MATERIALS USED IN THE CONSTRUCTION OF SHIPS FOR THE CARRIAGE OF CHEMICALS AND LOW TEMPERATURE CARGOES

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The recent rapid expansion of the chemical and petrochemicals industry, superimposed on the availability and demand for natural gas as a basic fuel, the exploitation of mineral deposits, etc., has led to requirements for bulk shipments by sea of a very wide variety of products.

Ships now in service or on order vary widely in size and complexity; their cargoes may be carried in containers of almost every shape; at pressures ranging from atmospheric to 2000 lb/in^2; temperatures ranging from -319°F (-195°C) to 302°F (150°C) and may be stable, unstable, corrosive, inert, dielectric or conductive in varying degrees.

Materials currently available to handle these cargoes range from conventional mild steel at about £50 per ton, through clad and coated steels to a wide range of nickel alloy steels culminating in 36 per cent Ni (Invar) at about £850 per ton; also aluminium, copper alloys, plastics, glass and rubber.

Compared with the materials, design and fabricating techniques that have been available in the past (for chemicals have been transported in bulk by sea for many years) the designer now has a wealth of data from which he can evaluate and select from an ever increasing range of materials; but the variety and complexity of products, size of ship and commercial pressures to reduce costs have also increased, thus the final optimum selection is no easier to arrive at than before.

Mr. Ffooks

INTRODUCTION

It is still possible for experts to argue at length about the analysis, production techniques, welding and painting of mild steel as it is applied to the structures of conventional size ships carrying conventional cargoes in a medium we have lived with for thousands of years.

It is hardly to be expected, therefore, that a paper covering materials used for the carriage of chemicals and low temperature cargoes—today a vast range of products—can be other than a very general introduction to the materials problem in this very rapidly developing field.

As an indication of the rate of development—consider LNG. The first ocean-going prototype ship (5000 m^3 capacity) was built in 1959; the first commercial ships—three of 25 000/27 500 m^3—commenced operation in 1964/5. Two ships of 75 000 m^3 capacity have recently entered service. Ships of 125 000 m^3 are currently under negotiation with shipyards for delivery in 1974/5, a fifteen-fold increase in ship capacity in just over ten years.

Of the ten ships now in service, there are four quite different and independently developed technologies employed, each incorporating three quite different materials. Next year a ship using a fifth technology will enter service, and a sixth has been ordered.

Chemical tankers have also developed rapidly in size and complexity in the last five to ten years, although they have a longer history. For example, the Shell tanker *Agnita*, built in 1931, was designed to carry 3780 tons of sulphuric acid in 12 mild steel riveted bottles; a number of relatively small carriers operated in Europe between and immediately after the Wars; similarly there was quite extensive barge traffic in the Mississippi and other U.S. waterways as well as some coastal traffic.

With the recent growth of large fertilizer plants and the plastics industry, relatively large shipments of petrochemicals have been carried by sea; in addition, several sulphur carriers of substantial capacity have been in service for a number of years. If ores, bauxite, etc., are included in the term "solid chemicals" then the last ten years has seen a similar rapid increase in the marine transportation of these materials.

It is a fascinating, if sometimes confusing, field of activity.

THE PRODUCT TO BE CARRIED

It is beyond the scope of this paper to provide a definitive list of all the products and their characteristics, that are currently carried by sea; this information may be found in a number of publications—some of which are given in the list of references. These publications are of considerable value in enabling the designer to make a rapid evaluation of his essential working parameters; from these data he can quickly determine the volumetric requirements of his ship, type of container required, range of materials at his disposal, extent of heating, insulation, gas blanketing, cargo separation, etc. By subsequent cross reference to the Rules of the Regulatory Bodies, in so far as they may be published for the product under consideration, he will quickly discover additional precautions which will be required

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* Shell Marine Department.

