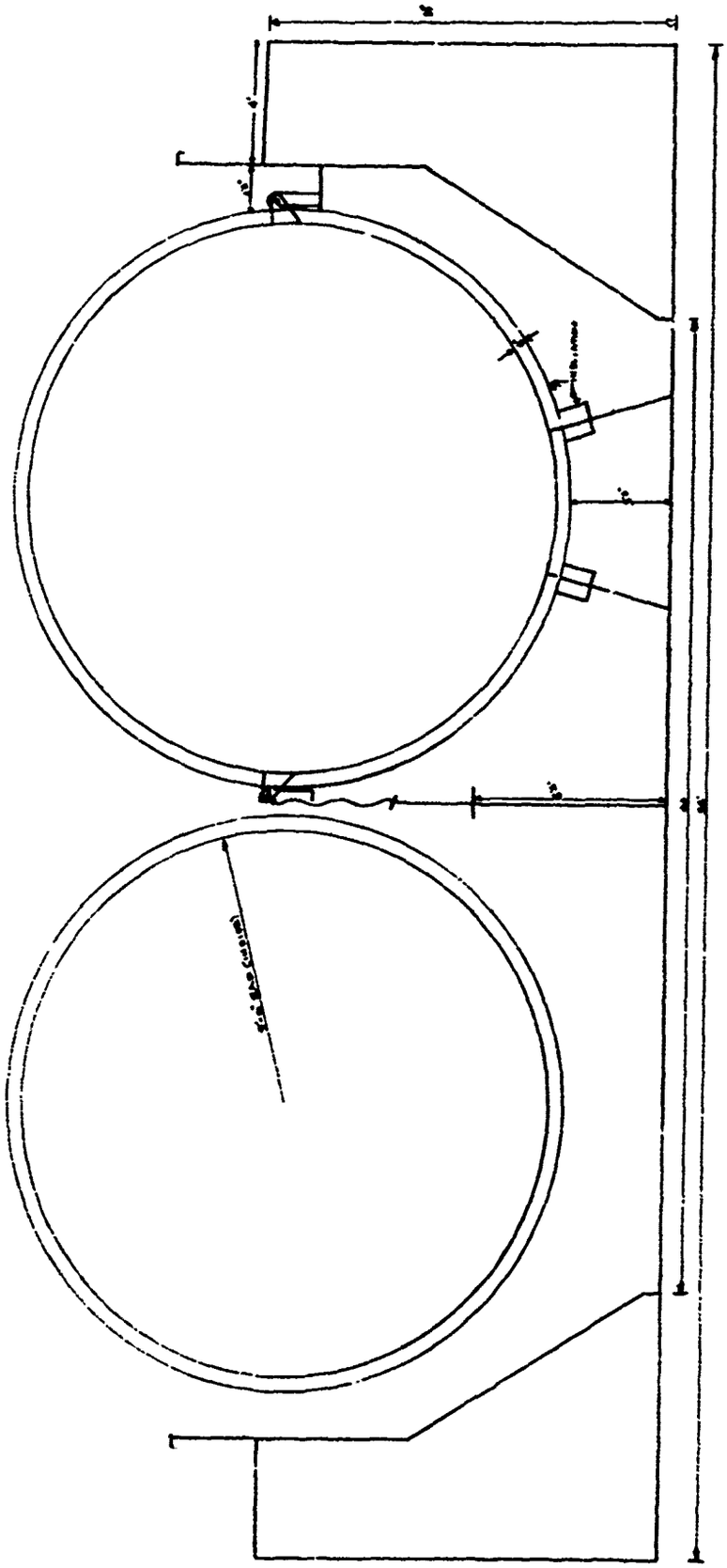

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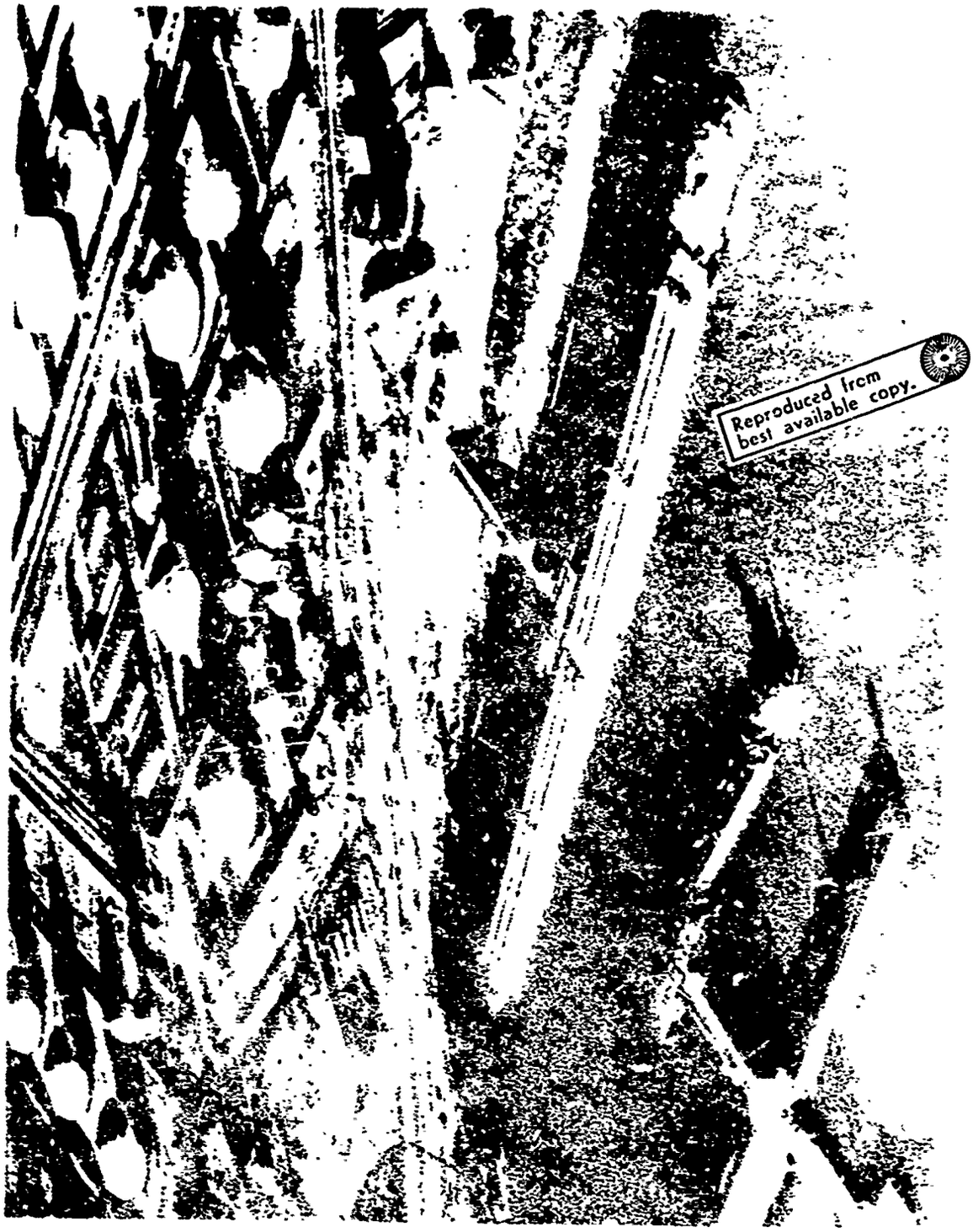

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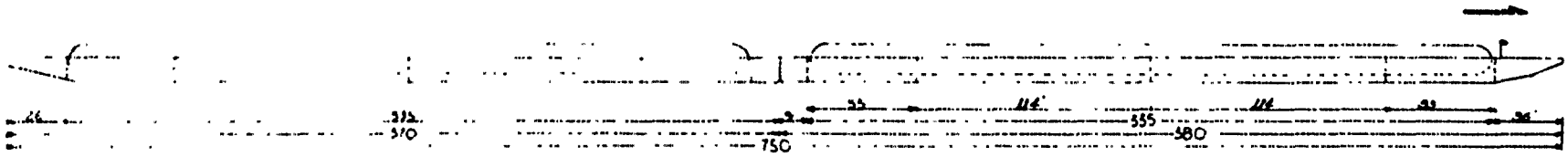
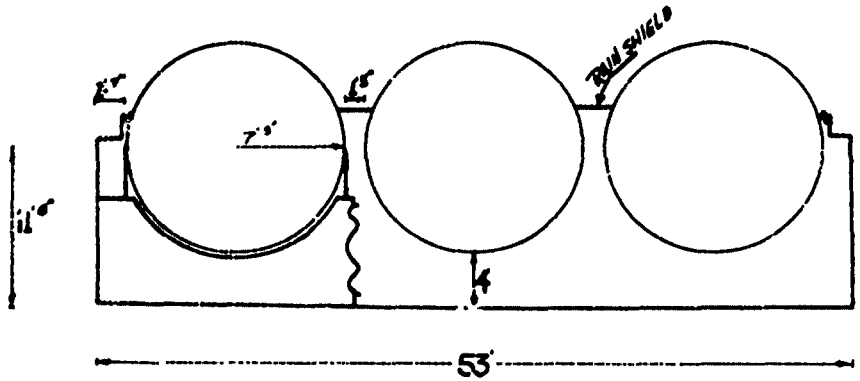
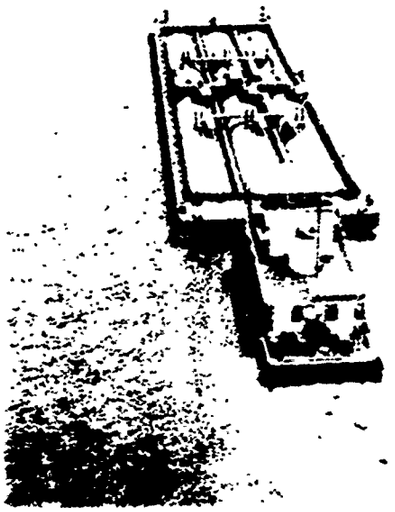
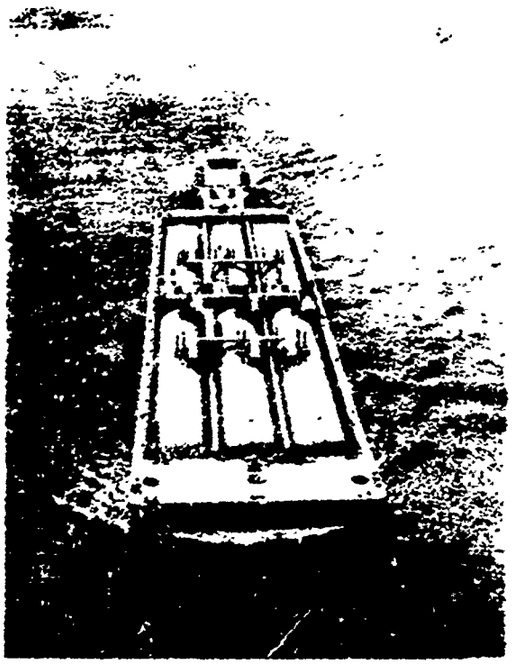




SECTION





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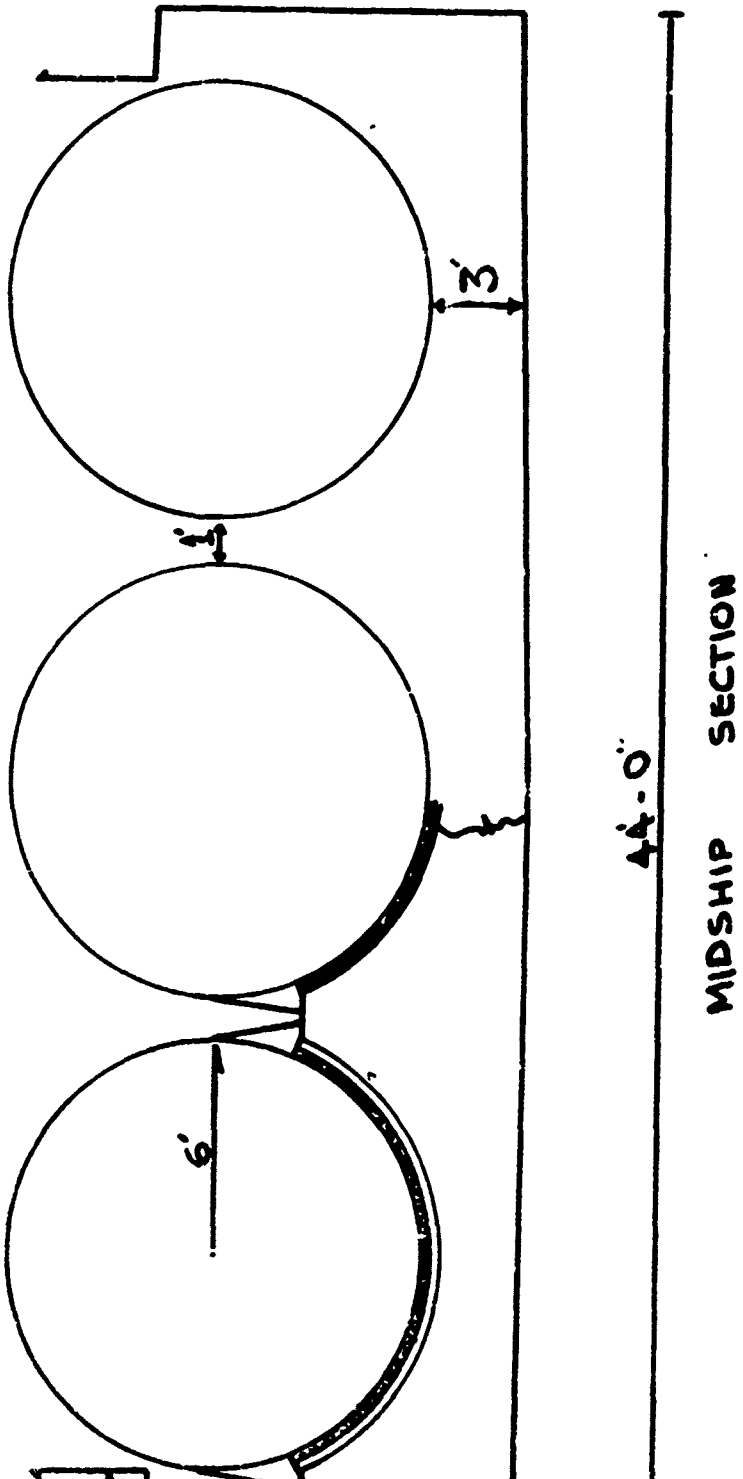
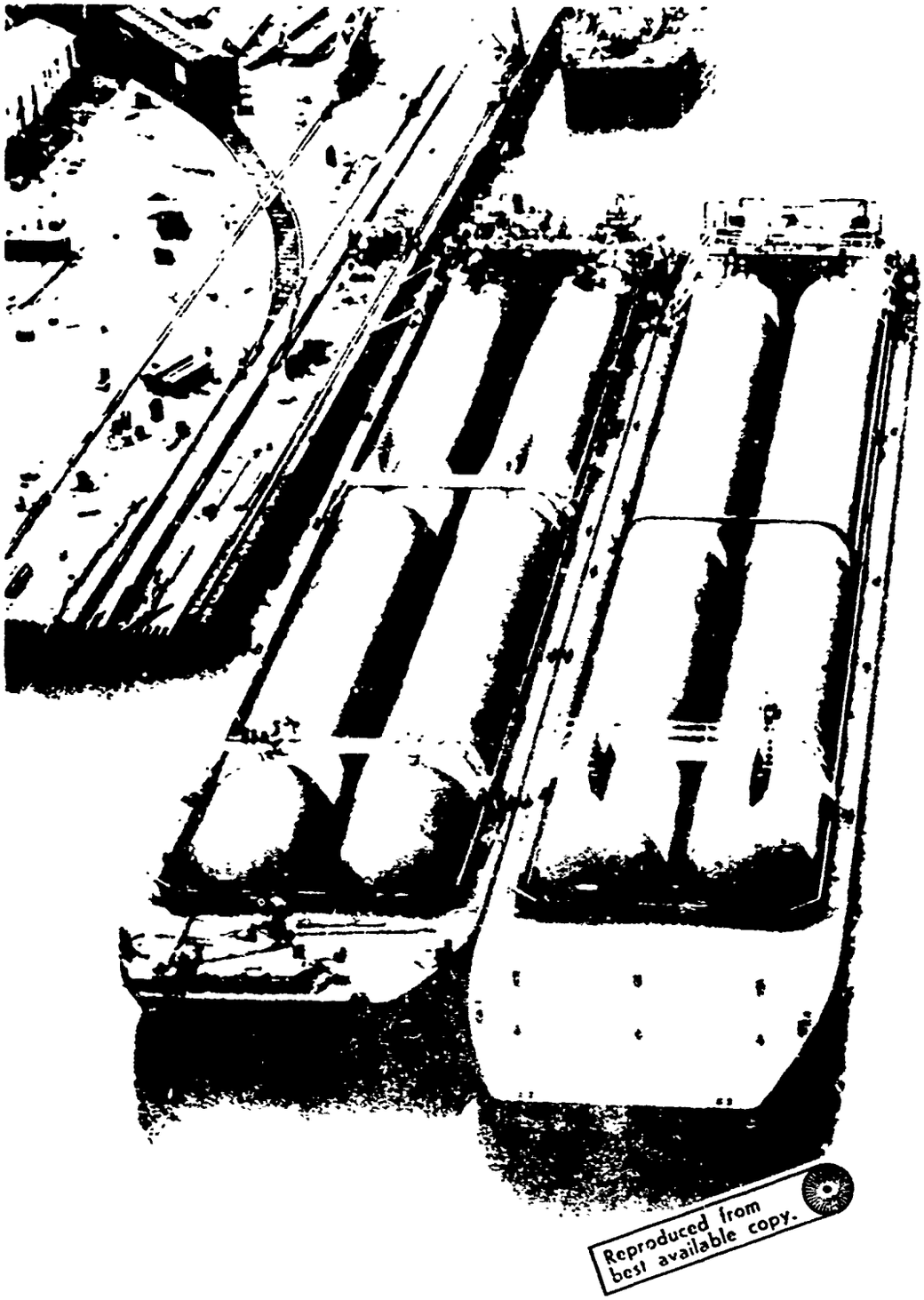


MIDSHIP SECTION



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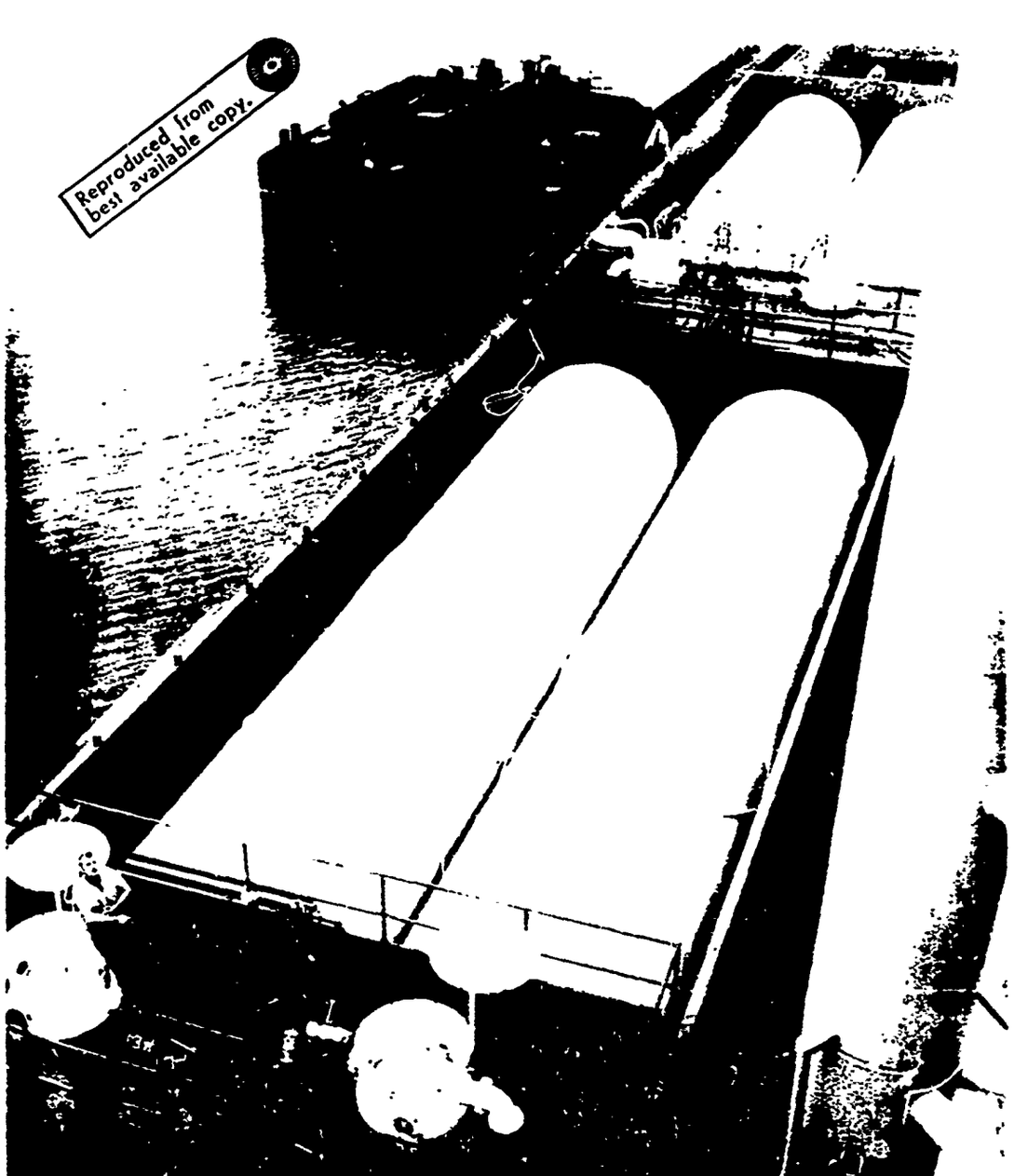