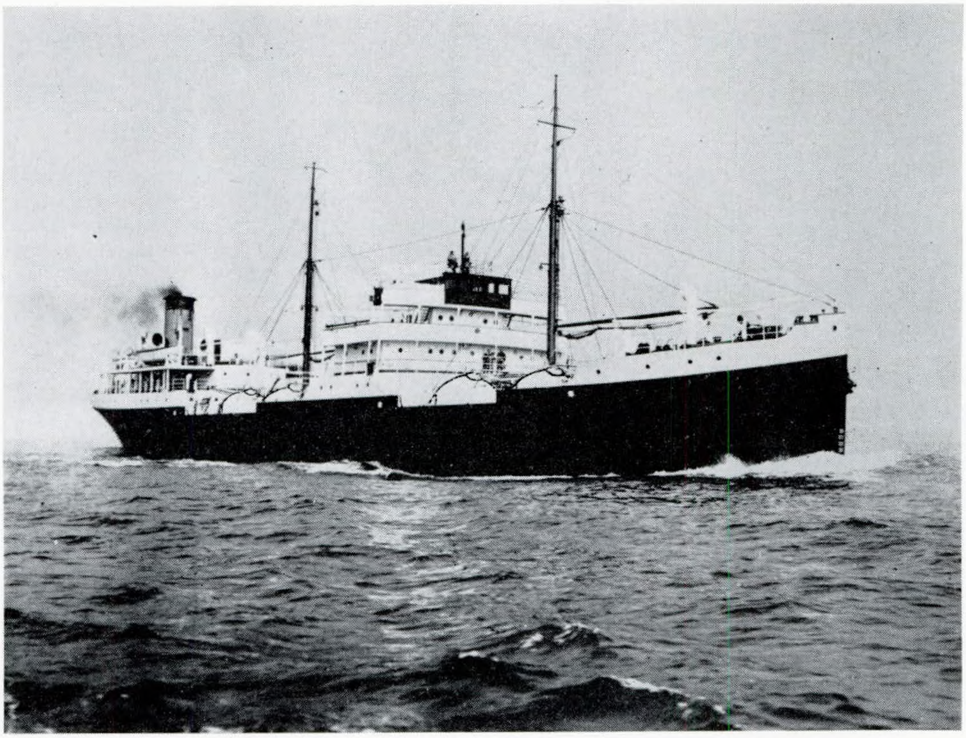

FIG. 1—MV Agnita—*owned by the Anglo Saxon Petroleum Co.*

to be built into his ship, such as secondary containment, positive separations, corrosion allowances, precautions against fire and collision.

He will thus find little difficulty in establishing preliminary "specifications" for products on which service experience has been gained. (See Fig. 3)

He will find more difficulty, however, when he studies products which though perhaps frequently handled in small quantities ashore, have not previously been stored or shipped in bulk; or newly developed products—and this applies particularly to the petrochemical field. Here data is sketchy, sometimes contradictory and often non-existent.

The following examples are typical:

LNG—if LNG (a hydrocarbon mixture—predominantly methane) is stored in bulk, does it stratify into separate layers? Do the top layers which, being at a lower pressure may become colder and denser, cause the whole mass of liquid to "overbalance" at some stage with consequent agitation, rapid evaporation, etc.? That this does *not* happen was clearly established and published in 1959—but the question is still being asked today.

Butadiene—in 1958 it was required to know under what conditions polymerization took place, particularly in contact with iron oxide, and what proportion of inhibitor was required to prevent this. Contact with several manufacturers failed to produce an answer, although butadiene had at that time been produced commercially for some years; very considerable quantities of polymer "stalactites" had been found in storage tanks but their formation appeared to be quite unpredictable.

More recently the possibility of caustic residue during the manufacturing process created a potential hazard if the product was to be carried in aluminium tanks—a material otherwise entirely suitable for this product. No published information was available on this question.

Anhydrous Ammonia—in 1962 it was necessary to establish the effect of water content on copper attack in order to produce a cargo specification: no information was available and a laboratory test programme was the only remedy.

In general, therefore, while reference books and other

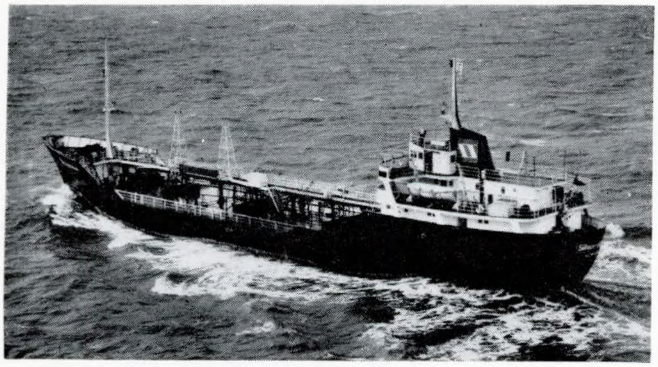

FIG. 2—M.V. Silverfalcon—*a British-owned chemical tanker—operating mainly in the North Sea*