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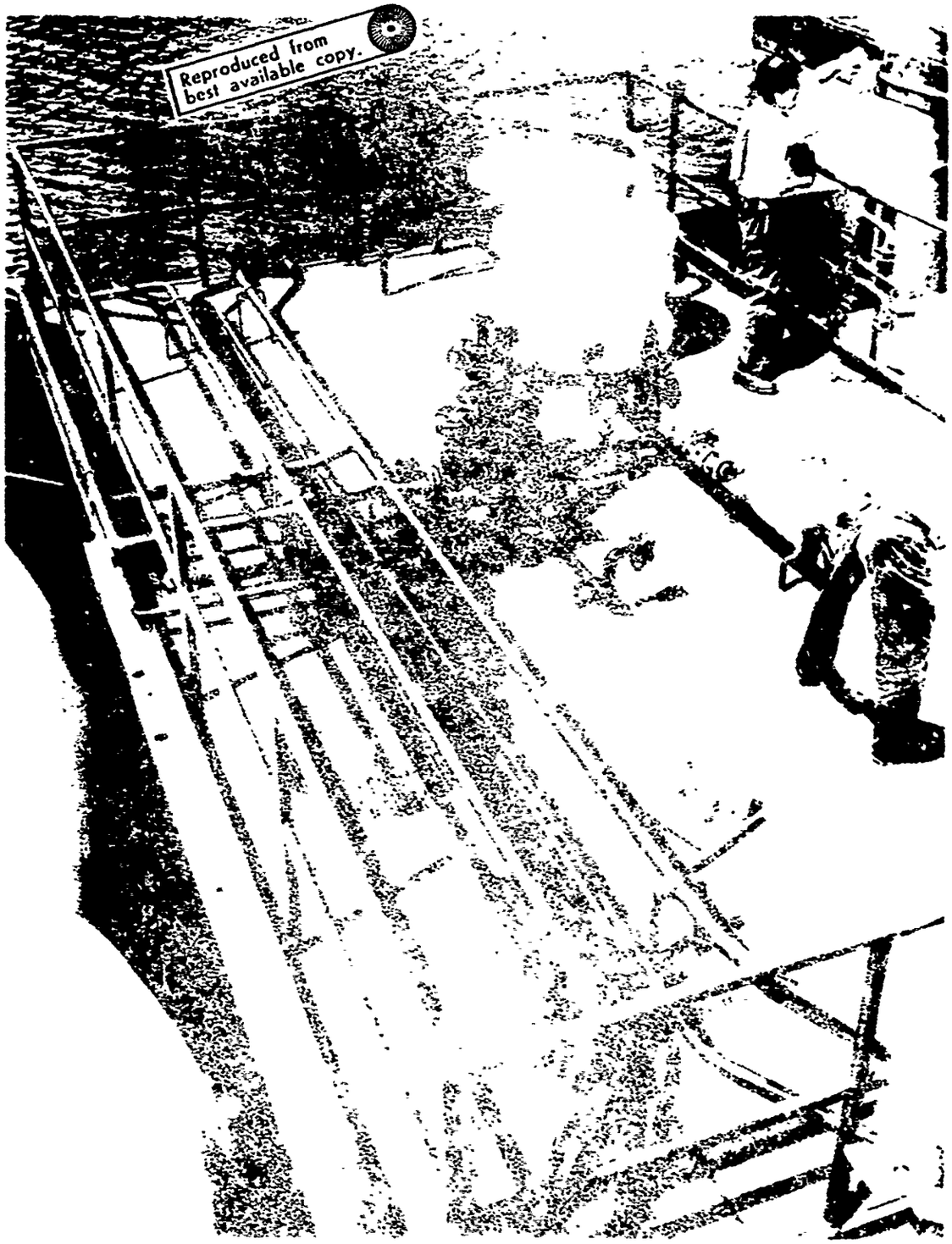

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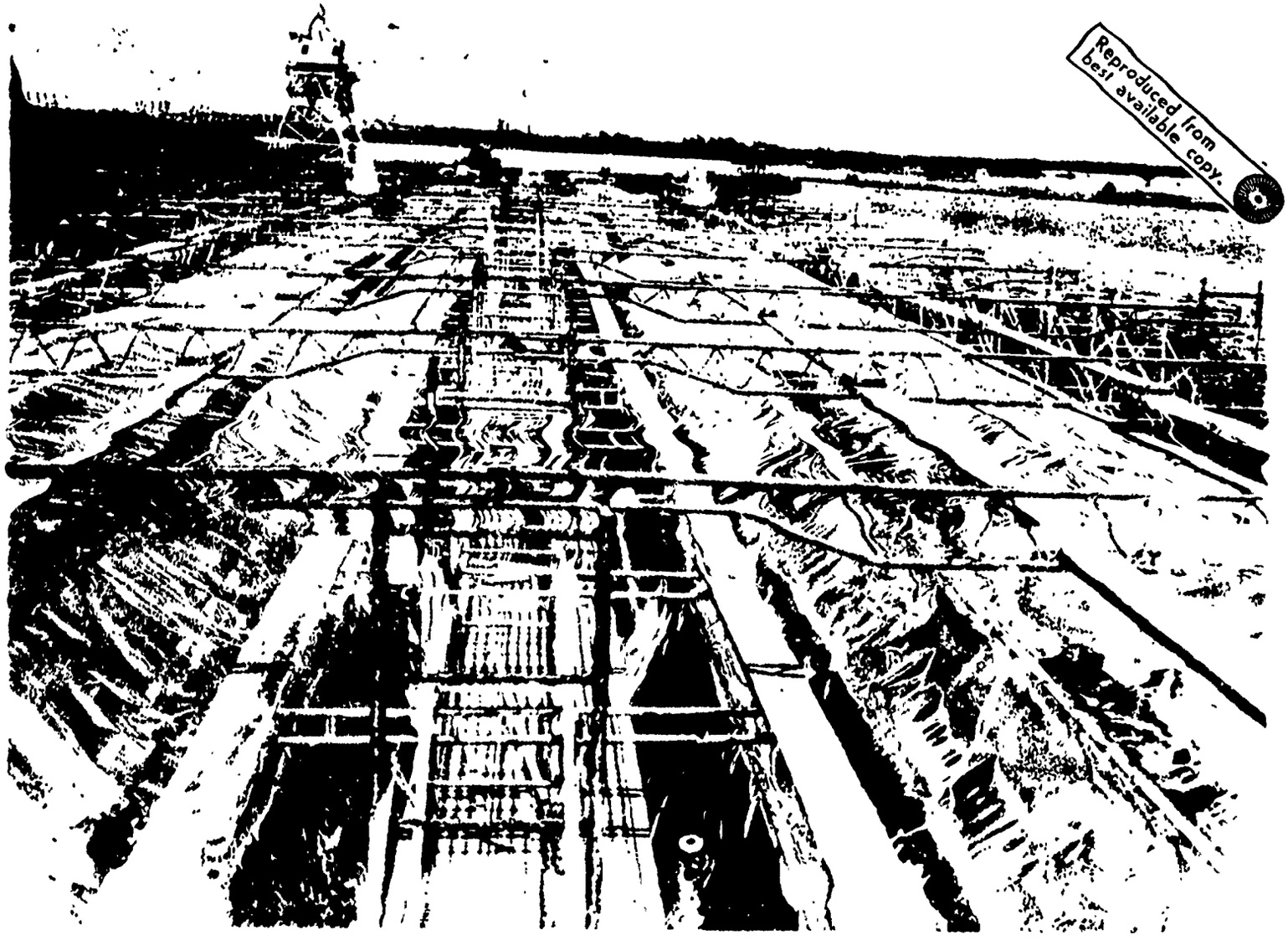

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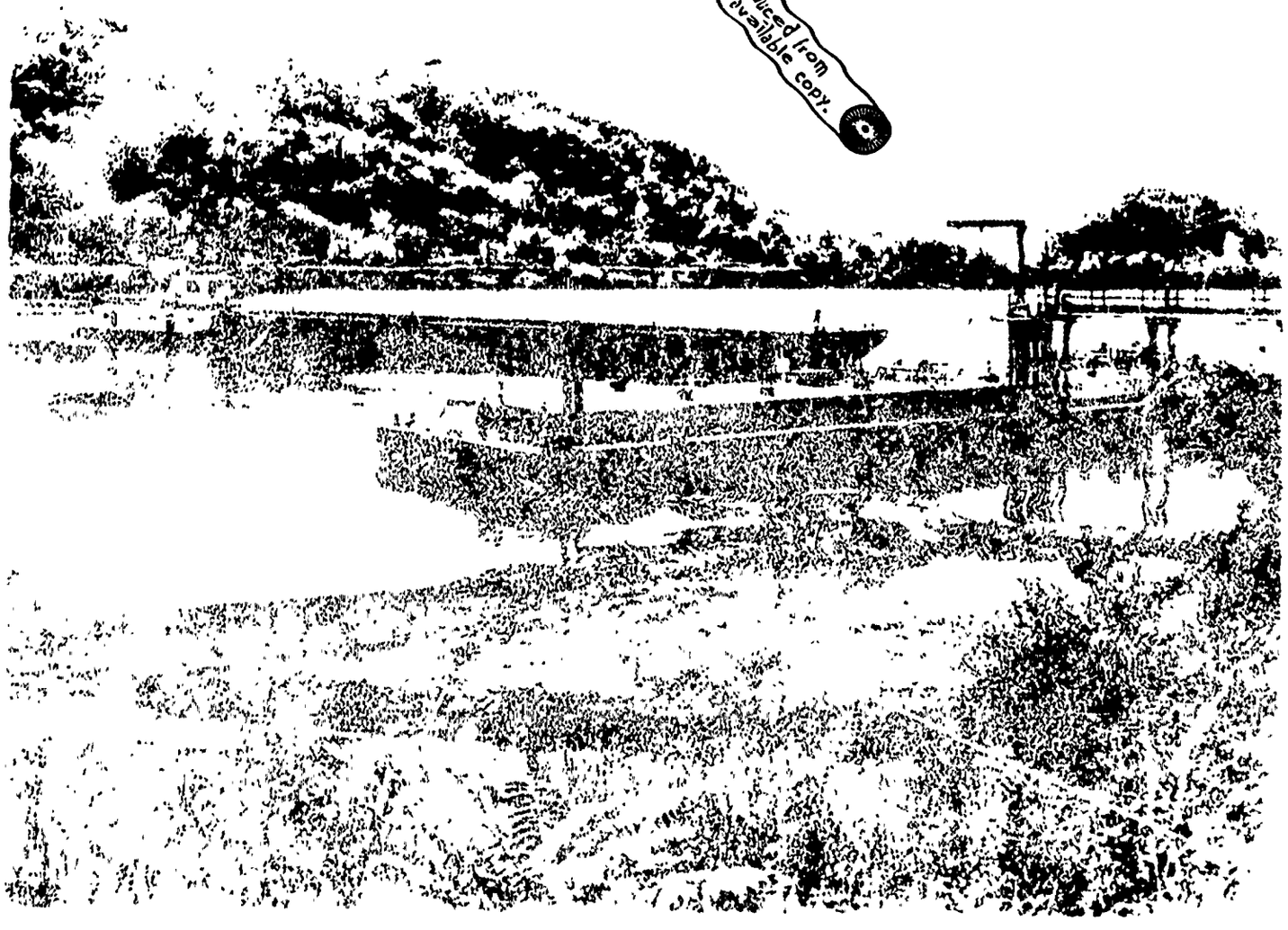

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Section C - Integral Tank Barges

1c View of an integral tank barge, adrift and afire

2c Cross-section and profile of an old integral tank barge

3c Aerial view of a double skin integral tank barge

4c Cross-section and profile of a double skin integral tank barge

5c View of inside of integral tank barge

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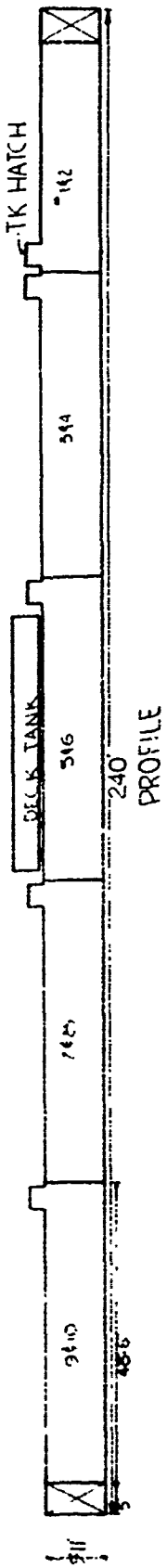
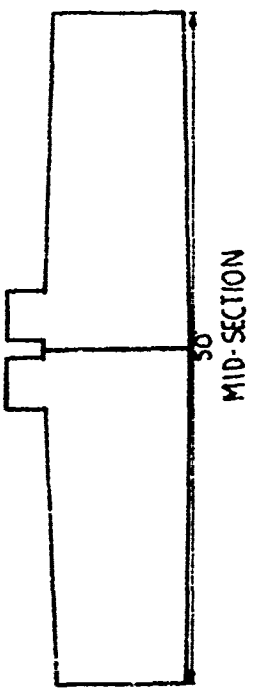

TK HATCH
DECK TANK
240'
PROFILE


50'
MID-SECTION

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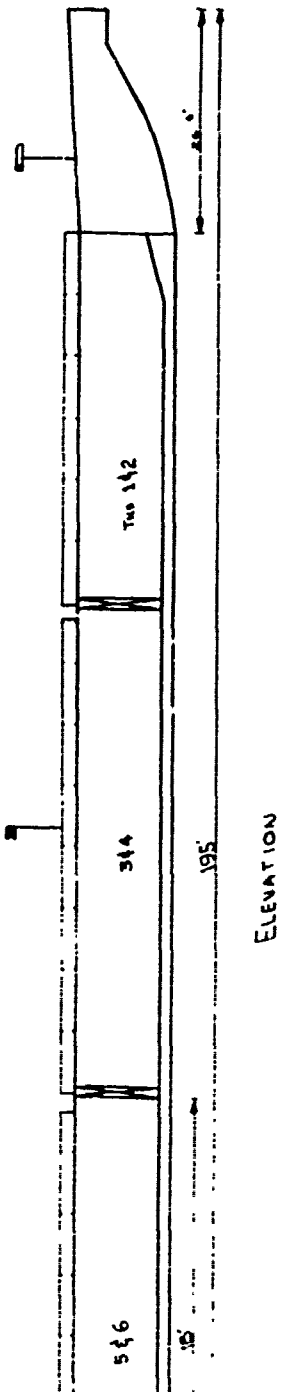
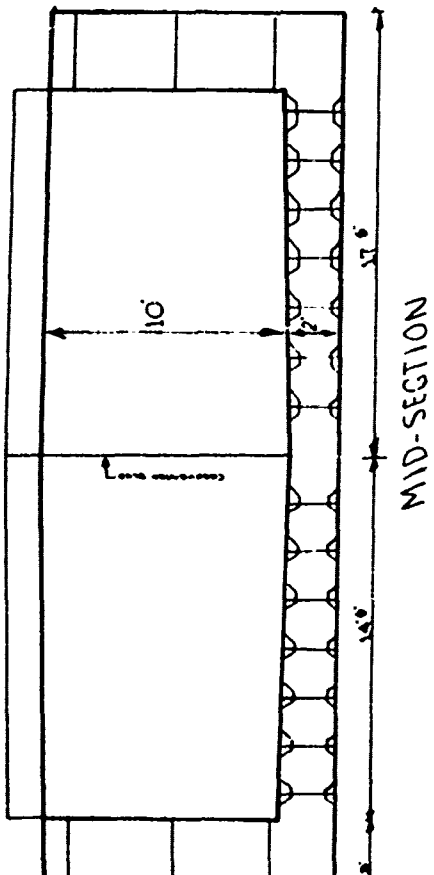

Tan 1&2
3&4
5&6
195'
15'
ELEVATION


10'
2'
17'6"
14'9"
MID-SECTION

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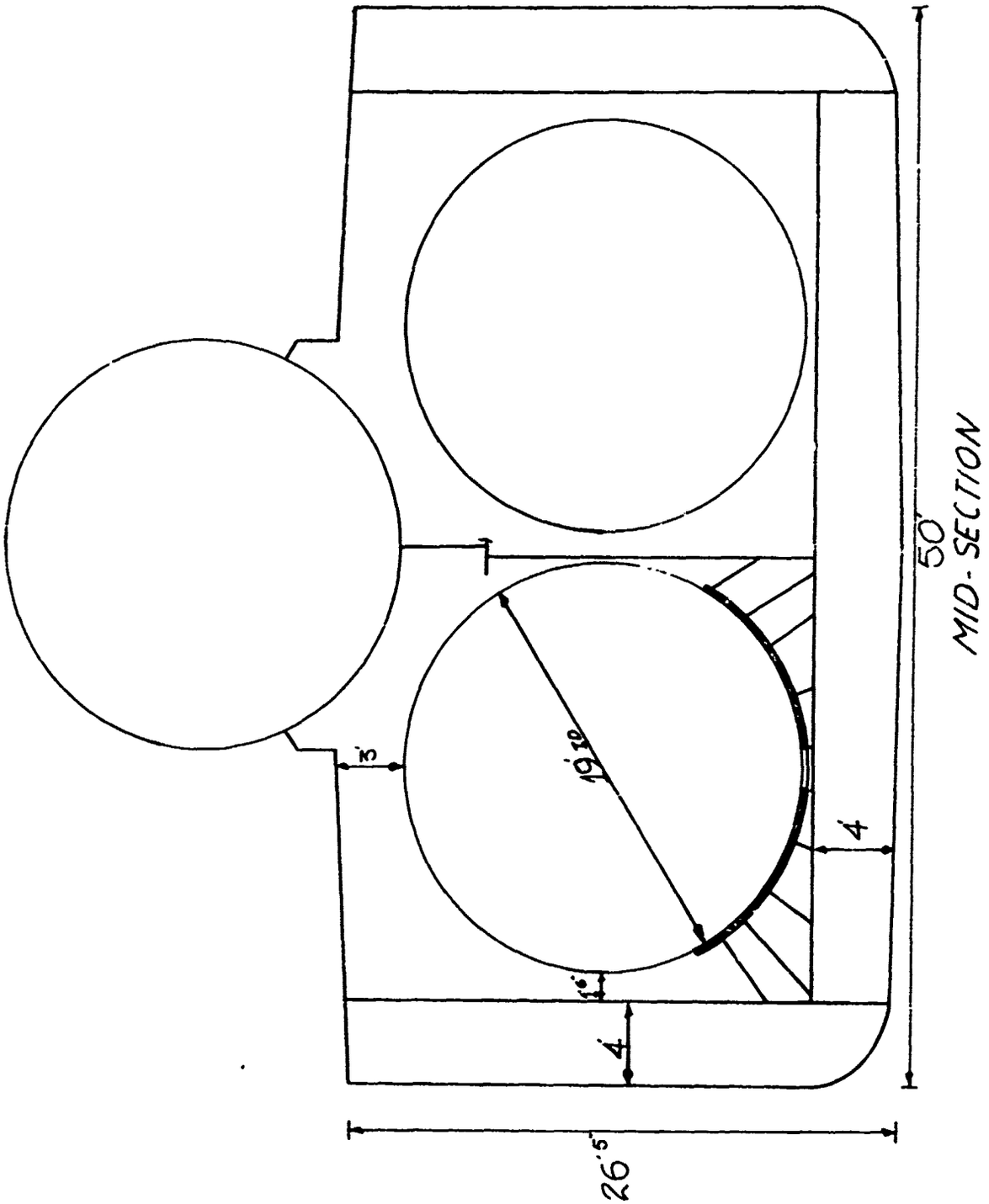
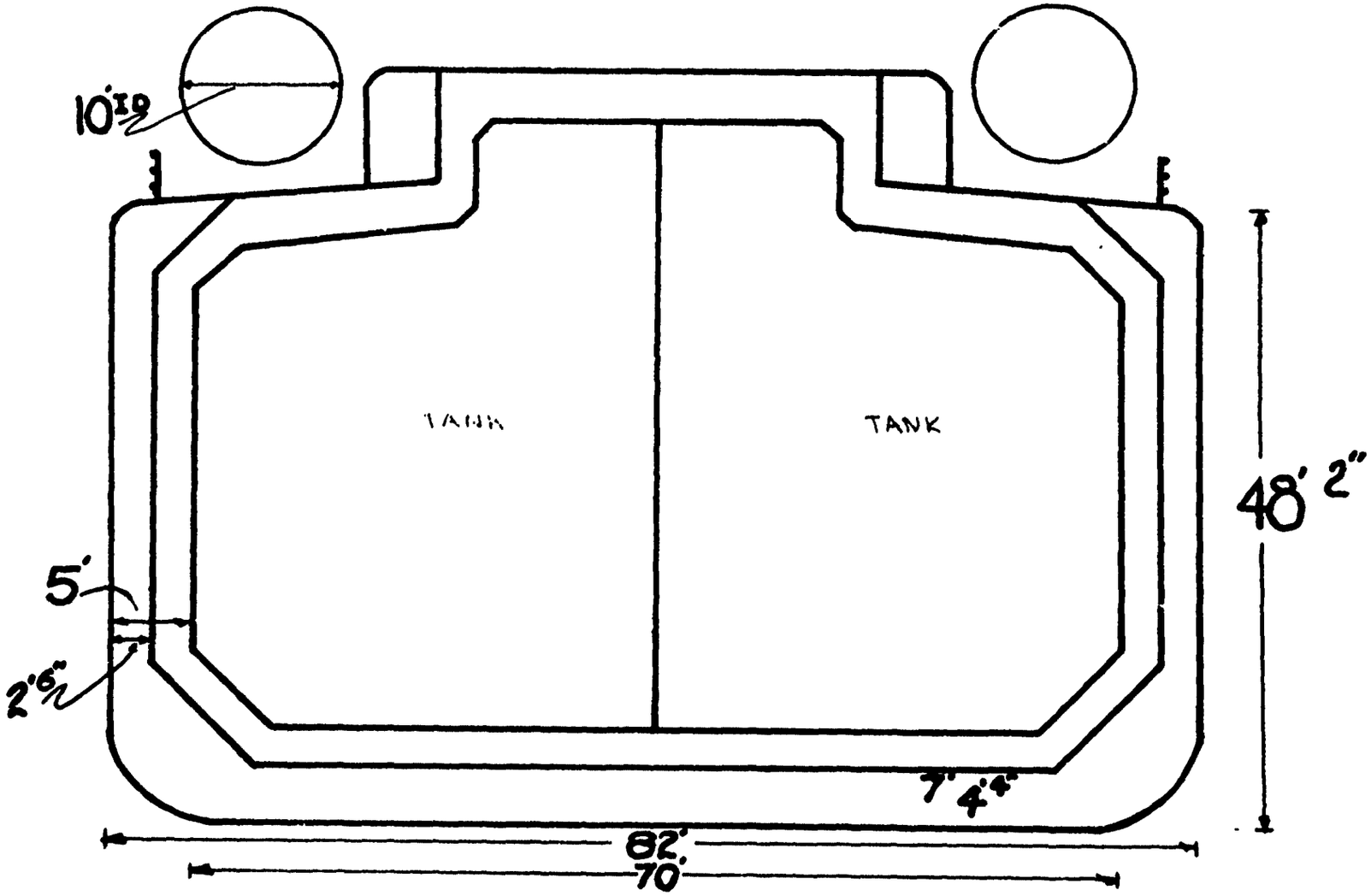
Section D - Tank Ships

1d Cross-section of a ship - carries refrigerated LPG, NH_3, butadiene, etc.

2d Cross-section of a ship - carries Ethylene oxide, LPG, NH_3, vinyl chloride, butadiene, etc.

3d View of ship - carries molten sulfur


3'
19'10"
1'
4'
4'
26'5"
50'
MID-SECTION



MID-SECTION

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APPENDIX 2: FORMULAE FOR CALCULATION OF VAPOR FLOW CAPACITY IN PRESSURE RELIEVING SYSTEMS

The tabulations and analysis which follow were prepared by Mr. Alan Schneider, working under the direction of the Technical Advisor to the Hazardous Materials Division of the U. S. Coast Guard, as an input to the more complete understanding of the various formulae which have evolved over the years for calculations of pressure relief capacity.[69]

Since the first organized presentation in 1925, a number of investigators and authors have used various approaches to calculate the amount of vapor or gas which must be released to avoid excessive pressure build-up and eventual rupture of a vessel containing bulk liquid and gases. Adequate venting would insure that time for emergency control would be extended, hopefully to permit necessary action to prevent rupture.