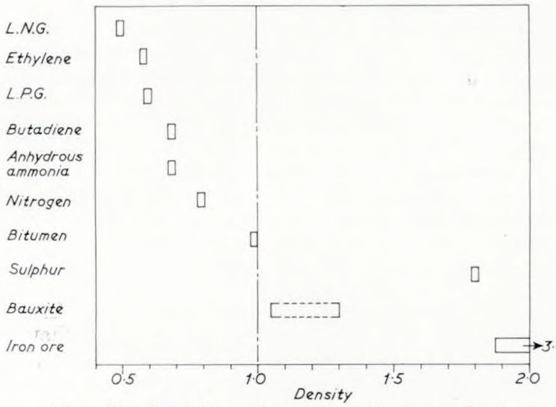

FIG. 3—*Density of some typical products*

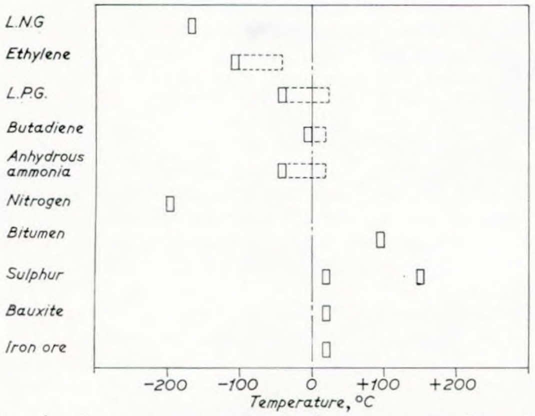

FIG. 4—*Temperatures at which some typical products are carried in bulk form*

publications now provide a very good general guide to the basic properties of chemicals and their reaction to various commercially available materials, they do not yet provide a complete answer to their satisfactory or safe shipment in bulk by sea.

MATERIALS FOR CONTAINMENT

It is both obvious and trite to state that the material selected for the containment and handling of a specific product must be suitable for the purpose; as already mentioned, it is in designing systems and selecting materials for "unconventional" cargoes, that the problem of selection becomes less elementary. Attention must be given to the following:

1) *Function*—structural, protective, insulant, lubricant, etc;
2) *Physical Properties*—strength, compatibility, liquid tightness, electrical properties, coefficient of expansion, method of application, weldability, bondability, toxicity, suitability for shipyard conditions, etc;
3) *Inspection and Repair Techniques*—during construction and service;
4) *Cost*—quantity, specification;
5) *Availability*—maximum plate size, rolled or extruded sections, etc;
6) *Existing Experience*—in similar applications, etc.

LOW TEMPERATURE CARGOES

When work began in the completely new field of LNG transportation in the mid 1950's there were three commercially available materials which retained their mechanical properties at the boiling point of LNG −265°F (−165°C), stainless steels, copper and some of its alloys and aluminium; and also some plastics like p.t.f.e. Every aspect was examined. At the same time there had recently been a catastrophic failure of a large land storage tank and the industry was "jumpy"; this was the direct result of the "borderline" use of 3½ per cent nickel, at a temperature of −265°F (−165°C). This tank, which also incorporated a number of what would immediately be recognized today as stress raisers, failed after a few months' service, resulting in explosions, widespread fire and loss of life.

Relevant information on the properties of material which would be reasonably economic to use at cryogenic temperatures and, more important, the properties of their welds was very scanty.

Experience in building large structures of these materials was similarly sparse—if it existed at all. Additional and vital information on *existing* materials was built up by:

a) the manufacturers—who saw a potential market for their products;
b) the companies engaged in the design of the ships and structures;
c) classification societies.

In certain cases, where existing alloys were deficient in strength, ductility, weldability, or availability, new alloys were developed; new welding rods, wires and new testing techniques were devised (e.g. different mechanical test techniques are needed for aluminium than stainless steel): expertise in welding and inspection techniques, developed in the laboratory, was passed to constructors.