It will be noted that most presentations use some specified heat flux, multiplied by an area factor. This area is frequently discounted by using a fractional exponent. In the tabulation, the various formulae or specifications have been approached to reflect these various requirements, and special note taken of the <u>intended</u> purpose of the method, as well as any environmental factors used to modify the calculations.

Sections of Appendix 2 are as follows:

	Page
Organization of the Tabulation	A2-2
Tabulations of Formulae*	A2-4
Formula References	A2-17 - A2-21

*Tabulations of Formulae:

1 thru 5	A2-6
6 thru 10	A2-7
11 thru 15	A2-8
16 thru 20	A2-9
21 thru 25	A2-10
26 thru 30	A2-11
31 thru 35	A2-12
36 thru 40	A2-13
41 thru 44	A2-14
45 and 46	A2-15
47 thru 51	A2-16

ORGANIZATION OF THE TABULATIONS
APPENDIX 2

	Formula No.	
1. Function of Area Convertible to Btu/hr		
A. Area to the 2/3		
Stroop-Maker - 1925	1	
B. Area to the .80		
Bureau Veritas - 1962	2	(1)
Det Norske Veritas - 1962	3	
Bureau Veritas - 1962	4	(2)
C. Area to the .82		
Petroleum Administration for War - 1943	5	
Nippon Kaiji Kyokai - 1964	6	
USCG - 1956	7	
American Petroleum Institute, Standard 2510 - 1957	8	
USCG - 1969	9	
American Standards Assoc., K61.1, CGA - 1960	10	
USCG - 1968	11	
Rubber Reserve	12	
National Fire Protection Assoc. - 1966	13	
USCG - 1968	14	
Cummings, API Proposed - 1960	15	
Cummings, Report to API, 1950	16	
Heller, Phillips Petroleum Co. - 1954	17	
American Bureau of Shipping - 1965	18	

Organization of the Tabulations (cont'd)

	Formula No.	
2. Various Methods Not Convertible to Btu/hr		
A. Interstate Commerce Commission Formulae		
1. Valve Size Directly		
ICC - 1962	37	
ICC - 1962	38	
ICC - 1969	39	(1)
ICC - 1969	40	(2)
ICC	41	
ICC	42	
B. Miscellaneous Non-ICC Methods		
1. Giving Results in cu. ft. air/min		
CGA - 1963	43	
2. Giving Results in Valve Sizes		
Duggan, Gilmour & Fisher - 1943	44	(1)
State of California, Dept. of Industrial Relations - 1934; revised 1946	45	
Fetterly, John F., Bureau of Explosives, Annual Report No. 22, Nov. 27, 1928	46	
3. Non-Liquefied Gases		
Duggan, Gilmour & Fisher - 1943	47	(2)
4. Fixed Valve Size Method		
National Fire Protection Assoc. - 1962	48	
5. Maximum Pressure Methods		
Lloyds of London - 1964	49	
3. Valve Equations		
Davidson McArdle - 1929	50	
USCG - 1968	51	

C. Area to the .82, continued — Formula No.

USCG - 1968 19

Compressed Gas Assoc. - 1963. 20

Association of American Railroads - 1968. . . . . 21 (1)

French Government - 1968. 22

D. Area to the 1.00

National Fire Protection Association - 1962 . . . . . 23 (1)

National Fire Protection Association - 1962 . . . . . 24 (2)

National Fire Protection Association - 1962 . . . . . 25 (3)

Association of American Railroads - 1968. . . . . 26 (2)

American Petroleum Inst.Suggested (F.L.Maker) 1956. 27

Handbook Butane Propane Gases - 1942. 28

National Fire Protection Association - 1954 . . . . . [illegible]

Lauderback, Eastman, Texas - 1964 30

Rubber Reserve - 1944 31

Lauderback, Eastman, Texas - 1964 . . . . . 32 (2)

Lauderback, Eastman, Texas - 1964 . . . . . 33 (3)

Dow Chemical, Diss, Karam, Jones, 1961. 34

E. Mixed

American Petroleum Institute RP2000-1966 35

National Fire Protection Assoc.

(Table based on Am. Petroleum Inst.RP2000-1966) 36

TABULATIONS OF FORMULAE

Explanation of information presented in rows (A) through (J) of the following tabulations:

(A) Original Equation

The original form of the equation is presented as in the publication cited, using the original symbols and the original units.

(B) Equivalent Equation

This form results from converting the original equation into a form which sets a rate of heat input (in Btu per hour) equal to a constant times the area raised to a power. The area is that considered significant in the original equation and does not necessarily include the total tank area. (see Row D, Area Considered)

(C) Originator; Date

The originator cited is the person, company, or group wh [illegible] proposed this formulae; the date is that of the publication in which it can be located.

(D) Area Considered

Since various methods consider areas in different ways, this column defines area cited by the original publication, in ft^2.

(E) Environmental Factors

In some equations, consideration is given certain environmental factors, such as insulation. These are defined where appropriate.

(F) Flame Height

The portion of the tank walls exposed to fire is in some formulae limited by indicating a flame height above which the tank surface will not be included in the exposed area.

(G) External Temperature

Actual temperature close to the outer surface of the tank, where given, in degrees F.

(H) Use by Various Groups

Indicates who required or endorsed the equation, including such advisory groups as the Compressed Gas Association and the National Fire Protection Association.

(I) Scope of the Method

Limitations of the method such as type of tank and type of cargo are indicated.

(J) Units Calculated

This row states the unit in which the numerical results of the calculation is stated.

Explanation of Information

Each vertical column contains an equation which has been developed for estimation of heat input to a tank exposed to fire from which vapor generation can be calculated, or an equation which in some other way relates fire exposure to vapor relieving capacity.

The conversions of formulae to evolve equivalent equations have been estimated, using the best available information. However, the resulting equivalent equation are believed sufficiently accurate to permit comparisons among the various estimation procedures.

	1	2	3	4	5
(A) ORIGINAL EQUATION	$Q = 48{,}000A^{2/3}$	$W = 49S^{.8}$	$Q = FS^{.8}$	$W = 6 \times 10^{4} .FS^{.8}$	$Q = 16{,}000A^{.82}$
(B) EQUIVALENT EQUATION X 10^{-3}	$Q = 48\ A^{2/3}$	$Q = 7.25\ A^{.8}$ PROPANE PROP.	$Q = 29.6A^{.8}$	$Q = 35.4\ A^{.8}$	$Q = 16.0A^{.82}$
(C) ORIGINATOR DATE	STROOP MAKER 1925	BUREAU VERITAS 1962	DET NORSKE VERITAS 1962	BUREAU VERITAS	PETROLEUM ADMINISTRATION FOR WAR 1943
(D) AREA CONSIDERED	INTERNAL WETTED SURFACE	LATERAL WALLS	TOTAL OUTSIDE SURFACE	TOTAL EXTERNAL AREA	TOTAL SURFACE EXPOSED
(E) ENVIRONMENTAL FACTORS			.5 INSUL. ON DECK .5 HOLD .24 HOLD, INERT GAS	$\frac{3K}{1+3K}$ ABOVE DECK K=TOTAL THERMAL CONDUCTIVITY .5 IN HOLD	.2 for 2" WELL BOUND INSULATION
(F) FLAME HEIGHT	50 FT ABOVE GRADE				20 FT ABOVE GRADE
(G) EXTERNAL TEMPERATURE					
(H) USE BY VARIOUS GROUPS		BUREAU VERITAS	REQUIRED IN NORWAY	REQUIRED IN FRANCE	
(I) SCOPE OF METHOD	GENERAL	SHIPS CARGO LPG TANKS	SHIPS CARGO TANKS	SHIPS	GENERAL
(J) UNITS CALCULATED	TOTAL HEAT INPUT, Btu/hr	CUBIC M/HR AIR AT STANDARD CONDITIONS	TOTAL HEAT INPUT, Kcal/hr	TOTAL HEAT INPUT, Kcal/hr	HEAT INPUT TOTAL, Btu/hr

	6	7	8	9	10
(A) ORIGINAL EQUATION	$Q = 37,[illegible]A^{.82}$	$Q = 21,[illegible]A^{.82}$	$Q_a = 32.6FA^{.82}$	$Q = 56.526A^{.82}$	$CFM = 22.1A^{.82}$
(B) EQUIVALENT EQUATION X 10^{-5}	$Q = 20.[illegible]A^{.82}$	$Q = 21.6A^{.82}$	$Q = 21.0A^{.82}$ PROPANE PROP.	$Q = 34.5\ A^{0.82}$ Only CHLORINE	$Q = 34.5\ A^{0.82}$ Only AMMONIA
(C) ORIGINATOR DATE	NIPPON KAIJI KYOKAI 1963	U.S.C.G. TENTATIVE STANDARDS 1956	API STANDARD 2510 1957	USCG 1968	ASA K61.1 CGA 1960
(D) AREA CONSIDERED	35% OF VERTICAL SIDE WALL AREA	35% VERTICAL SIDE WALL AREA	WETTED SURFACE	TOTAL OUTSIDE SURFACE	TOTAL EXTERNAL AREA
(E) ENVIRONMENTAL FACTORS	.5 FOR METAL SCREEN	F = .5 FOR METAL SCREEN WALL	.3→ 1" INSUL. .15→ 2" INSUL. .075→ 4" INSUL. WITH 1"→ 4 BTU / HR FT^2 °F		$CFM = 2.8UA^{.82}$ U=TOTAL THERMAL CONDUCTIVITY
(F) FLAME HEIGHT			25 FT ABOVE GRADE		
(G) EXTERNAL TEMPERATURE			1700°F		
(H) USE BY VARIOUS GROUPS	TENTATIVE REQUIREMENTS IN JAPAN	TENTATIVE USCG (USED IN 1963) NIPPON KAIJI KYOKAI	API	46 CFR 98.20-45 UP TO 1969	ASA CGA
(I) SCOPE OF	LIQ. ATM. PRESS. FLAM. GASES, BELOW 0°C. SHIP CARGO TANKS	GRADE A INFLAM. LIQ. LPG, PRESSURIZED TRANSPORT BY SHIPS	LPG	LIQUID CHLORINE	ANHYDROUS AMMONIA
(J) UNITS CALCULATED	TOTAL HEAT INPUT, Kcal/hr	TOTAL HEAT INPUT, Btu/hr	FT^3 AIR/MIN AT STANDARD CONDITIONS	TOTAL HEAT INPUT, Btu/hr	FT^3/MIN AIR AT STANDARD CONDITIONS

	11	12	13	14	15
(A) ORIGINAL EQUATION	$Q = 26.8A^{.82}$	$Q = 32{,}000A^{.82}$	$(cfm)_a = 53.632A^{0.82}$ For propane at 300psig	$Q = 21.63A^{.82}$	$\frac{Q}{HA} = Q_f E F_1 F_2$
(B) EQUIVALENT EQUATION X 10^{-5}	$Q = 27.6A^{.82}$ E.O.* $Q = 29.4A^{.82}$ P.O.**	$Q = 32.0A^{.82}$	$Q = 34.5A^{0.82}$ PROPANE PROP.*	$Q = 33.5A^{.82}$ AMMONIA PROP.	$Q = 34.5A^{.82}$
(C) ORIGINATOR DATE	USCG 1968	RUBBER RESERVE	NFPA ASA 1966	USCG 1968	CUMMINGS API PROPOSED 1951
(D) AREA CONSIDERED	TOTAL OUTSIDE SURFACE	TOTAL EXTERNAL AREA	TOTAL OUTSIDE SURFACE	TOTAL OUTSIDE SURFACE	WETTED SURFACE AT 100% CAPACITY
(E) ENVIRONMENTAL FACTORS		.75 FOR WATER APPLICATION; .20 FOR 2" WELL BOUND INSULATION	*(for propane at conditions: T = 600° R, L = 110 Btu/lb M = 44.09, Z=0.70 C = 330, P=300psig)	.5 FOR INSULATED TANK	THERM. COND. F_2: 2.0→.3, 1.0→.15, .2→.075; F_1 = .6 DRAINAGE: FOR CONTROLLED FIRE ONLY
(F) FLAME HEIGHT		20 FT ABOVE GRADE			
(G) EXTERNAL TEMPERATURE					1800°F
(H) USE BY VARIOUS GROUPS	46 CFR 40.05-60 40.10-60 UP TO 1969		NFPA 58-98 59-39 ASA Z106.1 UNREFRIG. LPG 49 CFR 173-315	46 CFR 98.25-60 UP TO 1969	
(I) SCOPE OF METHOD	* ETHYLENE OXIDE ** PROPYLENE OXIDE SHIP CARGO TANKS	GENERAL		ANHYDROUS AMMONIA SHIP CARGO TANKS	GENERAL
(J) UNITS CALCULATED	HEAT INPUT Btu/hr	HEAT INPUT, Btu/hr	FT^3/MIN AIR	FT^3/MIN AIR	HEAT INPUT, Btu/hr

	16	17	18	19	20
(A) ORIGINAL EQUATION	$Q = FGA^{.82}$ $G = \frac{633,000}{LC}\sqrt{ZT/M}$	$Q = FGA^{.82}$ $G = \frac{633,000}{LC}\sqrt{ZT/M}$	$Q = FGA^{.82}$ $G = \frac{633,000}{LC}\sqrt{ZT/M}$	$Q = FGA^{.82}$ $G = \frac{633,000}{LC}\sqrt{ZT/M}$	$Q = GA^{.82}$ $G = \frac{633,000}{LC}\sqrt{ZT/M}$
(B) EQUIVALENT EQUATION X 10^{-3}	$Q = 34.5A^{.82}$	$Q = 34.5A^{.82}$	$Q = 34.5A^{.82}$	$Q = 34.5A^{.82}$	$Q = 34.5A^{.82}$
(C) ORIGINATOR	CUMMINGS	BOLLIER, PHILLIPS PET. CO.	AM BUREAU OF SHIPPING	USCG	CGA
DATE	1954	1954	1965		1959
(D) AREA CONSIDERED	TOTAL OUTSIDE SURFACE	TOTAL OUTSIDE SURFACE	TOTAL EXPOSED SURFACE	TOTAL EXPOSED TO FIRE	TOTAL OUTSIDE SURFACE
(E) ENVIRONMENTAL FACTORS		NOT DESCRIBED	.1 OR METAL SCREEN BULKHEAD; .2 NON-PRESSURE TANK IN HOLD	.5 INSUL; .2 NON-PRESSURED TANKS IN HOLD; .1 NON PRESSURE IN HOLD, INSUL.	$Q = GA^{.82}$ $G = \frac{73.2}{LC}(1200-t)\sqrt{ZT/M}$
(F) FLAME HEIGHT					
(G) EXTERNAL TEMPERATURE					1200°F
(H) USE BY VARIOUS GROUP	CGA	ASME 59 11.45 (NON-REFRIGERATED)*	AMERICAN BUREAU OF SHIPPING	46 CFR 38.10-15	CGA PAMPHLET S1, PARTS 2,3; ICC MC 331 49 CFR 178.337-9
(I) SCOPE OF METHOD	GENERAL	LPG at UTILITY GAS PLANTS	GENERAL SHIP CARGO TANKS	GENERAL SHIP CARGO TANKS	CARGO, PORTABLE TANKS FOR COMPRESSED GAS, COMPRESSED GAS STORAGE CONTAINERS
(J) UNITS CALCULATED	FT^3/MIN AIR	FT^3/MIN AIR	FT^3/MIN AIR	FT^3/MIN AIR	FT^3/MIN AIR
		*Other than DOT specification containers			

	21	22	23	24	25
(A) ORIGINAL EQUATION	$Qa=\frac{633,000}{LC} A^{.82} \sqrt{\frac{ZT}{M}}$	$Q=640\ S^{.82}$	$Q=6,000\ A$	TABLE Gal. Cap Ft^3/hr 1000 25,300 100,000 363.000 Unlimited 648,000	TABLE Gal. Diam. In* 1,000 2.5 100,000 8.75
(B) EQUIVALENT EQUATION X 10^{-5}	$Q=34.5A^{.82}$	$Q=89.4A^{.82}$ PROPANE PROP.	$Q=6.0A$	$Q=6000A$	$Q=6000A$
(C) ORIGINATOR DATE	Asso. of Amer. Railroads 1962	French Gov't 1968	NFPA 1962	NFPA 1952	NFPA 1952
(D) AREA CONSIDERED	Total Outside	Total Surface	Wetted Surface	Volume(Not Area). For Tanks of 1,000 Gal. or More	Volume(Not Area). For Tanks of 1,000 Gal. or More
(E) ENVIRONMENTAL FACTORS	$Qa=\frac{44UA(1200-t)}{LC}\sqrt{\frac{ZT}{M}}$	Granted by M. M. Minister	Implies Heat Flux of 6,000 Btu/hr/ft^2		
(F) FLAME HEIGHT					
(G) EXTERNAL TEMPERATURE	1200°F				
(H) USE BY VARIOUS GROUPS	AAR; ICC 49 CFR 179.100-15 179.300-15 179.200-16 179.300-18	French Gov't	NFPA No.30	NFPA No.30; also NBFU PAMPHLET No. 30 p. 16	NFPA No. 30; also NBFU PMAPHLET No. 30 p. 23
(I) SCOPE OF METHOD	TANK CARS	LIQ. GAS IN TANKS [illegible]	FLAM. LIQ.	ABOVE GROUND FLAM.LIQ. ATM. PRESSURE	ABOVE GROUND FLAM. LIQ. ATM. PRESSURE
(J) UNITS CALCULATED	Ft^3/Min Air	M^3/Hr Air	Heat Input Btu/hr	Ft^3/Hr Air	Diameter In Inches Of Free Circular Opening

*Values are given for 3 inches of H_2O, and 1, 2 1/2, 5 PSIG

	26	27	28	29	30
(A) ORIGINAL EQUATION	Qa = 12A	Q = 10,000A	W = 100A	Q =20,000A	$Q+KF\left[A+\frac{A_2}{2}+\frac{A_3}{4}\right]$
(B) EQUIVALENT EQUATION X 10^{-3}	Q = 6.96A PROPANE PROP	Q = 10.0A	Q = 15.0A BUTANE PROP	Q = 20.0A	Q = 20.0A
(C) ORIGINATOR DATE	Asso. of American Railroads	API [F.L. MAKER] SUGGESTED 1956	HANDBOOK BUTANE-PROPANE GASES 1942	NFPA 1962	LAUDERBACK, TEXAS EASTMAN 1964
(D) AREA CONSIDERED	TOTAL OUTSIDE AREA	ABOVE WATERLINE SIDE WALL AREA	TOTAL OUTSIDE AREA	WETTED SURFACE	TOTAL WETTTED SURFACE
(E) ENVIRONMENTAL FACTORS	Qa = 3UA	REDUCE Q PROPRTIONATELY TO REDUCTION IN HEAT ABSORBTIONS WITH INSULATION			F = .5 for insulation (2" calcium silicate
(F) FLAME HEIGHT					$A_1 \rightarrow$ 0-25 FT $A_2 \rightarrow$ 25-50 FT $A_3 \rightarrow$ 50-75 FT
(G) EXTERNAL TEMPERATURE					
(H) USE BY VARIOUS GROUPS	AAR; also 49 CFR; 179.100-15; 179.330-15 179.200-18; 179.400-18			NFPA	
(I) SCOPE OF METHOD	CAR TANKS > 400 SQ.FT.	LPG, ATM, COOLED SHIPS	PROPANE, BUTANE	FLAM. LIQ. SMALL TANKS*	GENERAL
(J) UNITS CALCULATED	FT^3/MIN AIR	HEAT INPUT Btu/hr	WEIGHT OF VAPOR GENERATION lb/hr	HEAT INPUT Btu/hr	HEAT INPUT Btu/hr
				*Under 100,000 Gal Cap.	

	31	32	33	34	35
(A) ORIGINAL EQUATION	$W = \frac{\left(\frac{Q}{A}\right)^{A}}{L}$ For Uninsulated Vessel	[illegible]	$Q = 40{,}000F\left(\frac{A_1+A_2}{2}+\frac{A_3}{4}\right)$	$Q = KA$ A — K Btu/hr/ft^2 0-100 — 20,000 100-500 — 15,000 500-1000 — 10,000 1000-5000 — 6,000 5000-7000 — 4,000	CFH = [illegible] For Areas over 2,800 sq.ft
(B) EQUIVALENT EQUATION X 10^{-3}	Q = 21.0A	Q=31.0A	Q=40.0A		
(C) ORIGINATOR DATE	RUBBER RESERVE 1944	Same as 30	Same as 30	Dow Chemical Co. Biss, Karam & Jones 1947	API RP2000 1965
(D) AREA CONSIDERED	Wetted Area Times Factor From .5 to 1.0	Same as 30	Same as 30	Total Outside Surface	.5 Sphere [illegible] 0.0-1.0 for cylinders area Exposed Wetted Area
(E) ENVIRONMENTAL FACTORS	$\frac{Q}{A}$ = Heat Flux in Btu/hr/ft^2 Generally 20 to 22,000 Btu/hr/ft^2 A= surface of vessel exposed to fire, sq.ft. L= latent heat at allowable pressure for capacity rating Btu/lb	Same as 30	Same as 30	F — K 0-100 — 10,000 100-500 — 9,000 500-1000 — 8,000 1000-5000 — 5,000 5000-7000 — 3,000 With Insulation	.5 → 1" Insul → 2" Insul .075 → 4" Insul With 1" → 4 Btu/hr ft^2 .5 Drainage
(F) FLAME HEIGHT		Same as 30	Same as 30		[illegible] Ft Above [illegible]
(G) EXTERNAL TEMPERATURE					
(H) USE BY VARIOUS GROUPS	RUBBER RESERVE			Dow CHEMICAL	API RP2000 (FLAME [illegible]) Amer. Insurance Assn.
(I) SCOPE OF METHOD	GENERAL	[illegible]	GENERAL		[illegible] PS. [illegible] STORAGE
(J) UNITS CALCULATED	[illegible]		HEAT INPUT Btu/hr	[illegible]	[illegible]

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	36	37	38	39	40
(A) ORIGINAL EQUATION	TABLE BASED ON API RP 2000	A =1.25 in^2 +.0025 Water Cap. in Gal	<40 PSIG 1 $in^2/35\ ft^2$; 30 PSIG 1 $in^2/350\ ft^2$+ 9 $in^2/350\ ft^2$	<1 Gal, $\frac{.0055\ in^2 \text{ vent area}}{\text{LBM } H_2O \text{ CAPACITY}}$ <30 Gal >1 Gal, $\frac{.0012\ in^2 \text{ vent area}}{\text{LBM } H_2O \text{ Capacity}}$	Safety Vent .1023 in. Diam.
(B) EQUIVALENT EQUATION X 10^{-3}	NONE	NONE			
(C) ORIGINATOR DATE	NFPA	ICC	ICC 1962	ICC 1962	ICC 1962
(D) AREA CONSIDERED	75% Exposed Area Basis	Not Considered	Total Externul Area	Volume Basis	Independent of Tank Size
(E) ENVIRONMENTAL FACTORS	INSULATION: 12,000 Cu Ft/hr or 6,000 cu Ft/hr For Each 350 sq.ft Surface Whichever is Greater TIMA Only			LAGGED STEEL DRUMS upt to 61 gal. capacity, Use Fused Plug, Not Vent	Vent Closed With Fusible Metal Yielding at 157°F
(F) FLAME HEIGHT					
(G) EXTERNAL TEMPERATURE					2 Coats of flame-retarding paint required
(H) USE BY VARIOUS GROUPS	NFPA 385-15; 30-23 ICC MC 307, 306 TIMA RP 22-196	ICC MC 305 300 302 303	ICC MC304	49 CFR 173.124 (a)(2) (a)(3) (a)(4)	49 CFR 173.124 (a)(1)
(I) SCOPE OF METHOD	CARGO TANKS, MOTOR VEHICLES	FLAM. LIQ. POISON LIQ. B POISON		ETHYLENE OXIDE COMPRESSED GAS CYL.	ETHYLENE OXIDE METAL CONTAINER 12 oz. Capacity
(J) UNITS CALCULATED	Ft^3/Min Air	Vent Area, Inches	Vent Area, Inches	Vent Area, Inches	Vent. Area, Inches