Because of the high cost of austenitic stainless steel and its welding a completely new material, 9 per cent nickel steel, was developed to compete with aluminium which had soon established itself as the most attractive material. Very sophisticated, original and quite dramatic test techniques were used to establish confidence in this new material.

Much more recently, in fact currently, the pressure of competition and the high cost of nickel is encouraging studies on 8 per cent nickel—aimed specifically at the LNG market for operating temperatures of −265°F (−165°C) (9 per cent is acceptable for −319°F [−196°C]).

Within the last few days one has read of a new Hitachi/Esso technique to evaluate 9 per cent Ni.

The above remarks apply to low temperature cargoes, but apply equally to "less low" temperatures because one is looking for the *cheapest* acceptable material and clearly 9 per cent Ni tanks are an uneconomical solution for, say, LPG tanks, which operate at −40°F (−40°C). It is, perhaps, interesting to note that the first fully refrigerated single purpose LPG carrier, built in 1961, used 3½ per cent Ni tanks with a 2¼ per cent Ni inner hull which acted as a secondary barrier. Sufficient confidence and knowledge has now been gained and steel production techniques have developed to the point when one can now safely use 2¼ per cent nickel for such tanks or perhaps 0·8 per cent Ni—or even low carbon, grain refined, controlled X-rolled mild steel? This is a subject in itself and will be discussed in a separate paper.

It is significant that no single test yet exists which in itself provides an answer to the question, "will this material be suitable for this or that specific application?" One may therefore be faced with carrying out a multitude of tests—or awaiting successful operating experience.

CHEMICALS

For chemical carriers the problem is primarily one of corrosion and, forgetting those products which, suitably specified as to impurities, or "inhibited", etc., can be carried in ordinary mild steel tanks, the almost universally adopted material is still stainless steel, the grade depending on the corrosivity of the cargo.

This statement ignores coatings, again the subject of a separate paper, which are rapidly developing as a means of using cheaper structural materials. In this category one has Epoxy paints, rubber, etc.

The use of stainless steel in itself poses a number of interesting problems. The most versatile alloy so far as corrosion resistance is concerned, is 316L and, as might be expected, it is one of the most expensive. For large structures, requiring a thickness of say ⅜ in or above, for reasons of strength, it is possible to apply a stainless steel coating by welding thin sheets on to a grid work of stainless steel strips, spot welded on to a mild steel plating; alternatively, one can readily obtain clad steels; these introduce, however, welding problems involving alloy dilution, etc. Both have the disadvantages that if corrosion is likely to take the

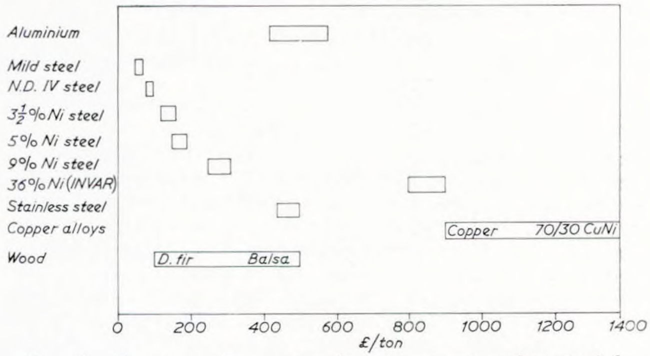

FIG. 5—*Comparative costs of some structural materials*

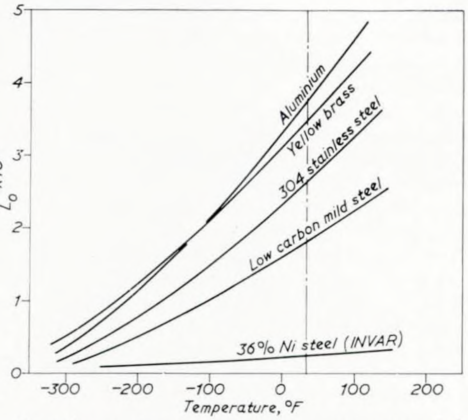

FIG. 6—*Thermal expansion of some materials—variation with temperature*

form of pitting—the life of the tank can be short; and this is likely to occur in the weld areas which thus become the weak points. Again one must assess the likelihood of corrosion taking this form and considerable work has been done on the development of representative accelerated ageing and corrosion techniques.