	41	42	43	44
(A) ORIGINAL EQUATION	CAPACITY TO PREVENT BUILD UP A PERCENTAGE OF TANK TEST PRESS.	CAP. TO REDUCE PRESS. IN TANK FROM 70% to 30% IN 3 MIN.	$Q_a = .00308^{PWc}$	$d = (97.35S_w/P+14.7)^{1/2} \frac{T}{Mr^2}^{1/4}$
(B) EQUIVALENT EQUATION X 10^{-3}				
(C) ORIGINATOR DATE	ICC CURRENT	ICC	CGA 1963	DUGGAN, GILMOUR,, FISHER 1943
(D) AREA CONSIDERED			BASED ON WATER CAPACITY IN LBS(NOT LESS THAN 12.5p.)	WETTED SURFACE EXPOSED 585 SQ FT.
(E) ENVIRONMENTAL FACTORS	82.5% TEST PRESSURE PRESS. TANK CAR, VINYL FLUORIDE, INHIB. LIQ. CO_2 85% TEST PRESSURE liq. H_2 90% TEST PRESSURE LPG and NH_3	AIR USED AS TEST PRESSURE	.5 FOR INSULATION. Qa = .00154 PW_c FOR NON-LIQ. GASES	
(F) FLAME HEIGHT				
(G) EXTERNAL TEMPERATURE				
(H) USE BY VARIOUS GROUPS	49 CFR 179.100-15 .102-14 .102-11 .400-18 ETC.	49 CFR 179.500-12 (ICC [illegible])	CGA	FIA (1963)
(I) SCOPE OF METHOD	PRESSURE TANK CARS AND FOR VINYL FLUORIDE, INH	SEAMLESS	NON LIQ & LIQ. GAS, IN ICC, BTC CYLINDERS 1000 POUNDS WATER CAPACITY	GENERAL
(J) UNITS CALCULATED	NOT SPECIFIED		FT³/MIN AIR	DIAMETER OF VALVE, INCH

	45	46
(A) ORIGINAL EQUATION	$A = \frac{.77A}{P}$	$A = \frac{[(B\pi U)+2E]C(t_1-t_3)}{LP50}\sqrt{\left(\frac{W_3}{W_1}\right)}$ (uninsulated unmachined steel containers) A = the area in sq. inches for a valve having a seat of any angle.
(B) EQUIVALENT EQUATION X 10^{-3}		
(C) ORIGINATOR DATE	STATE OF CAL. DEPT. OF INDUSTRIAL RELATIONS 1946	FETTERLY, BUR. OF EXPLOSIVES 1928
(D) AREA CONSIDERED	TOTAL SURFACE OF TANK	TOTAL OUTSIDE AREA UNDERNEATH INSULATION
(E) ENVIRONMENTAL FACTORS		$D = \frac{[(B\pi U)+2E]C(t_1-t_3)}{110LPN}\sqrt{\frac{W_3}{W_1}}$ (insulated containers) (assume insulation will not lose more than 50% of heat insulating properties when exposed to a temperature of 1200°F) D = the diameter of the safety valve in inches
(F) FLAME HEIGHT		
(G) EXTERNAL TEMPERATURE		1200°F
(H) USE BY VARIOUS GROUPS		USED IN 1942 BY ICC, NFPA: ICC 73.315; 49 CFR 173.315
(I) SCOPE OF METHOD	SMALL LPG TANKS	CYLINDRICAL TANKS
(J) UNITS CALCULATED	AREA OF RELIEF DEVICE In^2.	AREA OF RELIEF DEVICE, inches

	47	48	49	50	51
(A) ORIGINAL EQUATION	$d = \sqrt{\frac{.80355}{\sqrt{P+14.7}}}$	$d \geq 1.5$in	SAFETY VALVE CAPACITY TO PREVENT PRESSURE RISE ABOVE 110%	$W = 315ap^{C}\ \frac{M}{T}$	$Q = \frac{418\ AP}{T}$
(B) EQUIVALENT EQUATION X 10^{-3}					
(C) ORIGINATOR DATE	DUGGAN, GILMOUR, FISHER 1943	NFPA 196.	LLOYDS OF LONDON 1964	DAVIDSON McARDLE API - ASME 1929	USCG SAFETY VALVES 1968
(D) AREA CONSIDERED	TOTAL SURFACE AREA IN SQ.FT.			a = theo. area sq. in for C=1.0 = actual area, sq.in., for other values of C	A = valve discharge area in sq. in. T = temp. at flow conditions °R P = max. pressure psia Q = theo. flow of air, cu. ft./min STP
(E) ENVIRONMENTAL FACTORS					
(F) FLAME HEIGHT					
(G) EXTERNAL TEMPERATURE					
(H) USE BY VARIOUS GROUPS		FIRE PROTECTION HANDBOOK 1962, p. 9-14		46 CFR 162.018-7	46 CFR 162.018-7
(I) SCOPE OF METHOD	NON-LIQUEFIED GASES	UNENCLOSED FUEL OIL TANKS	GENERAL	VALVE EQUATION	VALVE EQUATION
(J) UNITS CALCULATED	d = DIAMETER OF RELIEF DEVICE, INCHES p = PRESSURE IN psig.	VENT DIAMETER, INCHES			

FORMULA REFERENCES

Reference No.		Formula No.
2.1	Stroop-Maker, 1925. This formula was suggested as a graphical curve by Mr. D.V.Stroop, American Petroleum Institute. Mr. F.L.Maker, Standard Oil Company of California, derived the equation form as presented here.[73] (Attempts to secure a salutation of the original publication of this formula have been unsuccessful.)	1
2.2	Bureau Veritas, International Register for the Classification of Shipping and Aircraft, Paris, Sept. 1962. General Technical Conditions Covering the Sea Transport of Liquefied Natural Gas, With Annex Concerning the Sea Transport of Liquefied Petroleum Gas Under Atmospheric Pressure.	2,4
2.3	Det Norske Veritas Research Department, Oslo, Norway, April, 1962, p. 20 Recommendations for the Design and Construction of ships for Transport of Liquefied Gas.	3
2.4	Office of the Petroleum Administration for War, Wash.,D.C. Jan.4-5, 1943. Wartime Recommendations of the Safety Valve Standardization Conference.[73]	5
2.5	Nippon Kaije Kyokai, Tokyo, Japan, 1964. Tentative Requirements for the Construction and Survey of Ships Carrying Liquefied Flammable Gases at Low Temperatures.	6
2.6	U.S.Coast Guard. Revised by API, Special Committee on the Transportation of LNG by Water thru Aug. 22,1956, and edited by the Sub-Committee on October 30, 1966. Tentative Standards for Transportation of Liquefied Inflammable Gases at Atmospheric Pressure.	7

Reference No.		Formula No.
2.7	American Petroleum Institute, Standard 2510, June, 1957. The Design and Construction of Liquefied-Petroleum-Gas Installations at Marine and Pipeline Terminals, Natural-Gasoline Plants, Refineries and Tank Farms.	8
2.8	U. S. Coast Guard. Code of Federal Regulations, Title 46, 98.20-45. This formula was in effect in 1968 but removed in 1969 in favor of the more generalized formula No. 18.	9
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2.10	U. S. Coast Guard. Code of Federal Regulations, Title 46, 40.05-60 and 40.10-60, 1968. This formula was in effect in 1968 but was removed in 1969 in favor of the more generalized formula No. 18. (Although the same formula was used for both EO and PO they have different properties)	11
2.11	Rubber Reserve. Tests by Rubber Reserve at Baytown, Texas (Nov. 19, 1943) caused by the Petroleum Administration for War (P.A.W.). Test showed that a heat flux of 16,000 Btu/hr. sq. ft., was inadequate, resulting in the change to 32,000 Btu/hr. sq. ft.[73]	12
2.12	National Fire Protection Assoc., 58-98; 59-38; 1966. Code of Federal Regulations, Title 49, 173.315. 1966.	13
2.13	U. S. Coast Guard. Code of Federal Regulations, Title 46, 98.25-60, 1968. This formula was in effect in 1968 but was removed in 1969 in favor of the more generalized formula, No. 18.	14

Reference No.		Formula No.
2.14	Cummings, L. W. T., American Petroleum Institute Bulletin, RP520, 2nd ed., Sept. 1960.	15
2.15	Cummings, L. W. T., Report to API Committee on Pressure Relieving Systems, Nov. 8, 1950.	16
2.16	Heller, Frank J., Phillips Petroleum Bulletin E-2, Jan. 1954. How to Size Safety Relief Devices.	17
2.17	American Bureau of Shipping, Feb. 9, 1965. Proposed Section 44. Vessels Intended to Carry Liquefied Gases.	18
2.18	U. S. Coast Guard. Code of Federal Regulations, Title 46, 38.10-15 1968.	19
2.19	Compressed Gas Association. Pamphlet S-1, Parts 2 and 3, N. Y. 1963. Safety Relief Device Standards.	20
2.20	Association of American Railroads. 1962, Chicago, Illinois. Specifications for Tank Cars. (Code of Federal Regulations, Title 49, 179.100-15; 179.200-18; 179.300-15; 179.400-18.1968)	21
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Reference No.		Formula No.
2.23	Association of American Railroads. (Ref. Same as 2.20)	26
2.24	American Petroleum Institute Suggested (F. L. Maker) Comments for the API Subcommittee on Liquefied Petroleum Gases on the Proposed Revisions to the U. S. Coast Guard Standards for Transportation of Liquefied and Flammable Gases. Wash. D. C. April 23, 1956, p. 22.	27
2.25	Handbook Butane Propane Gases. 3rd ed., edited by Arthur Rohman and Justus M. Krappe, 1942	28
2.26	National Fire Protection Assoc. Fire Protection Handbook, 11th ed., 1954. Chpt. 12, p. 258	29
2.27	Lauderback, W. H., Safety Director, Texas Eastman Co. Longview, Texas, 1964. Test to Determine Relief Valve Sizing	30
2.28	Rubber Reserve, 1944. This method has been used by a large refining company for about twenty years. The Office Reserve advocated the use of this method during recent years.[73]	31
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2.34	ICC. Agent T. C. George's Tariff No. 19, 78.325.9 (MC 304), 1962. (This specification is now obsolete)	38
2.35	ICC. Code of Federal Regulations, Title 49, 173.124. 1969	39,40
2.36	ICC. Code of Federal Regulations, Title 49, 179.100-15, 179.102-4, 179.102-11, 179.400-18, 179.200-18, 179.700-15. (This is a largely useless method in that it does not explain how to achieve the capacity in terms of actual dimensions)	41
2.37	ICC. Code of Federal Regulations, Title 49, 179.300-12 (Specification ICC-107A). (This method is virtually useless because it expresses valve capacity in terms of a test rather than a formula. This cannot be easily related to fire conditions)	42
2.38	Compressed Gas Assoc. CGA, 3rd ed., 1963. Safety Relief Standards, Part 1, Cylinders for Compressed Gases.	43
2.39	Duggan, Gilmour & Fisher. Chemical Engineering, June 1943. Requirements for Relief of Overpressure in Vessels Exposed to Fire.	44

Reference No.		Formula No.
2.40	State of California. Liquefied Petroleum Gases Safety Orders issued by Div. of Industrial Safety, Dept. of Industrial Relations of the State of California. Eff. March 12, 1934; revised, eff. Jan. 1, 1946.[73]	45
2.41	Fetterly, John. F. The Determination of the Relief Dimensions for Safety Valves on Containers in Which Liquefied Gas is Charged and When the Exterior Surface of the Container is Exposed to a Temperature of 1200°F. Nov. 27, 1928. Reprinted from Bureau of Explosives Annual Report No. 22.[73] Also ref. to CFR, Title 49, 173.315	46
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2.43	National Fire Protection Assoc., Fire Protection Handbook, 1962. p. 9-14	48
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2.45	Davidson-McArdle. Oil and Gas Journal, Aug. 29, 1929.[73,27]	50
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APPENDIX 3: FORMULAE FOR SIZING PRESSURE RELIEF VALVES

By assuming adiabatic and reversible flow and that the fluid follows the ideal gas law, the maximum mass flow rate of a safety or relief valve may be determined by application of the ASME Code[63]

$$W = CKAp \left[\frac{M}{T}\right]^{1/2} \qquad [3\text{-}1]$$

In this equation

W = mass flow rate of gas or vapor, lb/hr

C = constant (with dimension) for gas or vapor which is a function of the specific heats ratio, $k = c_p/c_v$

K = coefficient of discharge, dimensionless

A = actual discharge area, orifice or the nozzle throat area, sq.in.

p = upstream pressure. This is the set pressure multiplied by 1.10 or 1.20 (depending on the permissible pressure), plus the atmospheric pressure, psia

M = molecular weight of gas or vapor, lbm/lb mole

T = temperature of the gas at the relieving conditions, °R

Equation [3-1] assumes that the absolute upstream and downstream pressures permit critical flow which is the necessary condition for the maximum flow rate. For real gases an empirical correction can be made to Eq. [3-1] by using the equation state in the form

$$pv = ZRT \qquad [3\text{-}2]$$

where

v = gas specific volume, cu. ft./lb

R = gas constant

Z = compressibility factor, dimensionless

Consequently, Eq. [3-1] becomes

$$W = CKAp \left[\frac{M}{ZT}\right]^{1/2} \qquad [3\text{-}3]$$

Values of C for different k are given in Fig. 5.

For a liquid cargo the vapor flow rate through the pressure relief valve is given by

$$W = \frac{Q}{L} \qquad [3\text{-}4]$$

where Q is the amount of heat absorbed by liquid cargo, given by Eq. [2], page 29.

$$Q = qFEA, \text{ Btu/hr}$$

and

L = latent heat of vaporization at relieving conditions, Btu/lb

Assume that a given relief valve is tested with dry air at 60°F (520°R); the pressure differential is sufficient for critical flow. For this case Eq. [3-3] can be written as

$$W_a = C_a KAp \left[\frac{M_a}{Z_a T_a}\right]^{1/2} \qquad [3\text{-}5]$$

solving for KAp

$$KAp = \frac{W_a}{C_a} \left[\frac{Z_a T_a}{M_a}\right]^{1/2} \qquad [3\text{-}6]$$

where

C_a = 356 (for air k = 1.4)

M_a = 28.97, Z_a = 1.0

T_a = 520 °R

Substituting these values in [3-6] one obtains

$$KAp = 0.0119\ W_a \qquad [3\text{-}7]$$

When this relief valve is designed for use on a liquid cargo container, then the air rated capacity of the valve can be determined, by substituting [3-4] and [3-7] in Eq. [3-3], as

$$W_a = \frac{Q}{0.0119\ LC} \left[\frac{ZT}{M}\right]^{1/2} \qquad [3\text{-}8]$$

where,

W_a = air rated equivalent capacity, converted to pounds of air per hour at 60°F inlet temperature

This equation assumes that either K in Eq. [3-7] is independent of pressure p, or that the air rated capacity is determined under the pressure conditions of the equivalent vapor flow.

Air equivalent rate of discharge in cu.ft. per minute of air at standard conditions (60°F and 14.7 psia) is given by

$$(cfm)_a = \frac{W_a\ v_o}{60} \qquad [3\text{-}9]$$

v_o = 13.1 ft^3/lb, specific volume of air at 60°F, 14.7 psia

Substituting [3-8] in [3-9]

$$(cfm)_a = 18.34\ \frac{Q}{LC} \left[\frac{ZT}{M}\right]^{1/2} \qquad [3\text{-}10]$$

When the amount of heat to be absorbed by the liquid cargo, Q, is known, air equivalent capacity of the pressure relief valve can be calculated from Eq. [3-10].

If the specific heats ratio k or the isentropic expansion coefficient is not known, it is suggested to let C = 315, the smallest value in Fig. 5. This may result in somewhat larger relief valve size which is not objectionable. In addition if Z = 1 is used, Eq. [3-3] becomes

$$W = 315\ KAp \left[\frac{M}{T}\right]^{1/2} \qquad [3\text{-}11]$$

where

W is in lb/hr

A = discharge area, sq. in.

p = upstream pressure, psia.

Considering the saturated steam at atmospheric pressure

$T = 672°R$, $M = 18.016$

Substituting these values in [3-11]

$$W_s = 51.5\ KAp \qquad [3\text{-}12]$$

This equation is the ASME Code formula[63] for official capacity rating of steam pressure relief valves. The rated capacity W_s is given in pounds of steam per hour. At atmospheric conditions compressibility factor of saturated steam is slightly less than unity. The coefficient C, on the other side, is 350 (k= 1.329 for low pressure steam) rather than 315 used in Eq.[3-11]. This is not objectionable, since it allows about 10% additional discharge area.

When steam is superheated a correction factor is used in Eq.[3-12]. For further information concerning this matter see reference 2.

APPENDIX 4: TYPICAL PHYSICAL AND CHEMICAL PROPERTIES SUGGESTED FOR EVALUATION OF PRESSURE RELIEF REQUIREMENTS

The following list is not intended to be all inclusive, but it is suggested to illustrate the type of information on a cargo which the designer of a pressure relief system should have for full consideration of pressure relief requirements.

1. Name (Chemical name of major constituent; trade name). (If mixture give composition, or normal range.
2. Chemical formulae of principle constituents.
3. Inhibitors, antioxidants, and other additives (with amounts).
4. Thermodynamic Properties:

   Molecular weight

   Vapor Pressure @ 68°F (20°C)

   Boiling Point at 1 atm.

   Freezing point

   Critical temperature

   Critical pressure

   Critical density

   Specific volume of liquid at significant temperatures

   Specific volume of vapor at significant temperatures

   Specific heat of liquid and vapor at significant temperatures

   Latent heat of evaporation at normal boiling point

   Latent heat of fusion at freezing point

   Temperature at flowing pressure and start-to-discharge pressure.

   Compressibility factor

4. Thermodynamic Properties, continued:

   Coefficient of expansion for temperature range involved in shipment

   Flammable limits in air

   Heat of combustion

   Decomposition and pyrolysis products in air

   Autoignition (or AIT) temperature

   Shock sensitivity

5. Chemical Reactions

   a. Reactivity with air

   b. Reactivity with water/moisture

   c. Reactivity with normal material of construction

   d. Reaction with heat and/or catalyst (such as polymerization)

6. Physiological Effects

   a. Toxicity by inhalation and/or skin contact

      (1) maximum allowable concentrations and threshold limit values

      (2) short-term limits (acute effects)(employees) (general public)

      (3) lethal exposure

      (4) odor threshold

7. Ecological Effects

   a. Water

   b. Air

   c. Soil

8. Ignition from external source

   a. Flash point (closed-cup)

   b. Fire point

   c. Elevated Temperature

APPENDIX 5: HEAT TRANSFER TO CARGO CONTAINERS WHEN WALLS ARE SUBJECTED TO FIRE

Calculation of the radiant heat transfer rates from fires to the surrounding surfaces often involves considerable mathematical complexity. Therefore, in order to avoid the unnecessary rigor, the method of analysis should be chosen on the basis of the problem to be solved and the degree of accuracy required. For this reason, the present appendix is concerned mainly with a rather simplified analysis of the heat transfer from flames to a liquid cargo container. However, for a better understanding, the problem will be introduced first in a reasonably general form; then, after considering various assumptions, it will be simplified.

The presentation follows very closely the methods of Hottel and Sarofim.[48] Although these methods allow consideration of temperature gradients within the flame and along the enclosing surfaces, division of the system into isothermal zones results in large number of equations. Simultaneous solution of these equations provides the temperature distributions. Unless the problem is very simple, solution will require the use of a computer.

The sequence of procedures in the heat transfer calculations would be evident even with a much simpler model. Therefore, in the analysis it is assumed that:

1. An isothermal non-gray gas, temperature T_g, is surrounded completely by a gray and diffuse sink A_1 and a radiative equilibrium surface A_r, each at a uniform temperature, T_1 and T_r.

2. Surface of the cargo tank is represented by A_1, whereas A_r stands for the other surfaces enclosing the fire.

Matters concerning choice of the gas temperature T_g will be considered later. Although most engineering surfaces deviate to various degrees from the idealizations of being gray and diffuse, the assumption in item 1 above is adequate for purpose of the present discussion. A radiative equilibrium surface is one that absorbs radiant energy at the same rate at which it emits it. Any convection to the surface should be balanced by the heat loss through the wall. Use of this idealization for surfaces other than the surface of the cargo container simplifies the analysis and seems to be a reasonable approximation.

Following Hottel and Sarofim[48] the net heat flow from flames to the container surface A_1 can be written as

$$(\overrightarrow{GS_1})_R E_g - (\overleftarrow{GS_1})_R E_1 + h_1 A_1 (T_g - T_1) = \mathring{Q}_{net,1} \qquad [5\text{-}1]$$

$(\overrightarrow{GS_1})_R$ and $(\overleftarrow{GS_1})_R$ in this equation are "the directed-flux areas" between gas and the container surface A_1. Derviation of the directed flux has been given at the end of the present appendix along with the nomenclature.

The major contribution to the total heat transfer from flames and gases of conventional fuels is the thermal radiation from water vapor, carbon dioxide, soot and carbon monoxide. Calculation methods of the radiant heat flux from flames usually treat the luminous and the non-luminous contributions separately. Luminosity in flames originates either from pure chemical reaction or from glowing carbon particles at high temperatures. The presence of particles, at unknown quantities, in a luminous flame make the estimate of the flame emissivity rather difficult. When calculations are based on a mean flame temperature,total radiative transfer from gases to wall can be approximately estimated by adjusting the non-luminous gas emissivity to allow for the particle luminosity.

Experimental data indicate that the radiation from luminous flame is often much greater than that from non-luminous gases.[50] Therefore, the luminosity effects should be given proper consideration.

The total non-luminous radiation is obtained by adding the contributions from the individual gases. When the emission bands of two gases in a mixture do not interfere with each other, the emissive powers of two gases may be superimposed in order to get the total emissive power. If the emission spectra of these gases overlap, correction factors must be applied. For detailed information on the radiation properties of gases, see Ref. 59.

For engineering calculations the emissivity of any real gas can be visualized as due to the weighted sum of a sufficient number of gray gases

$$\epsilon_g = \sum_n a_{g,n}(1 - e^{-K_n L}) \qquad [5\text{-}2]$$

similarly absorption coefficient of the real gas is given by

$$a_{gs} = \sum_n a_{s,n}(1 - e^{K_n L}) \qquad [5\text{-}3]$$

$K=k_p p$, where the absorption coefficient k_p is based on partial pressure p of the radiating gas component. In Equation [5-2], a and k_p may be considered simply as the numbers which make the series in this equation fit the emissivity function of the real gas.

Similar to the total emissivity and the absorptivity expressions, the directed flux areas in Equation [5-1] can be written as

$$(\overrightarrow{GS}_1)_R = \sum_n [a_{g,n}(T_g)]\ [\overline{GS}_{1R}(K_n L)] \qquad [5\text{-}4]$$

$$(\overleftarrow{GS}_1)_R = \sum_n [a_{s,n}(T_1)]\ [\overline{GS}_{1R}(K_n L)] \qquad [5\text{-}5]$$

In these equations symbols "a" and "$\overline{GS}$" are functions of T and $K_n L$, respectively. Referring to Equation 8-20 of Hottel and Sarofim[48] for each gray gas component

$$\frac{1}{[\overline{GS}_1\ (K_n L)]_R} = \frac{1}{A_1}\left(\frac{1}{\epsilon_1} - 1\right) + \frac{1}{[\overline{GS}_1\ (K_n L)]_{R,black}} \qquad [5\text{-}6]$$

where

$$[\overline{GS}_1(K_n L)]_{R,black} = A_1 - (\overline{s_1 s_1}) - \frac{(\overline{s_1 s_r})^2}{A_r - \overline{s_r s_r}} \qquad [5\text{-}7]$$

If A_1 cannot see any part of itself, then $\overline{s_1 s_1} = 0$. In Eq. [5-7], the "directed-interchange areas, $\overline{s_i s_j}$" can be expressed in terms of "view factors, F_{ij}" as

$$\overline{s_1 s_1} = A_1 F_{11} \tau = (A_1 - A_r F_{r1}) \tau \qquad [5\text{-}8]$$

$$\overline{s_1 s_r} = A_r F_{r1} \tau \qquad [5\text{-}9]$$

$$\overline{s_r s_r} = A_r (1 - F_{r1}) \tau \qquad [5\text{-}10]$$

Using the same mean value of the transmittance $\tau = 1 - \epsilon_g$, the last four equations can be combined to give

$$[\overline{GS}_1 (K_n L)]_{R,black} = \epsilon_{g,n} \left[A_1 + \frac{A_r}{1 + \dfrac{\epsilon_{g,n}}{(1 - \epsilon_{g,n}) F_{r1}}} \right] \qquad [5\text{-}11]$$

where

$$\epsilon_{g,n} = \epsilon_{g,n} (K_n L, T_g)$$

References 49 and 71 contain tables of over 150 view factors that are available in the literature. For cargo containers $F_{11} = o$, thus $F_{r1} = A_1/A_r$ is obtained from Equation [5-8].

For this case Equation [5-11] becomes

$$[\overline{GS}_1]_{R,black} = A_1 \frac{\epsilon_{g,n} + M_n}{1 + M_n} \qquad [5\text{-}12]$$

where

$$M_n = \frac{\epsilon_{g,n}}{1 - \epsilon_{g,n}} \left(\frac{1 - N}{N} \right) \qquad [5\text{-}13]$$

$N = \frac{A_1}{A_1 + A_r}$ denotes the cold surface fraction.

Substitution of Equation [5-12] in [5-6] yields

$$\overline{GS}_{1R}(K_n L) = \frac{A_1}{\frac{1}{\epsilon_1} + \frac{1 - \epsilon_{g,n}}{M_n + \epsilon_{g,n}}} \qquad [5\text{-}14]$$

This equation is substituted in Equations [5-4 and 5-5]. Since each gas component is treated as a gray gas $\epsilon_{gs,n} = \epsilon_{g,n}$ is used in writing Equation [5-5].

As a special case if the real gas is completely surrounded by a black sink, $\epsilon_1 = 1$ and $N = 1$, then $M_n = 0$ for each component, and Equation [5-14] reduces to

$$\overline{GS}_{1R}(K_n L) = A_1 \epsilon_{g,n} = A_1 \epsilon_{gs,n} \qquad [5\text{-}15]$$

and from Equations [5-4 and 5-5]

$$(\overline{GS}_1) = \sum_n [a_{g,n}(T_g)] A_1 \epsilon_{g,n} = A_1 \epsilon_g \qquad [5\text{-}16]$$

$$(\overleftarrow{GS}_1) = \sum_n [a_{s,n}(T_1)] A_1 \epsilon_{gs,n} = A_1 \epsilon_{gs} \qquad [5\text{-}17]$$

Therefore, the net radiative heat transfer to the surface, in Equation [5-1] becomes:

$$(\overrightarrow{GS}_1)E_g - (\overleftarrow{GS}_1)E_1 = A_1(\epsilon_g E_g - \epsilon_{gs} E_1) \qquad [5\text{-}18]$$

This equation is true only when the sink surfaces are black and they enclose the gas completely.

As an approximation toward allowance for nongrayness, Equations [5-4, 5-5 and 5-14] may be based on the total gas emissivity and absorptivity, then

$$(\overrightarrow{GS}_1)_R = \frac{A_1}{\frac{1}{\epsilon_1} + \frac{1 - \epsilon_g}{M_\epsilon + \epsilon_g}} \qquad [5\text{-}19]$$

with,

$$M_\epsilon = \frac{\epsilon_g}{1 - \epsilon_g} \left(\frac{1-N}{N} \right) \qquad [5\text{-}20]$$

and

$$(\overleftarrow{GS}_1)_R = \frac{A_1}{\frac{1}{\epsilon_1} + \frac{1 - \alpha_{g1}}{M_\alpha + \alpha_{g1}}} \qquad [5\text{-}21]$$

where

$$M_\alpha = \frac{\alpha_{g1}}{1 - \alpha_{g1}} \left(\frac{1 - N}{N} \right) \qquad [5\text{-}22]$$

In this case $\epsilon_g \neq \alpha_{g1}$, since the gas, as a whole, is not gray. With this approximation Equation [5-1] can be written as

$$\frac{\dot{Q}_{net,\,1}}{A_1} = \frac{E_g}{1/\epsilon_1 + M_1} - \frac{E_1}{1/\epsilon_1 + M_2} + h_1 \left(T_g - T_1 \right) \qquad [5\text{-}23]$$

where

$$M_1 = \frac{1 - \epsilon_g}{M_\epsilon + \epsilon_g} \quad , \quad M_2 = \frac{1 - \alpha_{g1}}{M_\alpha + \alpha_{g1}} \qquad [5\text{-}24]$$

and

$$E_g = \sigma T_g^4 \quad , \quad E_1 = \sigma T_1^4 \qquad [5\text{-}25]$$

Equation [5-23] may be used for discussing, in a simplified manner, main characteristics of the heat flow from flames to the surface of a cargo container. Assuming that the overall heat transfer coefficient is large enough, the total heat flow $\dot{Q}_{net,\ 1}$ given by Eq. [5-23] will be absorbed by the liquid cargo inside the container. Eq.[5-23] shows that: (a) increasing the flame emissivity increases the heat flux, but not proportionately; (b) decreasing ε_1, when the flame emissivity is close to unity (i.e. very small M_1) produces a proportional decrease in heat flux; (c) increasing N (increased coverage of the walls by the sink surface A_1) decreases the heat flux $\dot{Q}/A_1$ in consequence of decreases in both M and the gas temperature.

The foregoing conclusions indicate that the radiant heat flux to a cargo tank can be reduced by: keeping the ratio of the fire exposed cargo container surface area A_1 as large as possible with respect to the adjacent enclosing surface areas; assuming that the insulation is used for reducing the heat flow; further reduction may be obtained by covering the insulation with a material of low emissivity. Large A_1 implies decreased space in the fire, thus enhancing occurence of the incomplete oxidation. This, in turn, may cause a decrease in the flame temperature, causing additional drop in the heat flux. The incomplete combustion, however, also tends to improve the flame emissivity by making the flame more luminous. Therefore, quantitative estimation of the effects of incomplete oxidation on the radiant heat flux is rather difficult without knowledge of the flame characteristics.

Discussion which follows is concerned with the estimation of the quantities involved in Eq. [5-23].

Flame Temperature T_g. Although the use of an average flame temperature may cause substantial errors in the heat flow calculations, the temperature distributions in flames cannot be predicted theoretically. When the heat flux distribution at the enclosing walls and the combustion patterns are known, it is possible to determine the flame temperature distribution by using the iterative zoning method as given by Hottel and Sarofim, page 375.[48] However, if the overall heat transfer coefficients at the enclosing walls are not known, as in the problem of the present study, this is not possible.

Under these conditions a heat transfer model which is more elaborate than that represented by Eq. [5-23] would not improve the predictions, although it would increase the computation time considerably.

Consequently, the average flame temperature should be chosen from the experimental data available. Even then the heat flux values obtained from Eq. [5-23] should be treated with some reservation. The main value of the equations obtained by using rather simplified models is to provide the design engineer with an orderly approach toward a reasonably sound engineering decision. In this effort carefully obtained experimental data is indispensable.

Gas emmissivities and absorptivities. Experimentally determined total emissivities of different gases are compiled in a number of references.[48,59] The total emissivity of a gas is usually presented

as $\epsilon_g = f(pL, T_g)$, and a correction factor C is introduced for pressure broadening effects dependent on the partial pressure and the total pressure. The overlapping of the emission bands of emitting species is accounted by a correction factor $\Delta\epsilon_m$.

As an example, the emissivity of a carbon dioxide and water vapor mixture is given by

$$\epsilon_m = [(C\,\epsilon_g)_{CO_2} + (C\,\epsilon_g)_{H_2O} - \Delta\epsilon_m] \qquad [5\text{-}26]$$

Charts for the emissivities and the correction factors C and $\Delta\epsilon_m$ are given in the mentioned references along with values of "the mean beam length L" for various gas-surface exchange.

For blackbody radiation from a surface at T_1 the absorptivity of a gas at T_g may be shown to be equal to

$$\alpha(T_g, T_1, pL) = \left(\frac{T_g}{T_1}\right)^m \epsilon_g\left[T_1,\ pL\left(\frac{T_1}{T_g}\right)^n\right] \qquad [5\text{-}27]$$

with m = 0.5

In this equation ϵ_g is evaluated at T_1 and at a partial pressure-beam length product equal to $pL\,(T_1/T_g)^n$. The absorptivities of CO_2 and water vapor are correlated by using Equation [5-27] with the following values of m and n

$m = 0.65,\ \ n = 1$ for CO_2

$m = 0.45,\ \ n = 1$ for H_2O vapor

In determining the total absorptivity of the mixture, ϵ_g in Equation [5-27] should be multiplied with the correction factor C, and in the absorptivity equation for the mixture $\Delta\epsilon_m$ should be accounted for.

In the study of real gas emission the mathematical formulation

which is based on a gray-gas system can be retained through the use of Equations [5-2 and 5-3] for representing the emissivity and the absorptivity of a real gas.

Since no method is available for predicting the particle concentration of a luminous flame analytically it is not possible to estimate the luminous flame emissivity by analytical means; one must rely on the experimental data. As an example, Godridge and Hammond[44] reported that the equation

$$\epsilon = 1 - (1 - \epsilon_g)e^{-K_m cL} \qquad [5\text{-}28]$$

can be used to predict total emissivity of residual fuel oil flames across sections where the carbon particle concentrations at N.T.P. exceed 1 mgm/. . In this equation, ϵ_g, is the non-luminous emissivity, K_m an absorption factor averaged with respect to the thermal spectrum, c the mean concentration of carbon particles, and L the flame thickness.

In the case of uncontrolled fires the main interest is in the prediction of total heat flow from flames to the cargo container. Therefore, an experimentally determined addition to the non-luminous gas emissivity to allow for particle luminosity is often sufficient when calculations are based on a mean flame temperature. However, it should be noted that when a cargo container is exposed to an uncontrolled fire, it is very possible that the combustion would very often be incomplete. Therefore, the flame luminosity would affect the radiant heat flow considerably.

Container surface temperature T_1. This temperature is closely related with the type and thickness of insulation used on the container surface therefore, it has been considered in Appendix 7.

Convective heat transfer from flames. Equation [5-23] includes the convective contribution to the total heat flux. In the present case the convective heat transfer coefficient h_1 is affected by both the chemical reaction and the interaction between radiation and convection. Generally speaking, information on the free convection heat transfer coefficients for non-reacting and non-radiating gases may not be applied directly to flames. As it has been reported in Reference 61 the rate of heat transfer in reacting gas systems is frequently substantially larger than the maximum rate predicted by using the convective heat transfer coefficients for non-reacting systems. In reacting gas systems a significant increase in the heat flux may arise from the motion of activated species across the boundary layer.

Until recently, little work of engineering nature has been done on heat transfer problems where convection and radiation occur simultaneously. As an example, it has been found in Reference 71 that for an optically thin laminar boundary layer flow over a flat plate, the maximum effect of radiation interaction was to increase the Nusselt number by almost a factor of two at a given Reynolds number and the Prandtl number of unity.

By assuming the physical properties of air for the flames at 2200°F, Neill[61] calculated the free convection coefficients from different correlations available in the literature. Computed

nvective heat transfer coefficients were varied from 0.76 to 1.72 Btu/(hr)(ft^{2}F) for cool surface temperatures between 300°F and 1800°F.

TABLE III

MAXIMUM HEAT TRANSFER RATES FOR OPTICALLY THICK FLAMES FROM SINGLE BURNERS[61]

Fuel	Optically Thick Flame Dept (inches)	Maximum Heat Transfer Rates to a Cold (200-300°F) Target (Btu/(hr)(ft^2) Radiant	Convective	Total
Methanol	35	5000	7000	12000
Acetone	35	10000	7000	17000
Hexane	70	22500	7000	29500
Cyclohexane	100	21000	7000	38000
JP-4	80	23700	7000	30700
Benzene (Benzol)	80	39000	7000	46000

Considering the effects of reactions and the interaction between convection and radiation, therefore, it is expected that the effective convective heat transfer coefficient for a buoyant diffusion fire should exceed 2 Btu/(hr)(ft^2)°F. Table III summarizes data by Neill[61] for the maximum heat transfer rates expected from optically thick flames of various fuels. The radiant heat transfer rates in this table are based on the non-specular data from the channel burners. It is seen that contribution to the total heat flux through convection is not negligible.

The laboratory data recently obtained by Welker and Sliepcevich[81] showed that, the maximum radiant heat flux from a JP-4 fire can be taken

as 31,000 Btu/(hr)(ft^2). A flame thickness of about 15 feet was required to obtain the maximum rate. The convective heat transfer coefficient was about 5 Btu/(hr)(ft^2)(°F) for the laboratory-scale heat transfer probe, and the average flame temperature was about 2450°F. It has been noted in the reference that the convective coefficient obtained could be extended to other situtations by standard techniques.

A. Directed total-exchange area $(\overrightarrow{GS_1})$ or $(\overleftarrow{GS_1})$.

The net rate of heat flow by radiation between any two black surfaces may be written as

$$\dot{Q}_{1\rightleftharpoons 2} = F_{12}A_1(E_1 - E_2) = F_{21}A_2(E_1 - E_2) \qquad [5\text{-}29]$$

F_{12} = view factor, fraction of isotropic radiation from surface A_1 intercepted directly by A_2, dimensionless.

The following equality from [5-29] is known as the reciprocity theorem

$$A_1F_{12} = A_2F_{21} = \overline{s_1s_2} \qquad [5\text{-}30]$$

$\overline{s_1s_2}$ = direct - interchange area; ft^2.

Thus

[5-29] can be rewritten as

$$\dot{Q}_{1\rightleftharpoons 2} = \overline{s_1s_2}\,(E_1 - E_2) \qquad [5\text{-}31]$$

Both F_{12} and $\overline{s_1s_2}$ are determined by geometrical configuration of radiating surfaces.

Equation [5-31] does not depend on the geometrical disposition or radiation characteristics of other surfaces completing the enclosure.

it represents the direct radiative interchage between A_1 and A_2. If the radiating surfaces are not black and the radiations from all of the surfaces completing the enclosure are considered, the total net radiative interchange between A_1 and A_2 is given by

$$\overset{\circ}{Q}_{1 \rightleftharpoons 2} = \overline{S_1S_2}E_1 - \overline{S_2S_1}E_2 \qquad [5\text{-}32]$$

where the intervening medium is non-absorbing, and

$\overline{S_1S_2}$ = total exchange area for the flux from A_1 to A_2, ft^2.

In the earlier treatments the nomenclature $A_1\mathcal{F}_{12}$ was used for $\overline{S_1S_2}$ as the "total view factor from A_1 to A_2."

In general, $\overline{S_1S_2}$ and $\overline{S_2S_1}$ will each be a function of T_1 and T_2 because of the temperature dependence of the surface emissivities and absorptivities. For gray surfaces, with grayness independent of temperature, Equation [5-32] becomes

$$\overset{\circ}{Q}_{1 \rightleftharpoons 2} = \overline{S_1S_2}(E_1 - E_2) = \overline{S_2S_1}\,(E_1 - E_2) \qquad [5\text{-}33]$$

For a gray system $\overline{S_1S_2}$ characterizes the radiative heat flow independent of other heat transfer mechanisms.

The net radiative heat flux to a surface which is in radiative equilibrium, or radiatively adiabatic is zero. This condition is approximately satisfied by the refractory walls of a furnace. If some of the zones of the enclosure are in radiative equilibrium, then Equation [5-33] can be written as

$$(\overset{\circ}{Q}_{1 \rightleftharpoons 2})_R = (\overline{S_1S_2})_R(E_1 - E_2) \qquad [5\text{-}34]$$

For a discussion of the radiative exchange among non-gray surfaces the reader is referred to Hottel and Sarofim.[48]

The foregoing nomenclature allows for the presence of the absorbing medium. Considering a gray isothermal enclosure A_1 containing a gray isothermal gas (g), the net radiative heat loss by the gas is

$$\overset{\circ}{Q}_{g \rightleftarrows 1} = \overline{GS}_1 \, (E_g - E_1) \qquad [5\text{-}35]$$

If the enclosure containes no-flux zones then in [5-35], $(\overline{GS}_1)_R$ should be used.

With real gases the absorptivity is dependent on both the gas and the surface temperature; the reciprocity relation for exchange areas is not longer valid. This dependence on temperature is shown by using "the directed total exchange areas" $\overrightarrow{GS}_1$ and $\overleftarrow{GS}_1$; source and sink at foot and head of arrow, respectively. Consequently the net radiative heat exchange from an isothermal non-gray gas to an isothermal surface A_1 will be given by

$$\overset{\circ}{Q}_{g \rightleftarrows 1} = \overrightarrow{GS}_1 \, E_g - \overleftarrow{GS}_1 E_1 \qquad [5\text{-}36]$$

When radiative equilibrium surfaces are present, [5-36] becomes

$$(\overset{\circ}{Q}_{g \rightleftarrows 1})_R = (\overrightarrow{GS}_1)_R \, E_g - (\overleftarrow{GS}_1)_R E_1 \qquad [5\text{-}37]$$

This relation is used in Equation [5-1]. For detailed discussion the reader is referred again to Hottel and Sarofim.[18]

B. Nomenclature used in this appendix

a ($a_{g,n}, a_{s,n}$) - Weighting factors or energy - fraction in black body spectral region.

A - area, ft^2

E - hemispherical emissive power of a black body, $Btu/(hr)(ft^2)$

F_{ij} - view factor, dimensionless

$\overline{GS}_1$ - total exchange area between gas and surface A_1, ft^2

$\overrightarrow{GS}_1$ - directed total exchange area between gas and A_i, ft^2

K - extinction coefficient

k_p - absorption coefficient (pressure basis)

L - path length, ft.

p - partial pressure of radiating gas component

$(\overline{s_i s_j})$ - direct interchange area between surface zones i and j, ft^2

$\overline{S_i S_j}$ - total interchange area between surfaces i and j, ft^2

α - absorptivity

ϵ - emissivity

σ - Stefan-Boltzmann constant

Subscripts

g,s - gas, surface

R,r - Allowing for radiative equilibrium or re-radiation surfaces

APPENDIX 6: RATE OF BURNING OF FUEL FROM A FREE LIQUID

A review of several papers on the burning rates of liquid provides a basis for reasonably sound predictions of burning rates.

Blinov and Khudiakov writing in Russia in 1957 [9] considered burning rates. Hottel has prepared an excellent English review of the results of the Russian paper as applied to burning rates.[47] The tests were extensive, covering fires from 3.7 mm to 22.9 meters in diameter. Data indicated that three burning regimes were present, as shown in Figure 6. For burners less than 3 cm in diameter the flames were laminar and the burning rate decreased as the diameter increased. Turbulence in the flames increased as the diameter increased until the diameter reached about 130 cm. The burning rates leveled off between 3 cm and 10 cm; the minimum burning rate was reached at about 10 cm and then increased with the diameter until the burners were about 130 cm in diameter. Beyond this size, the burning rate was constant.