Metal and plastic coatings do have the advantage that leaks, or local failures, are easy to locate and repair.

GENERAL

In selecting a material for use in extremes of temperature its coefficient of expansion plays an important part. Fig. 6 shows the wide range in materials commonly used. If the rigid tank structure technique is to be adopted, beyond a certain temperature it is advisable, if not mandatory, to completely divorce the tank from the hull of the ship.

This is carried out in both low and high temperature ranges, i.e. LNG −265°F (−165°C)/LPG −40°F (−40°C) and sulphur carriers 302°F (150°C) although, interestingly, bitumen has been carried at temperatures of 248°F (120°C) and above for many years in tankers of conventional structure with few problems. In this latter case an insulating layer of solid bitumen is allowed to form on the tank's surface during the voyage; this no doubt reduces the stress levels due to temperature differential during the period when the ship is subjected to maximum stressing in a seaway.

In the low temperature field, and in an effort to reduce capital costs, recent developments in LNG transport have resulted in the adoption of the "membrane" technique. Two such designs are on the market, both similar in principle but they differ in their use of material for the "primary containment". One uses low carbon (304 L) stainless steel lining 1·2 mm thick with cross corrugations; these corrugations counteract expansion and contraction due to temperature and also the superimposed expansion and contraction of the hull structure of the ship itself, which occurs when the ship is at sea.

The other uses 0·5 mm thick Invar (36 per cent Ni) which has the special characteristic of a very low coefficient of expansion (see Fig. 6). It is installed without any intentionally built-in expansion means, i.e. in a fully restrained condition. Invar is less corrosion resistant than the stainless steel, but as the cargo is non-corrosive, the only problem from this point of view arises during construction and at dry dockings and, possibly, if leakage of ballast water occurs through the inner hull of the ship. Two ships built to this technique have very recently entered service between Alaska and Japan and their performance is being watched with much interest by builders, owners and designers alike. Both these membrane designs were subjected to extensive component testing for corrosion and fatigue life.

As a further general comment, it is useful to be on guard against situations where apparently suitable materials present problems due to a combination of properties in unfamiliar conditions. As an example, austenitic stainless steel, essentially suitable for use at low temperatures, has a high coefficient of expansion and this, in combination with its low thermal conductivity, led to many problems in low temperature applications, due to the unforeseen distortion of heavy piping connexions.

INSULATING MATERIALS

Similar considerations as those generally described earlier apply to the selection of insulating materials; e.g. compatibility with the cargoes carried and the normal operating environment, compressive strength, thermal expansion, long term stability, ease of application and repair, effect of material convection cost, availability.

As previously stated, however, many properties of those materials which appear suitable for a specialized application may not be available. To evaluate the suitability of newly developed materials for special applications, the author's company have developed a series of standard tests; these provide a quick and inexpensive initial screening, followed by more sophisticated and larger scale tests which vary according to the specific use required of the material.

Some such routine is essential when very specialized products are shipped and experience is limited. In this particular case the selected material may be required to combine thermal insulating properties, with compressive strength, a defined measure of resistance to liquid and gas penetration. Abnormal considerations, such as resistance to immersion in seawater, fire, etc., must also be taken into account.

CARGO HANDLING SYSTEMS

It would be unnecessary to repeat here that all equipment installed on board ship should be most carefully selected and be compatible with the products to be handled, were it not for the fact that this area seems always to produce a substantial proportion of the problems associated with the carriage of specialized products:

i) It seems most difficult to forecast, from manufacturers' drawings, the performance in service—thus it is advantageous for the first production unit to undergo as near a realistic test as possible;
ii) It is difficult to establish tests which truly represent service conditions and incorporate the time element;
iii) It is often difficult for the owners' superintendent to establish whether the "modified" unit (if adapted from the standard, for a specialized product) incorporates all the modifications specified.

Part of the problem may be that, when selecting materials for component parts, too great an emphasis tends to be given to their compatibility with the product. Certainly the problem is often rather a complex one involving, for example, the effects of thermal expansion on a combination of materials in a complicated casting and this may have an unexpected effect on sensitive working clearances. The effect of wear on claddings or coatings, instability, creep, grain growth of working parts, etc., the effect of contaminants, foreign matter, the marine environment, vibration, etc., all add to the difficulty in anticipating smooth performance in service.