Hottel suggested that the burning rates could be explained qualitatively by considering the mechanism of heat feedback from the fire to the liquid fuel. The burning rate is the fuel vaporization rate. The energy for vaporizing the fuel comes mainly from the fire except for the early burning period with fuels with low boiling points (such as LNG). Hottel expressed the heat feedback rate as

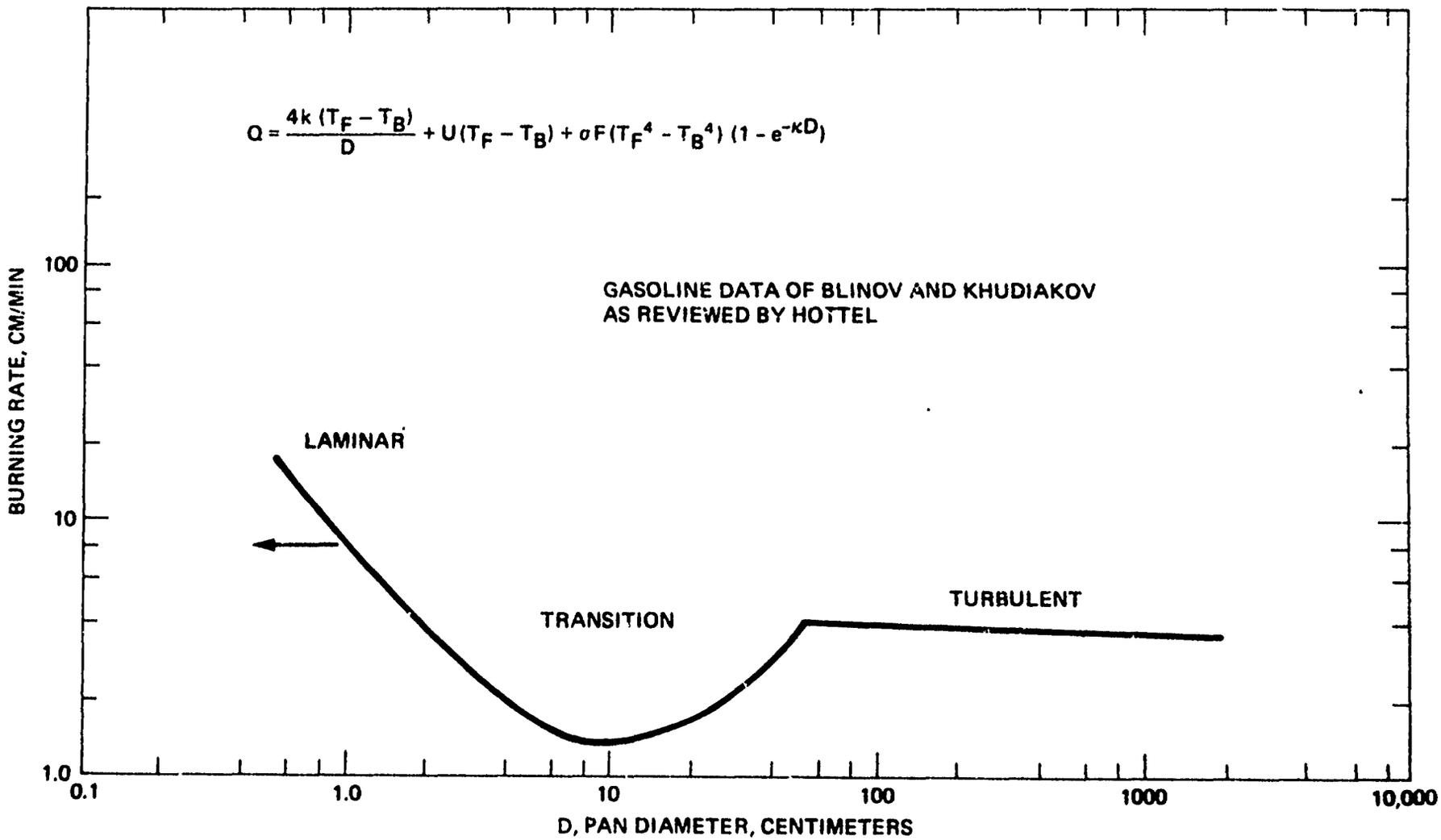

FIGURE 6

BURNING RATE OF GASOLINE

A6-2

$$q = \frac{4k(T_f - T_b)}{D} + U(T_f - T_b) + \sigma F(T_f^4 - T_b^4)\,(1 - e^{-\chi D}) \qquad [6\text{-}1]$$

where

q = heat feedback rate per unit area
D = pan diameter
k = conduction coefficient
U = convection coefficient
σ = Stephan-Boltzmann constant
F = view factor the fuel has of the flame
χ = Beer's law extinction coefficient to account for increasing flame opacity with diameter
T_f = absolute flame temperature
T_b = absolute temperature of the fuel, usually the boiling point.

The first term in the right side of Eq. [6-1] is related to conduction, the second to convection, and the third to radiation. The conduction term is dominant for small fires but decreases with larger fires. Convection plays an important part in intermediate fires and non-luminous large fires. Large fires with luminous flames are dominated by radiant heat feedback. Eq. [6-1] predicts constant burning rates for large fires. Emmons[38] later showed that the conduction term was made up of four succeeding mechanisms.

Burgess and coworkers at the Bureau of Mines made burning rate measurements for several fuels. Refs. 3,4,5,13,14. They showed that the liquid regression rate during burning could be expressed as

$$v = v_{\infty}(1 - e^{-kD}) \qquad [6\text{-}2]$$

where

v = liquid regression rate for burner diameter D
v_{∞} = liquid regression rate for large fires
k = a constant, depending on fuel type.

Figure 8 shows a typical result of some of their measurements. The liquid regression rate is related to the mass burning rate by

$$m = v \rho_L \qquad [6\text{-}3]$$

where m is the mass burning rate per unit area and ρ_L is the liquid fuel density. The burning rate is also related to the heat feedback rate by

$$m = \frac{q}{\Delta H_v} \qquad [6\text{-}4]$$

where ΔH_v is the heat of vaporization of the liquid fuel. Equation [6-2] can be obtained from Eq. [6-1] by neglecting conduction and convection in Eq. [6-1]. Therefore, it applies to fuels and fire sizes for which the heat feedback is primarily by radiation and it is more representative of fuels which burn with more luminous flames.

If the mass evaporation rate for a large fire is written as

$$m_{\infty} = v_{\infty} \rho_L \qquad [6\text{-}5]$$

the liquid fuel regression rate for a large fire can be given as

$$v_{\infty} = \frac{q_{\infty}}{\rho_L \Delta H_v} \qquad [6\text{-}6]$$

where q_{∞} is the heat feedback rate for a large fire. If it is further assumed that q_{∞} is always a constant fraction, f, of the heat of combustion ΔH_c for any fuel,

A6-5

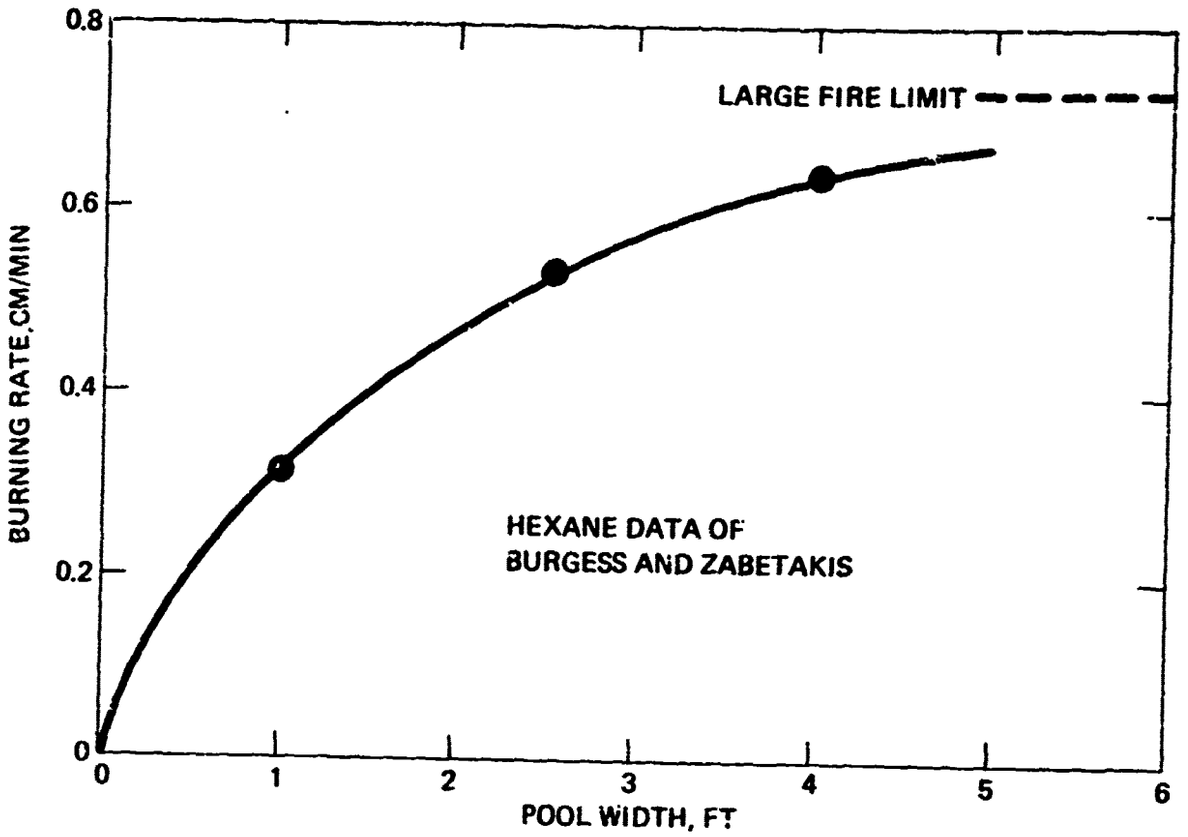

FIGURE 7

BURNING RATE OF HEXANE

$$v_{\infty} = \frac{f \cdot \Delta H_c}{\rho_L \ \Delta H_v} \qquad [6\text{-}7]$$

Burgess and coworkers presented a correlation of burning rate data based on Equation [6-7]. The result is shown in Figure 9, and can be summarized by

$$v_{\infty} = 0.0076 \ \frac{\Delta H_c}{\Delta H_v} \qquad [6\text{-}8]$$

where v_{∞} is expressed in cm/min. The data in Figure 3 follows the relationship quite well, even though the assumption of constancy of f/ρ_L is tenuous. Measurements of the fraction of the heat of combustion released as radiation range from less than 20 percent to more than 40 percent for various fuels.

Welker [80] measured the burning rates of liquid fuels in conjunction with his studies on flame bending and used the resulting data to estimate the burning rates of large fires. He concluded that the burning rates for large fires could be estimated from

$$v_{\infty} = 0.02 \ \frac{\Delta H_c}{\Delta H_v} \qquad [6\text{-}9]$$

where v_{∞} is in cm/min. A "large" fire was estimated to be about 15 ft in diameter. Welker's result showed burning rates more than twice as large as those of Burgess, and he suggested that a more thorough study of burning rates be undertaken. Unfortunately, such a study has not been made to date, and dependable burning rate data are still not available for large fires, except for a few isolated cases. The data that are available are sometimes questionable due

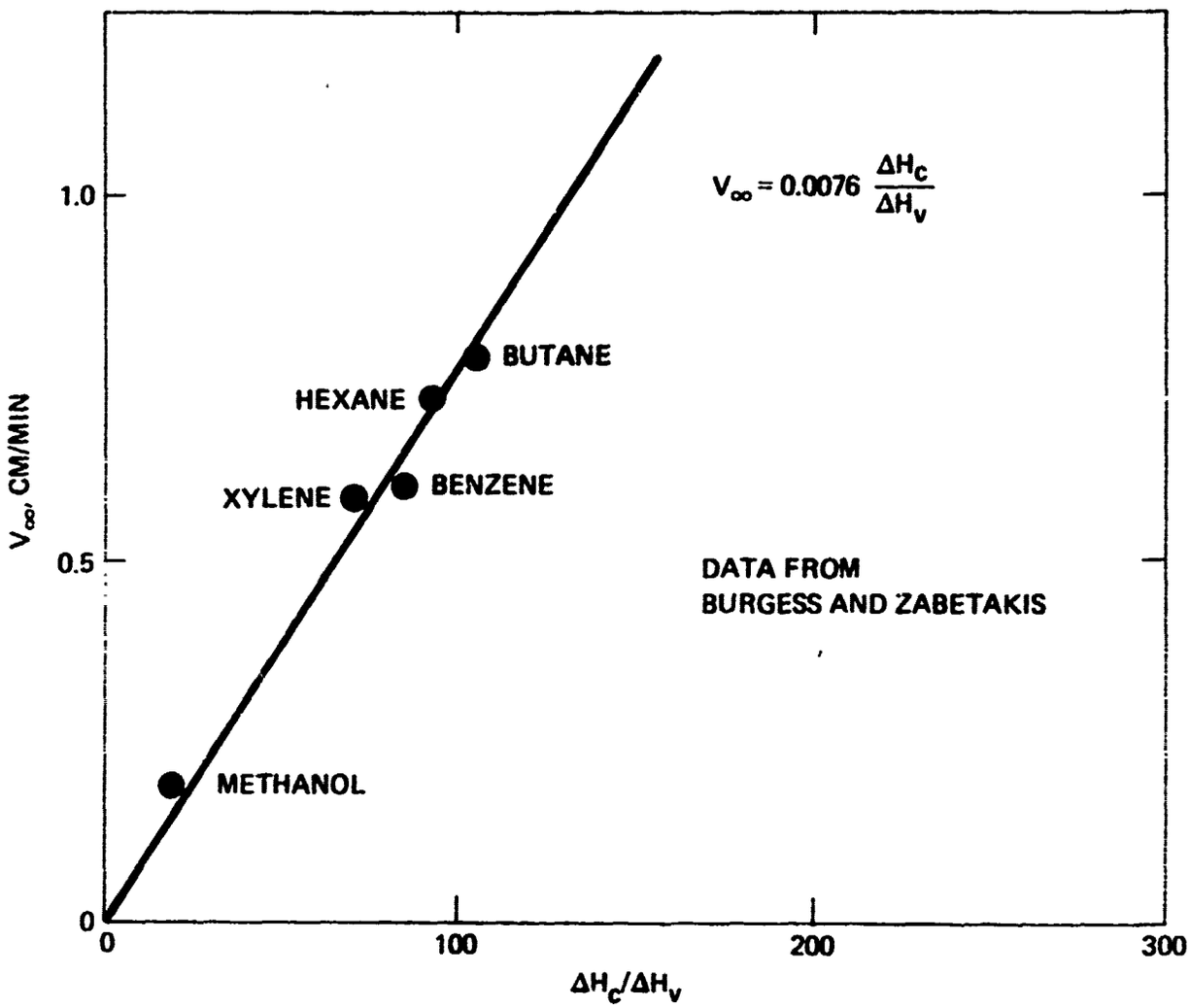

FIGURE 8

BURNING RATES FOR LIQUID-FUELED FIRES.

to inadequate instrumentation.

Welker observed that the burning rate of liquid fueled fires up to a few feet in diameter decreased at higher wind velocities if the wind was steady. In later work[51] it was shown that the decrease in burning rate was due largely to a decrease in the geometric view factor from the fuel to the flame as the flame was bent by the wind. This decrease in burning rate is probably limited to small or intermediate fires. Once the flame becomes large enough to be opaque, i. e., the Beer's law term becomes unity, the view factor also becomes unity because the fuel can no longer "see" anything but optically thick flame.

Blackshear and coworkers (Ref.8) have started a detailed study on the burning rates of liquid fuels from fuel-soaked wicks. For diameters above about 30 ft, convection may be the dominant heat transfer mechanism. However, to date their results are not useful for predicting the burning rates of large fires. Methanol and acetone have been the principle fuels in their studies. These fuels release a smaller fraction of their combustion energy by radiation than do liquid hydrocarbons.

Measurements of burning rates of liquid fuels other than methanol, acetone, and liquid hydrocarbons have not been reported, even for small fires. It is known that highly oxygenated compounds,[12] such as organic peroxides or partially nitrated hydrocarbons, burn faster than would be suggested by any of the analyses presented above.

Another technique involves estimating the rate of heat transfer to the pool and calculating the evaporation rate. Since heat transfer rates are not well established for most fuels, this approach is also less than perfect.

The following table presents the results of calculations of burning rates by three methods, the Bureau of Mines[14] correlation given by Eq. [6-8], Welker's[80] extrapolated results given by Eq. [6-9], and heat transfer calculations based on the total heat transfer rates measure by Neill[61]. Five liquid fuels are listed which are representative of fuels for which burning rates have been measured.

Table IV

FUEL	BURNING RATE per UNIT AREA $\frac{LB}{(HR)(FT^2)}$		
	Burgess[14]	Welker[80]	Calculated from Heat Transfer Data Of Neill[61]
Methanol	12	32	23
Acetone	35	92	64
Hexane	60	157	147
Cyclohexane	62	163	173
Benzene (Benzol)	65	171	208

The results presented in the table are all based on experimental data, but none of the data can be considered ideal for making predictions. The Bureau of Mines data were obtained from unsteady state burning tests on shallow pools. The early portion of the unsteady state measurements has burning rates considerably lower than those at steady state, so the Bureau of Mines results are lower than those

for steady state measurements. Welker's data are based on steady state measurements, but they were obtained for fires less than 2 ft in diameter under windy conditions. A double extrapolation of the data was therefore required, and the results may suffer from some inaccuracy. Neill's heat transfer rates were measured for low-temperature objects located above the fuel surface, directly in contact with the flames that surrounded them. They include both convective and radiative heat transfer. Although the radiative portion of heat transfer to the fuel surface can be related to that in the flame, the convective portion may differ because of the layer of evaporating fuel on the liquid surface. Another difference is that the fuel surface is horizontal rather than vertical as in Neill's tests.

While the analysis leading up to Eq. [6-8 and 6-9] assume radiation heat transfer to be dominant, the data used to obtain the constants in the equations were obtained under conditions which included both convective and radiative heating.

Prediction of the burning rates of large fires presently depends upon extrapolation of data from smaller scale. For engineering purposes the steady state burning rate is usually the value to use, but the specific fuel should be considered to see if transient rates could be greater than steady state, as with liquefied natural gas spills.[15] Predictions based on Welker or Neill must suffice until experimental measurements on larger steady state pool fires can be made.

Experimental measurements of steady state burning rates for large pool fires are difficult and expensive. There is a possibility

that the same information can be obtained from measurements on smaller, interacting fires. Huffman, Welker, and Sliepcevich[51] have shown that the interaction effects of multiple pool fires increase the burning rate. It should be possible to use such data on interacting fires, which can be taken using smaller pool diameters, to predict burning rates for large single fires. Thus, the number of large single fires necessary in a research program could be reduced, with subsequent economies in the program.

A heat flux meter has been used to study radiation and convection transfers to the fuel surface in large pool fires[85] of n-hexane and gasoline.

APPENDIX 7: EVALUATION OF INSULATION EFFECTIVENESS

Insulation may provide very substantial protection to liquid cargos during fire exposure by reducing the heat flux from fire to the liquid cargo. This protection is provided only if the insulation sheath maintains its integrity during the fire. Evaluation of insulation effectiveness requires predictions of the heat fluxes and the outside surface temperatures of insulation at several flame temperatures. Surface temperatures higher than the safe maximum value could result in deterioration of the insulation material. Materials adequate for low temperature service may not be able to withstand high temperatures, and therefore fail under fire exposure.

The net heat flow from flames to the cargo container surface is given by Eq. [5-1] in Appendix 5. In order to use relatively simple expressions in the present discussion, the heat flux to the container surface can be written as

$$\frac{Q}{A} = h_r (t_g - t_r) + h_c (t_g - t_r) \qquad [7\text{-}1]$$

where,

h_r, h_c = average unit thermal conductance for radiation and convection, respectively, Btu/(hr)(ft^2)F

t_g = average flame temperature, °F

t_r = any convenient reference temperature, °F

A = wetted area completely exposed to fire, ft^2

It should be noted that Q/A in Eq.[7-1] is the heat flux q per unit wetted area completely exposed to fire, given by Eq. [2] in the main text.

Comparing [7-1] with [5-1] of Appendix 5, it is seen that

$$h_r = \frac{(\overrightarrow{GS_1})_R E_g - (\overleftarrow{GS_1})_R E_1}{t_g - t_r} \qquad [7-2]$$

$$h_c = h_1 \quad \text{and} \quad t_r = {}_1 \qquad [7-3]$$

Eq [7-1] can be rewritten as

$$\frac{Q}{A} = h(t_g - t_r) \qquad [7-4]$$

where

$$h = h_r + h_c$$

For additional information on this method, the reader is referred to F. Kreith, "Principles of Heat Transfer".[52] For a comparison between the heat transfer rates for insulated and uninsulated cargo containers for several insulations it is assumed that the flame will develop a reference heat flux of $(Q/A) = 34{,}500$ Btu/(hr)(ft^2) for uninsulated containers with a reference temperature, $t_r = 125°F$. Then

$$(Q/A) = h\,(T_g - 125) = 34{,}500 \qquad [7-5]$$

Heat flux to the insulated container can be written as

$$\frac{Q}{A} = h_i\,(t_g - t_{ins.}) \qquad [7-6]$$

where, the reference temperature is the outside temperature t_{ins} of insulation. At a given flame temperature h_i and h in the last two equations are not equal. For comparison purpose, however, the problem can be further simplified by assuming that $h_i = h$. Otherwise, h_i should be determined from [7-2], for tabulated values refer to F. Kreith.[52] By combining [7-5] and [7-6] one obtains

$$\frac{Q}{A} = 34{,}500\,\frac{t_g - t_{ins}}{t_g - 125} \qquad [7-7]$$

The heat flux through the insulation Q/A is also given by

$$\frac{Q}{A} = \frac{k_m}{\ell}(t_{ins} - t) \qquad [7\text{-}8]$$

where

k_m = mean thermal conductivity of insulation in Btu per hour per square foot per °F per inch

ℓ = thickness of insulation in inches

t = temperature of material of lading at pressure of flowing conditions in °F

The insulation temperature now can be obtained from [7-7] and [7-8],

$$_{ins} = \frac{\frac{k_m}{\ell} t + \frac{34,500}{t_g - 125} t_g}{\frac{k_m}{\ell} + \frac{34,500}{t_g - 125}} \qquad [7\text{-}9]$$

The insulation temperature and heat fluxes were calculated for flame temperatures of 1500, 1850 and 2000°F for one-inch thick insulations with mean thermal conductivities of 0.6, 1.8 and 4.0 Btu per hour per square foot per °F per inch. A flame temperature of 1850°F was selected on the basis of experimental work using JP-4 as the fuel.[6] Propane was assumed to be the material of lading. The results of these calculations are summarized in Table V. It should be noted that a different material of lading will alter these results.

Table V

OUTSIDE INSULATION TEMPERATURES AND HEAT FLUXES[57]

Material of Lading: Propane (t = 140°F)
Insulated Thickness: One inch

Flame Temp. °F	Mean Thermal Conductivity Btu/hr-ft^2/(°F/in)	Outside Temp. of Insulation °F	Heat Flux Btu/hr-ft^2
1500	0.6	1468	797
1500	1.8	1408	2280
1500	4.0	1312	4688
1850	0.6	1800	1000
1850	1.8	1710	2830
1850	4.0	1560	5680
2000	0.6	1940	1080
2000	1.8	1834	3050
2000	4.0	1666	6096

Comparison of Heat Transfer Rates

A comparison between the heat transfer rate of completely insulated containers and the heat transfer rate of an uninsulated container of equal area can be made by taking the ratio of the heat transfer rates. The ratio of heat transfer rates can be expressed as

$$r = \frac{(\text{Heat Flux x Area})_{\text{insulated}}}{(\text{Heat Flux x Area})_{\text{uninsulated}}} \qquad [7\text{-}10]$$

Since the containers have equal surface areas for heat transfer, the ratio of the heat transfer rates is simply the ratio of the heat fluxes. Thus,

$$r = \frac{(\text{Heat Flux})_{\text{insulated}}}{(\text{Heat Flux})_{\text{uninsulated}}} \qquad [7\text{-}11]$$

or

$$r = \frac{(Q/A)_i}{(Q/A)_u} = \frac{q_i}{q_u} \qquad [7\text{-}12]$$

where q_i is the heat flux in Btu per hour per square foot of wetted area completely exposed to fire for insulated containers and q_u is the heat flux for uninsulated containers.

If the container is only partially insulated, the ratio of the heat transfer rates can be expressed as

$$r = \frac{(\text{Heat Flux x Area})_{\text{exposed}} + (\text{Heat Flux x Area})_{\text{covered}}}{(\text{Heat Flux x Area})_{\text{uninsulated}}} \qquad [7\text{-}13]$$

where, area is the wetted area completely exposed to fire. Equation (7-13) states that the ratio of the heat transfer rate for a partially insulated container to the heat transfer rate for an uninsulated container of the same size is the sum of the products of a heat flux term and an area term for the exposed and covered portions of the container divided by the product of the heat flux term and the total exposed area term for an uninsulated container.

Assuming that the fire exposure factor E in Eq [2] of the main text is chosen as $E = A^{0.18}$ the area enveloped by flame will to the total wetted surface area of the container raised to the 0.82 power. Letting g represent the fraction of the tank which is insulated and using the above factor, (7-13) can be written

$$r = \frac{q_e \left[(1-g)A_T\right]^{0.82} + q_c (gA_T)^{0.82}}{q_u A_T^{0.82}} \qquad [7\text{-}14]$$

or

$$r = \frac{q_e (1-g)^{0.82} + q_c g^{0.82}}{q_u} \qquad [7\text{-}15]$$

where the subscripts c, e, and u refer to covered, exposed and totally uninsulated portions.

The ratio of heat transfer rates for insulated containers (both partially and completely) to the heat transfer rate for an uninsulated container of the same size has been calculated for 50, 80, 90, 95 and 100 per cent insulated containers with one-inch insulation having mean thermal conductivities of 0.6, 1.8 and 4.0 Btu per hour per square foot per °F per inch for flame temperatures of 1500, 1850 and 2000°F. In these calculations it was assumed that the heat flux to an uninsulated container (or any fraction of a tank uninsulated) is 34,500 Btu per hour per square foot regardless of the flame temperature. The results of these calculations are presented in Table VI and Figures 9, 10 and 11.

TABLE VI

COMPARISON OF HEAT TRANSFER RATES BETWEEN INSULATED AND UNINSULATED CONTAINERS[57]

Material of Lading: Propane
Insulation Thickness: One Inch
q_u = 34,500 Btu/hr-ft^2

Flame Temp. °F	Mean Thermal Conductivity Btu/hr-ft^2/(°F/in)	Outside Temp. of Insulation °F	Heat Flux q_c Btu/hr-ft^2	Ratio r
g: 100 Percent Insulated Containers				
1500	0.6	1468	797	0.023
1500	1.8	1408	2280	0.066
1500	4.0	1312	4688	0.136
1850	0.6	1800	1000	0.029
1850	1.8	1710	2830	0.082
1850	4.0	1560	5680	0.164
2000	0.6	1940	1080	0.031
2000	1.8	1834	3050	0.088
2000	4.0	1666	6096	0.176
g: 95 Percent Insulated Containers				
1500	0.6	1468	797	0.108
1500	1.8	1408	2280	0.149
1500	4.0	1312	4688	0.216
1850	0.6	1800	1000	0.114
1850	1.8	1710	2830	0.164
1850	4.0	1560	5680	0.244
2000	0.6	1940	1080	0.116
2000	1.8	1834	3050	0.170
2000	4.0	1666	6096	0.254

TABLE VI CONTINUED

Flame Temp. °F	Mean Thermal Conductivity Btu/hr-ft^2/(°F/in)	Outside Temp. of Insulation °F	Heat Flux q_c Btu/hr-ft^2	Ratio r
	g: 90 Percent Insulated Containers			
1500	0.6	1468	797	0.173
1500	1.8	1408	2280	0.212
1500	4.0	1312	4688	0.276
1850	0.6	1800	1000	0.178
1850	1.8	1710	2830	0.227
1850	4.0	1560	5680	0.303
2000	0.6	1940	1080	0.180
2000	1.8	1834	3050	0.232
2000	4.0	1666	6096	0.314
	g: 80 Percent Insulated Containers			
1500	0.6	1468	797	0.286
1500	1.8	1408	2280	0.322
1500	4.0	1312	4688	0.380
1850	0.6	1800	1000	0.291
1850	1.8	1710	2830	0.335
1850	4.0	1560	5680	0.405
2000	0.6	1940	1080	0.293
2000	1.8	1834	3050	0.341
2000	4.0	1666	6096	0.411

TABLE VI CONTINUED

Flame Temp. °F	Mean Thermal Conductivity Btu/hr-ft^2/(°F/in)	Outside Temp. of Insulation °F	Heat Flux q_c Btu/hr-ft^2	Ratio r
g: 50 Percent Insulated Containers				
1500	0.6	1468	797	0.579
1500	1.8	1408	2280	0.603
1500	4.0	1312	4688	0.644
1850	0.6	1800	1000	0.583
1850	1.8	1710	2830	0.612
1850	4.0	1560	5680	0.660
2000	0.6	1940	1080	0.587
2000	1.8	1834	3050	0.617
2000	4.0	1666	6096	0.665

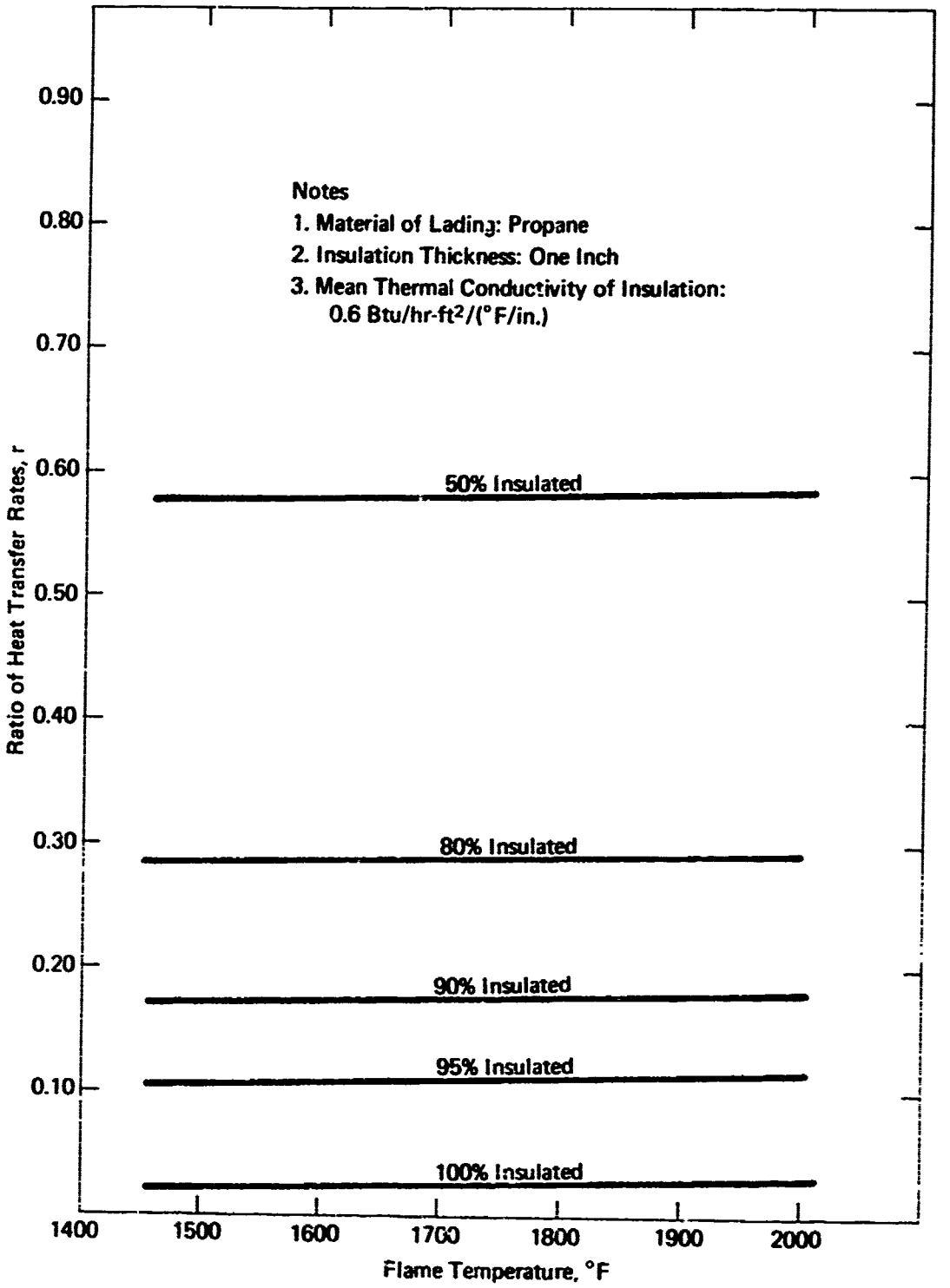

FIGURE 9

EFFECT OF INSULATION ON THE HEAT ABSORBED FROM FIRE

Plotted from Table VI

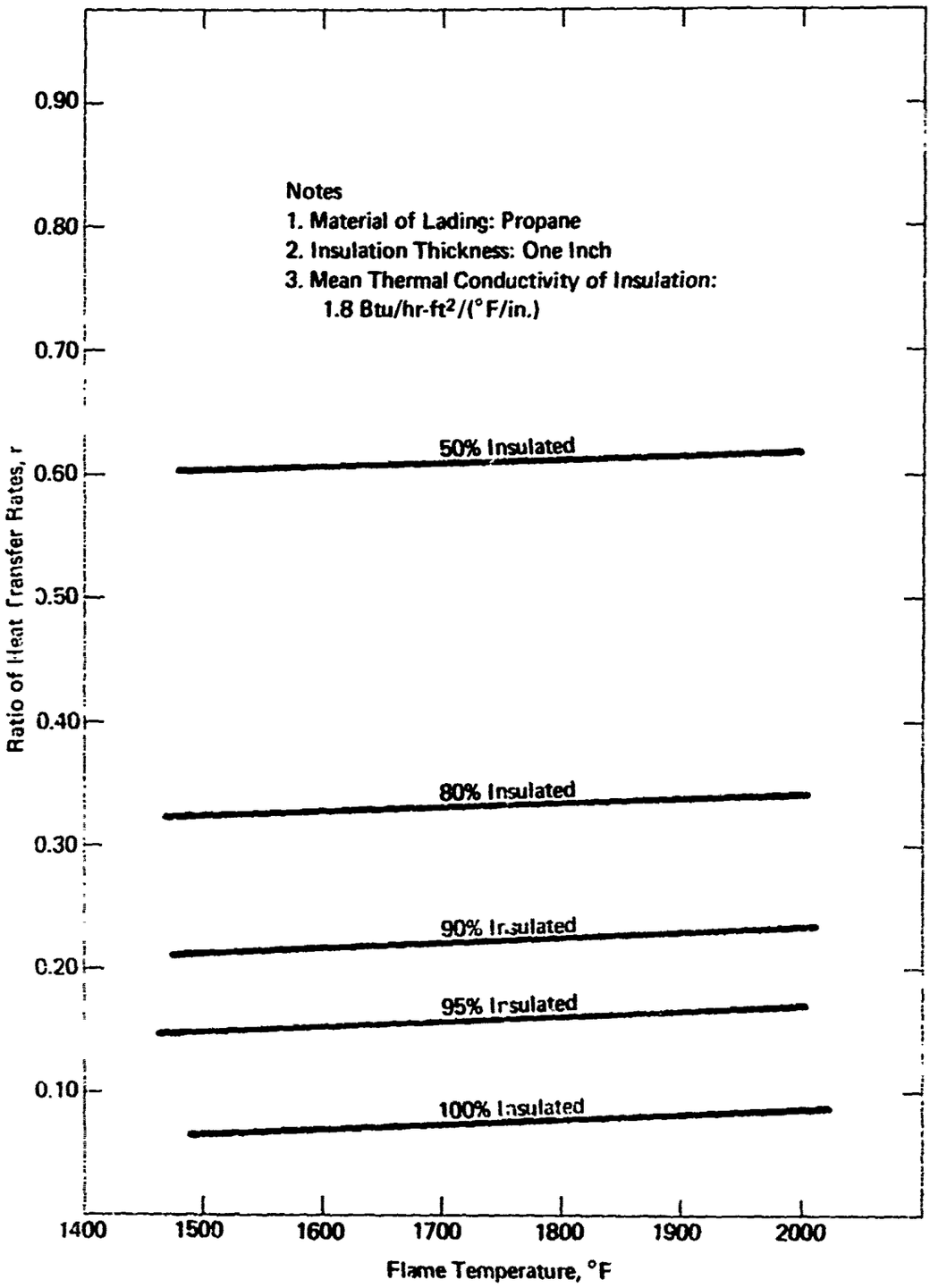

FIGURE 10

EFFECT OF INSULATION ON THE HEAT ABSORBED FROM FIRE

Plotted from Table VI

A7-12

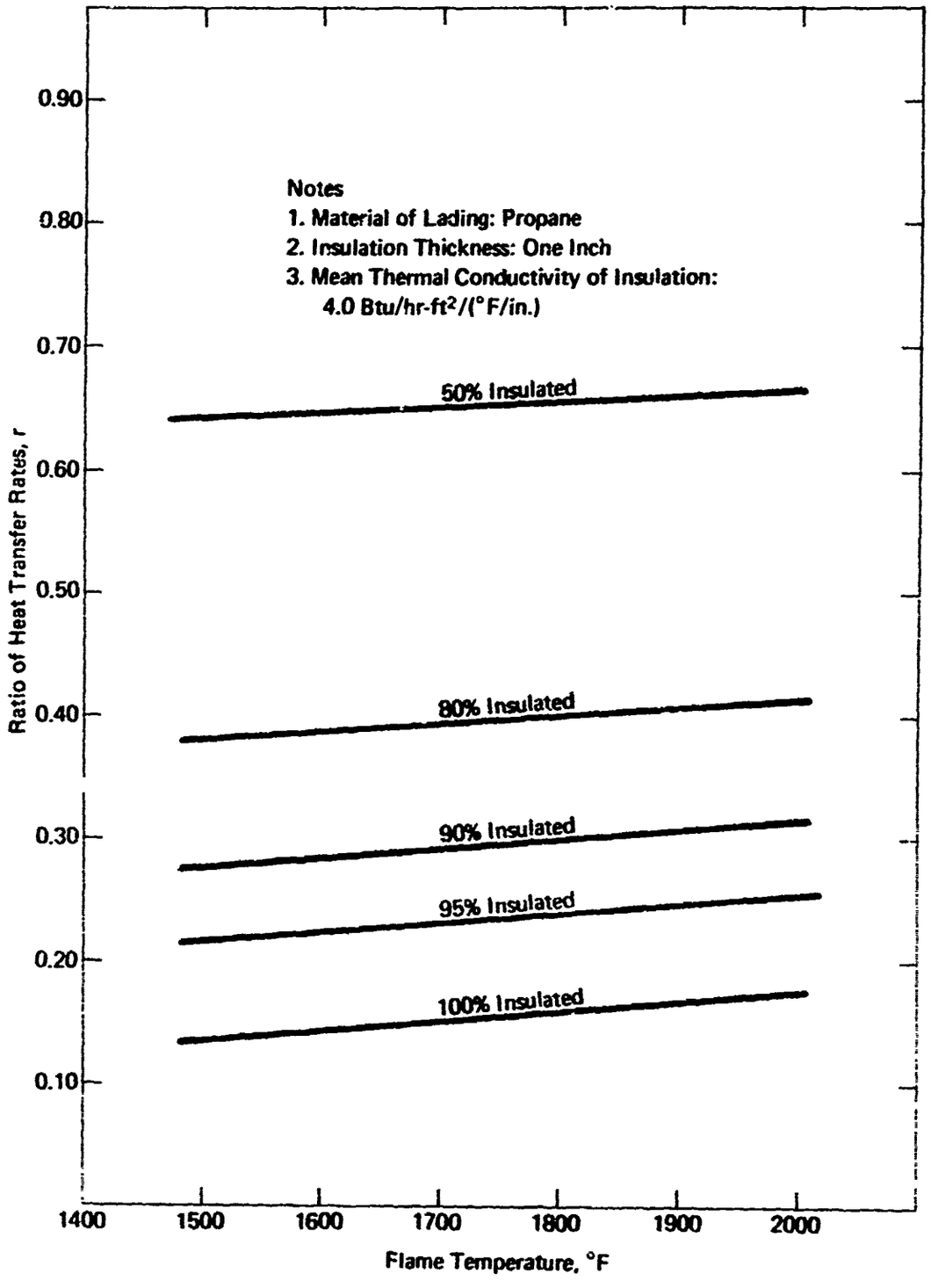

FIGURE 11

EFFECT OF INSULATION ON THE HEAT ABSORBED FROM FIRE

Plotted from Table VI

The results obtained indicate that insulation is very effective in reducing the heat flux from fire to the liquid cargo. Referring to the discussion in Part Four of this report, credit factor F for a given insulation system can be selected on the basis of the r values tabulated in Table VI or by a calculation similar to that presented in this appendix.

It is expected that for a given situation, the selected F Value for insulation coverage would be larger than the r value given in Table VI due to other factors which might affect the insulation effectiveness adversely.

If the integrity of insulation under fire conditions cannot be guaranteed, it is unwise to make large allowances for the insulation by using small F values.

The present calculations have indicated that temperature of the exposed insulation surface approaches closely that of the flame temperature. Therefore, it is important that the insulation be chosen to withstand the expected high temperatures without any degradation in its effectiveness. Selection depends also on the following factors: mechanical strength properties, moisture resistance, resistance to chemicals, and cost.

Some insulating materials are tabulated in the following table:

TABLE VII

Insulating Material[19]	Thermal Conductivity at 70°F Btu/(hr)(ft)(F)	Temperature Range °F Min.	Max.
Foam glass	0.0325	-400	800
Foam polystyrene	0.022	-400	175
Fiber glass	0.021	-300	600
Diatomaceous earth (with asbestos)	0.055	22	1,900
Mineral Wool (with binders)	0.0325	70	1,700
Calcium silicate (hydrous)	0.031	100	1,200

The first three materials in this table are used to insulate the refrigerated liquid cargo containers; their selections are made on account of their suitability as low temperature insulators. It is evident that the maximum temperatures for these three materials are much lower than that would be attained due to fire exposure. Exposure to fire could result in their decomposition, melting, or deformation.

Considering the other insulation materials in Table VII although these materials can stand high temperatures, their low temperature insulation characteristics are not adequate. For refrigerated cargos this problem can be resolved by using two different layers of insulating

materials, the inner layer being a low temperature insulation, whereas the outer layer is a high temperature insulation for protection against fire hazard. For non-refrigerated cargos one layer of high temperature insulation alone would be satisfactory.

Since most insulations are adversely affected by moisture, it is necessary, especially in marine transport systems, to cover the insulation with a waterproof material. For lasting protection, mechanical strength and chemical resistance of the insulation material should be taken into account.

Additional information on commercially available high temperature insulation materials may be obtained from P. E. Glaser.[43]

Another problem which needs special consideration is the effect of fire exposure on the unwetted surface of a container when this surface is not protected by insulation. Containers which have internal insulation or interior deposits of low conductivity material are subject to the same problem even if the surface is wetted. With the fire exposure such surfaces of a pressure container may assume a temperature high enough to cause failure of the metal within a few minutes. Figures 12 and 13 taken from API RP 520, Third Edition, November 1967, show, for a given heat input, the rate of temperature increase for various plate thickness and the time to rupture of a given steel in terms of the temperature and stress. From Figure 13, it appears that at a stress of 15,000psi, the steel plate might rupture in about 3 minutes after it reaches a temperature of 1,300 °F.

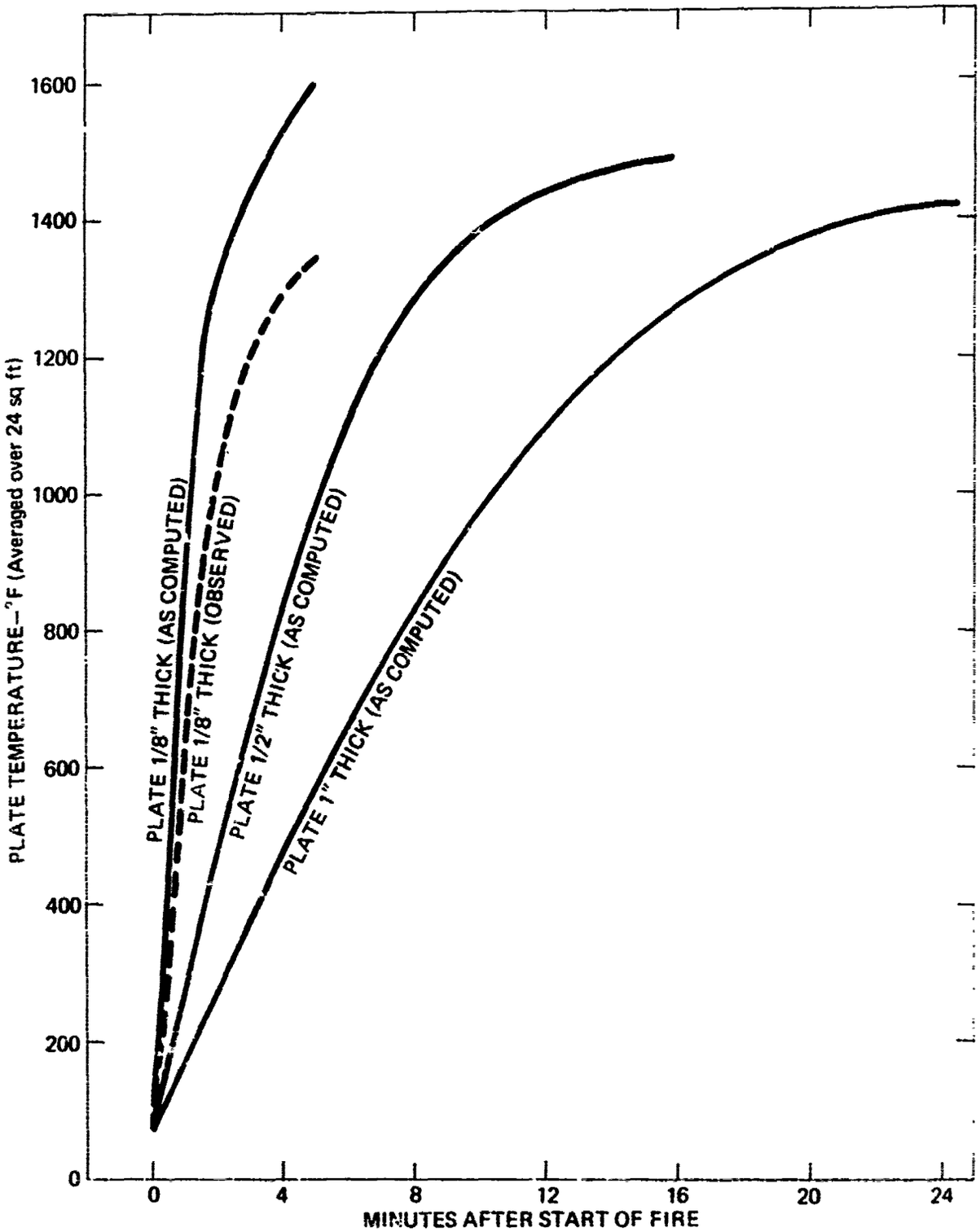

FIGURE 12

AVERAGE RATE OF HEATING OF STEEL PLATES EXPOSED TO OPEN GASOLINE FIRE ON ONE SIDE

Source: API RP520, 1967

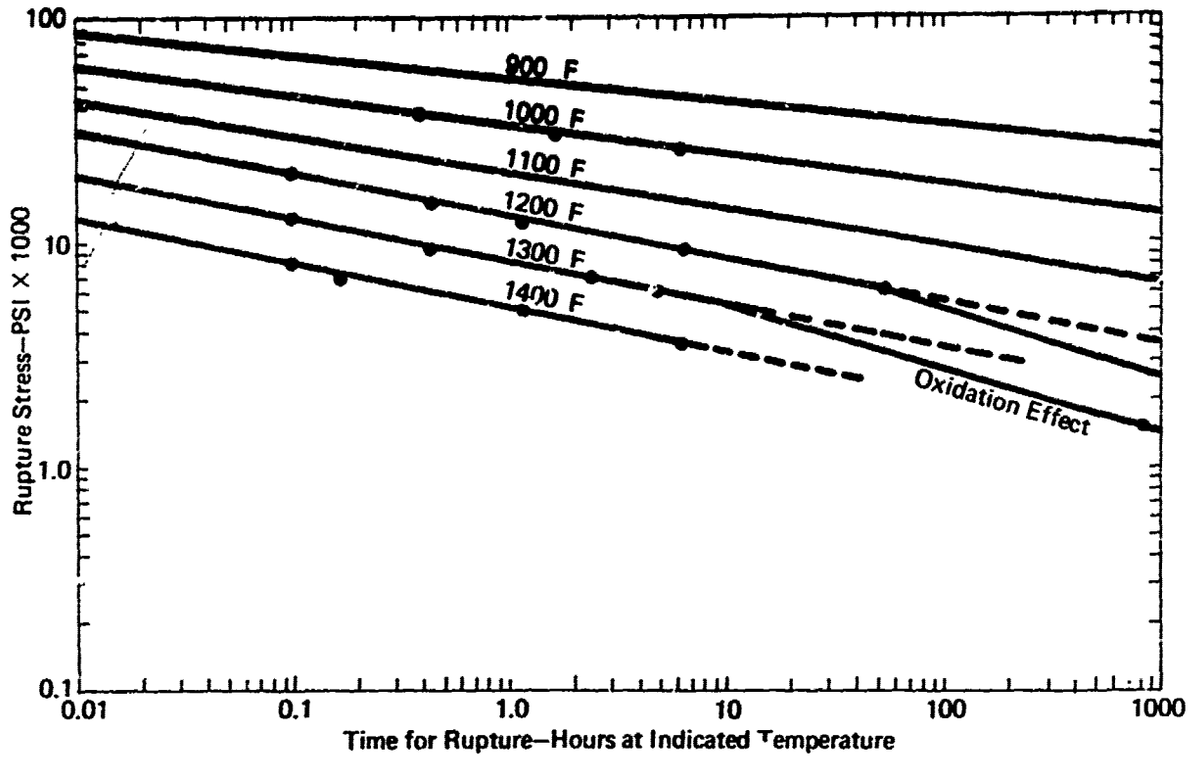

FIGURE 13

EFFECT OF OVERHEATING STEEL (ASTM A 212, GRADE B

70,000 psi MINIMUM TENSILE STRENGTH)

Source: API RP520, 1967

APPENDIX 8: BOILING CONDITIONS IN LIQUID CARGO CONTAINERS EXPOSED TO FIRE

When a liquid cargo container is first exposed to an uncontrolled fire, convective heating of the liquid takes place. If the heat flux is sufficiently large, liquid near the container surface starts to boil.