Inadequate operating instructions and maintenance manuals are another cause of trouble: if a piece of equipment fails to function the ship's engineer is forced to do his best to repair it, since service engineers may be many thousands of miles away: and often when at hand they are familiar with the standard rather than the modified unit.

Thus it is important that the designers' attention extends beyond the original specification and the initial selection of equipment.

CONCLUDING REMARKS

In considering the way in which ships for bulk transport of cargoes at low temperature and chemicals have developed, it is interesting to compare the different approaches made by the designers of LNG ships and chemical carriers.

In the first case, LNG was a completely new product to the naval architect, and has been followed by a very rapidly expanding market and increase in ship size. Designs had to be developed from first principles with, broadly speaking, new materials; the result is that existing ships and new orders incorporate a number of radically different designs. Materials have been used in the most unlikely environments, e.g. balsa wood for insulation and emergency liquid containment; ferritic stainless steel for ball bearings in the submerged pumps operating at −265°F (−165°C); iron laminations in the cargo pump motor windings, operating at the same temperature.

Conversely, in the second case, the chemical products have for the most part evolved over a period of years; the ships have developed by introducing new materials and/or coatings into conventional tankers; the size of ships has increased gradually. The transition has taken place in very much the same conventional way as riveting gave way to welding.

Is there now scope for a "first principle" approach to the shipping of chemicals?

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Discussion

MR. G. VICTORY, Member of Council, M.I.Mar.E. and the Chairman of the meeting, emphasized the problem of containment and the hazards involved, including not only the ship and crew, but in many cases, when the ship was in coastal waters or harbours the environment.

Although chemicals had been carried for many years, there had been some unfortunate incidents which had been under-emphasized. Hazards to human life could occur from the carriage of chlorine in bulk (proposed for the future), phosphorus, ethyl tetramethylead, carbon disulphate and acrylionitrile. It was conceivable someone might suggest the carriage of pesticides in bulk. The containment requirement was approaching that for a nuclear reactor on a ship. What would be the results of a massive release of LPG or LNG? The findings set out in a recent paper in America had been far from positive as only a restricted amount —some 800 gallons—of LPG had been released. It was hoped to scale this up to a more massive release; what would be the effect of scaling up such a release by a factor of 1000 or thereabouts?

At present, there were four different methods of containment of LPG in about ten ships, and under discussion were two more, thus, the best single method had yet to be established. He thought there might be certain advantages in starting from scratch. He advocated the use of the most suitable and proven materials, and to exercise extreme caution before changing a system.

The author had mentioned rules and regulatory bodies. Mr. Victory would mention some of the recommendations of the Standing Advisory Committee on the Carriage of Dangerous Goods, incorporated in the blue book, and the draught code recommendations now being produced by IMCO. The need for safe containment requirements was international and agreements must ensure that shipowners of one particular country should not be unduly penalized. It was essential that the fundamental problems be set down. He hoped the draught code produced by IMCO for the carriage of dangerous liquids in bulk would be implemented in the near future and be of great assistance.

Regarding the second barrier concept for LNG, obviously the temperature was low or very low. Unless it could be ensured that the second metallic barrier would never be exposed to the temperature at which the primary barrier had to maintain the cargo, that second barrier must be of a metal which would stand that temperature. It was fairly obvious that in a ship the external hull could not function thus, and this stressed the necessity of ensuring that the insulation must protect the secondary barrier.

Did the author consider that further developments might be made in this field? It was obvious that the present method, where the primary barrier had to be capable of accepting the very low LNG temperature, was a costly one.

MR. B. TODD M.Eng., M.I.Mar.E. said the author had mentioned that "it was necessary to establish the effect of water content on copper attack in order to produce a cargo specification", the inference being that it was necessary to keep the water to a very low level. In Mr. Todd's joint paper it was stated: "The presence of CO_2 and O_2 seem to be necessary for promotion of cracking whilst moisture has an inhibitive effect." Opinions appeared contradictory. What figure would the author indicate for a desired moisture content?