At the initial stage of fire exposure, it is reasonable to assume that the main body of the liquid in the container is below saturation temperature. Boiling at the container wetted wall under this condition is called "subcooled boiling", where the vapor bubbles either collapse without leaving the surface by transfer of heat to the adjacent subcooled liquid, or else they collapse immediately after leaving the surface. In either case, the heat transfer is improved over convection without phase change, due to agitation caused by the growing and collapsing vapor bubbles.

It has been shown[56] in many experiments that, over most of the nucleate boiling range, the surface temperature excess above saturation is a function of heat flux only, regardless of the subcooling. Therefore, with a sufficiently high heat flux the nucleate boiling may start even though the bulk of the liquid is at below saturation temperature. However, subcooling influences the start of the nucleate boiling and has a significant effect on the maximum

heat flux for nucleate boiling.

When a subcooled liquid cargo is exposed to fire, nucleate boiling may start as soon as the surface temperature excess above saturation ΔT reaches a specific value. The kinds of boiling processes found for subcooled boiling are similar to those existing for saturated liquids. At small ΔT values, the heating surface is in contact with both liquid and vapor, and the nucleate boiling exists. Beyond a maximum heat flux, a vapor film blankets the surface, thus resulting in the film boiling.

With subcooled boiling, the heat flux values usually are higher than those which would be found for a nucleate boiling process of the saturated liquid under similar conditions.[42]

Therefore, it would be conservative to treat the liquid cargo as saturated although at earlier stages of fire exposure the cargo might be subcooled.

Up to the maximum heat flux(i.e. critical heat flux) nucleate boiling exists at the container surface, provided that vapor generated can be removed freely from the surface. A considerable amount of data has been collected concerning the values of the maximum heat flux, q_{max}, in pool boiling. For different correlations, the reader is

referred to Rohsenow and Tong.[67,74] Some observed maximum heat flux values for various liquids, reported by Gebhart[42] are shown in Table VIII. It is seen that ΔT for various liquids vary from about 5°F to 100°F. In this table the highest surface temperature can be easily determined; it is 442.2°F for ethyl alcohol at 657 psia.

Referring to Fig. 14 within the nucleate boiling region ΔT assumes its maximum value ΔT_c at point a where the heat flux is a maximum. As a result, for a given fluid and for specified conditions, the maximum temperature of the container surface which contacts the liquid is obtained by using ΔT_c. Values of q_{max} and ΔT_c can be correlated in terms of reduced pressure as in Fig. 15. This correlation was obtained[20] for a number of organic substances, including ethanol, propane, benzene, n-pentane. However, it is also approximately valid for many other pure substances and mixtures.

The ΔT_c in Fig. 15 decreased from a high value at small reduced pressures toward zero at the critical pressure P_c.

Considering the usual pressure levels in liquid cargo containers, it can be assumed that ΔT_c is usually less than 50°F. In consequence, with the nucleate boiling the surface temperature excess above saturation temperature will be less than 50°F. This determines, for a given fluid, the highest surface temperature on the liquid side when nucleate boiling exists. As an example, saturation temperature of propane at 295 psia is 139°F (P_c = 42.0 atm). Therefore, with the nucleate boiling the

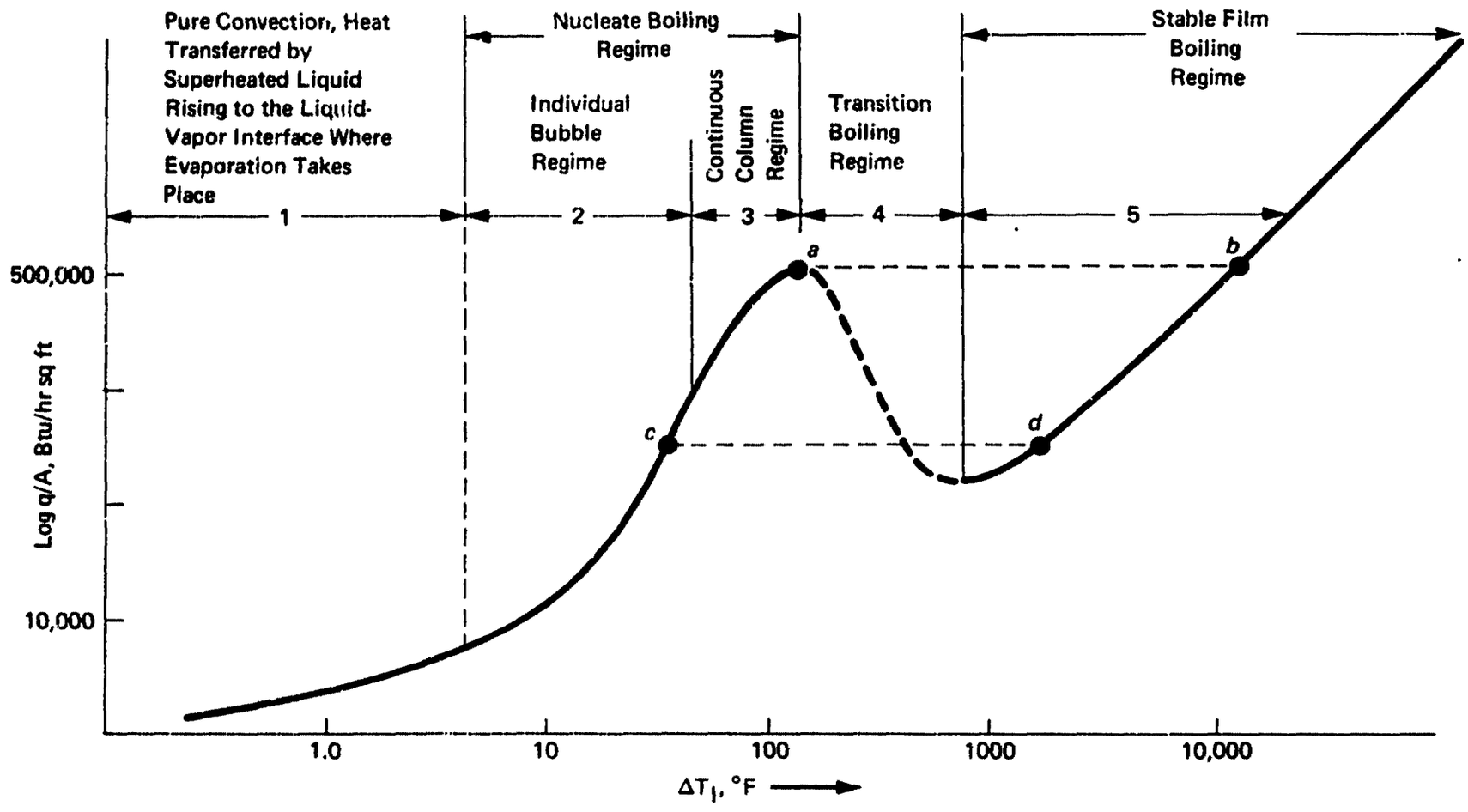

FIGURE 14

TYPICAL BOILING CURVES FOR A WIRE, TUBE, OR HORIZONTAL SURFACE IN A POOL OF WATER AT ATMOSPHERIC PRESSURE· REF. 52.

A8-5

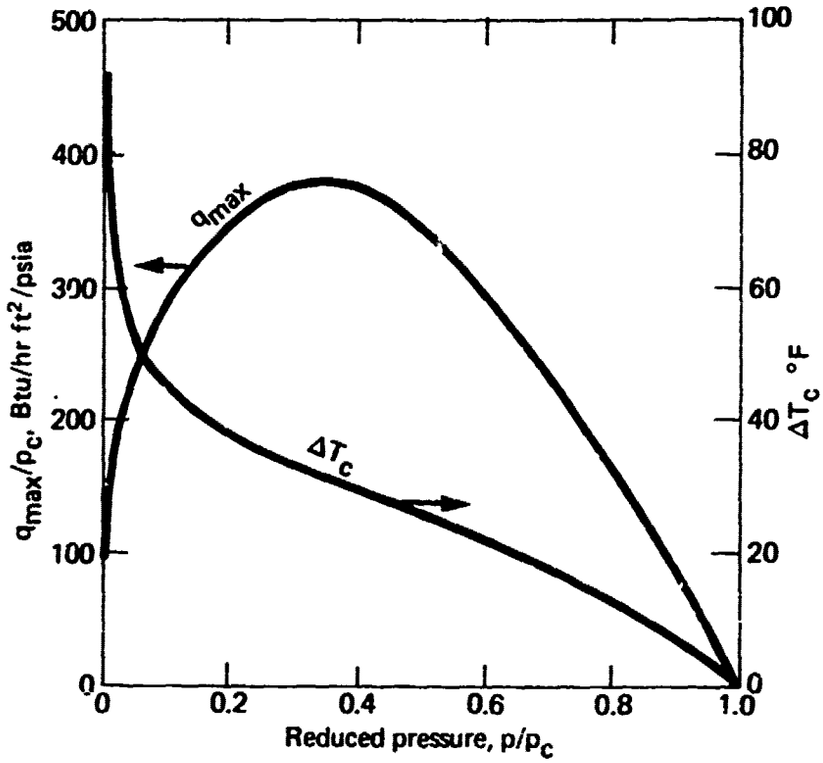

FIGURE 15

MAXIMUM HEAT FLUX AND TEMPERATURE DIFFERENCE AS A FUNCTION OF REDUCED PRESSURE

SOURCE: REF. 42

TABLE VIII - Observed maximum heat fluxes for various liquids, pool-boiling on submerged heaters

Liquid	Pressure, psia	Liquid temperature °F	Max. Heat Flux q_{max}	Critical temp. diff. ΔT_c, °F	Heater Surface and condition
Water	14.7	212	993,000	99.9	0.040-in.diameter Horizontal Chromel C wire
	64.7	297	906,000	39.5	
	114.7	337	1,590,000	12.8	
	14.7	212	210,000	42	0.004-in-diameter clean platinum wire
Propane, Comm.grade	555	196.8	36,200	6.1	
	14.7	172.6	192,500	53.2	Clean surface; horizontal plate electroplated with 0.002-in. chromium,polished
Ethyl Alcohol	375	379.3	350,000	22.6	
	657	432.2	261,000	10.0	
n-Pentane, 90+% pure	170	272.2	191,100	42.9	
	457	375.5	42,000	5.3	
	14.7	.....	109,000	.....	
n-Heptane, 70 +%pure	50	.....	157,000	.....	
	215	.....	205,000	.....	Dirty surface; horizontal plate, electroplated with 0.002-in. chromium, polished
	14.7	.....	139,000	.....	
Benzene, c.p.grade	355	.....	269,000	.....	
	667	.....	57,000	.....	

Source: B. Gebhart[42]

liquid side surface temperature will be less than 189 °F.

The variation of q_{max} in Figure 15 indicates that at very small and very large reduced pressures q_{max} values are small. Again for propane at 555 psia q_{max} is given in Table VIII as 36,200 Btu/(hr)(ft^2). The reduced pressure for this case is about 0.9. Assuming that the average heat flux from fire is 74,500 Btu/(hr)(ft^2), then at reduced pressures greater than 0.9 the flux q_{max} would be less than the heat flux from fire.

Under this condition, the liquid propane will not be able to absorb the heat flux from fire, a vapor film will start to blanket the surface and the film boiling will result. The system eventually starts to move, in Figure 14 from state "a" toward state "b" in the film boiling region, this causing a considerable increase in the heating surface termperature. The final surface temperature, of-course, depends on the fire temperature. Before state "b" is reached most likely the heated surface is subject to failure.

The q_{max} and T_c values in Figure 14 are given for the pool boiling of water at atmospheric pressure. The characteristic boiling regimes shown in this figure, however, are similar for other boiling liquids.

Considering the usual heat flux values from fire to liquid cargo containers, one can say that the problems associated with the film boiling may arise at pressures very close to the critical pressure.

Therefore, such cases require careful consideration. If pressures close to the critical value are expected, the use of proper insulation to reduce the heat flux from fire to a level below the predicted q_{max} is most desirable.

For moderate pressures it is expected that either the convection or the nucleate boiling will prevail. In this case, the liquid side surface temperature would be slightly above the liquid saturation temperature. In consequence, the container wall temperature is controlled by the heat flow characteristics on the fire side.

It is a possibility, with impinging flames, that the heat flux from fire is greater than 34,500 Btu/(hr)(ft^2). Average local (1/8 in. radius area around flame axis) heat flux values as high as 83,000 Btu/(hr)(ft^2) were reported in reference 4, for air-methane flames impinging on flat surfaces. Such heat flux levels may bring out the film boiling problem at reduced pressures much lower than the value of 0.9. However, in this case analysis of the problem is considerably complicated since the film boiling and the surface temperature increase are localized. A proper analysis should include the heat flow within the wall and the vapor film in the transverse direction from hot spots toward the cooler regions. This would help to reduce the wall temperature.

Another very important problem needs special consideration. It has been mentioned earlier that the nucleate boiling prevails as long as the vapor generated is readily removed from the heating surface.

For large liquid volumes, this removal occurs freely due to the buoyancy forces acting on the vapor bubbles. In the case of small liquid volumes and restricted container configurations, which makes the vapor removal difficult, a vapor blanket may form on the heating surface even at heat flux values much lower than the maximum flux. Referring to Figure 14 then, a system at state "c" moves toward the state "d" in the film boiling region without going through the state "a". A very informative example concerning this case was reported as a result of fire tests conducted at Baytown, Texas, in 1943, by the Rubber Reserve Co.[68] The paragraph below is quoted from that reference:

"Preparatory to the conduct of the test, there had been installed a 23 feet 8 inch length of 4 inch pipe connected to the bottom of the tank which extended outside of the diked area for the purpose of draining the water contents of the tank, either during the fire in case of emergency, or at the expiration of the test. After three minutes and thirty seconds, this drain pipe became sufficiently hot that it sagged 12 inches from level at a point 8 feet 6 inches from the center of the tank, which was about two feet inside the diked area, causing a leak to occur at the joint between the outlet nipple on the tank and the flanged elbow. This failure occurred even though this pipe was normally filled with water under approximately a 5 foot head."

This reference reported heat fluxes ranging from 40,000 to 45,000 Btu/(hr)(ft^2) as the maximum heat input to pipes exposed to

flame. These values are very small compared to the maximum nucleate boiling flux values for water given in Table VIII. Therefore, under normal conditions, the film boiling and the material failure should not occur. It is evident that with the piping arrangement used in these experiments free removal of the generated vapor was not possible, thus causing the film boiling.

This matter requires serious consideration in designing and in the protection of piping arrangements from fire exposures.

APPENDIX 9: BEHAVIOR OF A MONOMER CARGO DURING RAPID POLYMERIZATION AND PRESSURE RELIEF

Cargo containers carrying organic materials which have the potential for chemical reactions, such as polymerization, are subject to a unique hazard. A pressure rise may occur due to an internal reaction not necessarily associated with exposure to fire.

Polymerization reactions are exothermic in nature. The heat liberated causes the temperature to rise, resulting in an increasing rate of polymerization. Styrene, if heated to 239°F. will start to polymerize[32] liberating about 300 Btu/lb of polymer formed. Since the latent heat of vaporization is about 115 Btu/lb, the heat liberated from polymerization of one pound of material can result in the evaporation of two pounds of monomer.

The problem of designing a safety relief device for such a system is complex due to the unsteady state nature of the evaporation process. To illustrate, consider the special situation of styrene polymerization and follow the behavior of the tank contents as the polymerization gets underway. If the styrene monomer is at ambient temperature (77°F) and begins to polymerize due to the presence of traces of catalyst, and without external heat addition, then the amount of material which must polymerize in order to raise the temperature to the boiling point of styrene (298.4°F) can be obtained by heat balance

$$m\hat{Q} = Wc_p \Delta T$$

where

m =	amount of polymer formed	lbs
$\hat{Q}$ =	heat of reaction	Btu/lb
W =	total mass of material in the Vessel	°F
c_p =	specific heat	Btu/(lb)(°F)
ΔT	temperature rise, °F	

Since $\hat{Q}$ = 300 Btu/lb and c_p = 0.5 Btu/(lb)(°F)

ΔT = 298.4-77=221.4°F

$$m = \frac{0.5 \times 221.4}{300} W = 0.37W$$

More than one-third of the material should polymerize before styrene monomer starts to boil. This is overly simplified as in the initial stage of reaction perhaps only dimers or trimers would be formed and would have a much higher boiling point than the monomer. Vapor generation may be relatively low in volume but could entrain liquid and form foams as a result of high viscosity.

W. J. Boyle, Jr.,[11] discussing actual emergency rupture relief situations with polymerization reactors noted that in one instance a large quantity of liquid (monomer, polymer, and water) was observed to splash to the ground in the area surrounding the relief vent. This material was ejected as liquid slugs and not as vapor. It was also observed that the internal pressure of the container continued to rise after the safety disc had ruptured.

Since he could locate no references on two phase flow which could be applied to predict the behavior during venting of highly viscous syrups encountered in mass polymerizations (100,000-300,000 centipoises), Boyle conducted experiments on the one-quart size to check venting of such syrups. These confirmed calculations for liquid venting. If the required relief area is calculated on the assumption the batch will vent as a liquid (with the batch pressure at the designed failure pressure of the rupture disc), a factor of safety is believed to exist. For reactor designs, Boyle suggested that the relief area should be two to three times the area indicated by design calculations.

In an earlier study on the stability of butadiene, Robey et al [66] presented data on the two routes of polymerization, namely, dimerization (which is thermally activated) and polymerization to high-molecular-weight polymer (primarily in the presence of peroxides). For the dimerization in the vapor phase, the rate was found to be:[11] rate in (moles cc^{-1} sec^{-1}) = $9.20 \times 10^{9} \exp. (-23{,}690/RT)$ $[C_4H_6]$.

Commenting on the prevention of this reaction, the authors stated that no way was found for minimizing the dimerization reaction in concentrated butadiene other than the use of the lowest practical temperatures during storage and handling. Butadiene was shown to peroxidize in contact with oxygen, air or other substances. Noting that compounds such as hydroquinone, pyrogallol, and catechol are effective inhibitors of the peroxidation of the diene, it was determined that 300 cc of butadiene containing 0.1 weight per cent of hydroquinone completely resists the peroxidizing

action of a stream of air, at room temperature and 50 psi pressure, for more than 120 hours.

In a recent work, Harmon and Martin[45] studied polymerization of vinyl monomers, including ethyl acrylate (EA), methyl acrylate (MA) and methyl methacrylate (MMA), using a five-gallon apparatus. The MMA was uninhibited, while the EA and MA contained 15 ppm. of monomethyl ether of hydroquinone (MEHQ). Polymerization rates were measured as inhibitors were added. EA was found to polymerize more rapidly than MMA under similar concentrations and conditions. As the rate of polymerization increases, the pressure also increases and the rate of vapor formation increases, thus requiring a larger disc (orifice). Since the polymerization of EA, MA, and MMA is autoaccelerating, as the relief pressure is increased the rate of polymerization and the rate of temperature rise increase; the rate of pressure build-up is more rapid, requiring a larger relief area. Vessels containing materials capable of autoaccelerating or runaway reactions (e.g., vinyl monomers) should be protected with rupture discs having the lowest pressure rating feasible.

High heating rates may overpower the influence of the inhibitor. At present, there seems to be no general agreement on procedures or control methods to monitor inhibitors. Specified concentrations, even if added properly at time of manufacture, may not necessarily still be present days or weeks later, or during the prolonged shipment. In addition, the role of heat must be considered. Insulation will be important as it reduces the heat flux, especially in a fire emergency

Unresolved is the question of what level of inhibitor is needed at the boiling point of the monomer to prevent the monomer from beginning to polymerize.

In view of the sparce literature on this problem, it is necessary to examine each situation for potential difficulty, considering:

Reactivity of the monomer;

Presence of inhibitor and its concentration;

Possibility of loss of inhibitor;

Possibility of fire exposure to initiate polymerization;

Possibility of contamination as a result of an accident, with attendant onset of polymerization.

Rupture discs may be more satisfactory than spring-loaded relief devices since accumulation of polymer in relief valves could prevent them from functioning. It must be borne in mind in selecting the relief device that a small amount of vapor may emerge from the emergency vent as a viscous liquid-vapor mixture. The necessity for frequent inspection and cleaning of the rupture disc is clearly vital, since polymer which may coat the disc will, in effect, raise the relief pressure, without the change being apparent.

Styrene and vinyl chloride have been recently reviewed from the standpoint of loss prevention including detials of storage facilities.[70]

Butadiene has been known to explode its cylinder (container) when overheated by an electric heating tape. Temperature and pressure details are cited in the report.[31]

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