MR. H. J. MILLER, B.Sc., M.I.Mar.E., asked the author to enlarge on the subject of temperature in chemical carriers. He was convinced that one could not divorce materials from design. The author had stated: "If the rigid tank structure technique is to be adopted, beyond a certain temperature it is advisable, if not mandatory, to completely divorce the tank from the hull of the ship." Mr. Miller commented that at the present time, the temperature at which each ship operated had not been investigated. In a chemical tanker, for example the tanks were of stainless steel and the outside structure of mild steel. Problems had arisen because of the different expansion rates of these two different materials. He suggested that either the shipbuilder, the classification society, the owner or all three should co-operate on this problem. It was surprising the number of chemical tankers that did not have any stipulation as to maximum temperature.

The author had mentioned an insulating layer of solid bitument. In some recent designs Mr. Miller found that the way to insulate the cargo was to allow it to "congeal" and form the insulation itself. How did one unload the cargo "stuck" to the side of the ship? This would be a problem of design rather than of materials.

In the last paragraph Mr. Ffooks said: "Is there now scope for a 'first principle' approach to the shipping of chemicals?" Having reached such an advanced stage in technological achievements—Lloyds and IMCO's sets of rules—Mr. Miller would be loath to revert to first principles.

Author's Reply

The author in reply endorsed Mr. Victory's remarks especially the need for absolute security with the increasing hazard of larger ships and more noxious cargoes.

One of the problems in adopting proven designs was that one could only advance by attempting new techniques. When was something "proven"? Was it when it reached its first or second special survey? The end of the guarantee period would be about five or six years from the present time. In the LNG field, ship deliveries were envisaged for somewhere round about 1974/75; this was the earliest a ship of this size could enter service, so it would be six years before one started getting any answers. These ships were very expensive and the problem was to lower the price without decreasing the safety margin. Obviously, this was extremely important.

Regarding Mr. Victory's point of trying to reduce the operating temperature of the primary barrier, was it not so that one could only achieve this by putting some form of insulation on the inside? This would have to remain sufficiently liquid tight and homogeneous to prevent low temperature spots or local areas of sub-cooling, if not higher stresses would be introduced which was what should be avoided.

Mr. Todd had raised the problem of the water content of anhydrous ammonia. *Methane Pioneer* had completed her trials on LNG and was operating on a spot cargo basis. The ship had aluminium tanks, suitable for carrying anhydrous ammonia; three of the five pumps had bronze shafts and fittings and the water content had to be kept very low to avoid the reaction of anhydrous ammonia with the copper. There was no question of corrosion of the tanks. A quick test programme was carried out some years ago to define the level of water acceptable to the pump fittings, the figure decided was about two or three ppm. Another problem was that the cargo suppliers were unable to state the water content of their anhydrous ammonia so there was some initial confusion.

The author was intrigued by the fact that at least one major company had been transporting bitumen in conventional tankers for a long time at a temperature of 250°F, and if he remembered correctly, were loading it on occasions at somewhere near 300°F. There was no insulation on the tank walls. The bitumen, being heavy cargo, was carried entirely within the centre compartments which were wider than was normal for tankers at that time; the wing tanks were confined to ballast. At that time, without the aid of computers, a good deal less was known about the stresses and strains and the analyses of ships' structures. Although no problems had occurred to date, a maximum temperature was specified (if he remembered correctly it was about 258°F) to obviate the possibility of trouble when loading at too high a temperature. The self-developing insulating layer was achieved simply by turning most of the heated coils off once the ship had got under way, a cool viscous layer built up around the tank walls that in itself reduced the stresses in the immediate vicinity. Three or four days before the ship entered port, the heating coils were turned full on; the cargo was circulated within the tanks by a pumping system which drew cargo from the bottom and circulated it around to the top; this effectively removed the insulating layer before the ship reached port.

He agreed with Mr. Miller that a "first principle approach" was perhaps not a clear explanation. What he meant was, should not another basic look be taken to see whether there was something to be gained by standing back, and in a broad sense, re-looking? Certainly he did not mean literally starting from scratch.

In the LNG field one had had the experience of seeing a number of people starting with a new idea, advancing very rapidly and coming up with quite substantially different solutions to the same basic problems. When he said "first principle approach" in connexion with this field, he included the development of a completely new material or the use of an unlikely one. He did not think that anyone foresaw fifteen years ago that vast areas of forest would be cut down in Ecuador to build ships, but this was what was happening. The secondary barrier system, which was used in self-supporting tanks and also in one of the membrane tank solutions, used very considerable quantities of wood, which, in fact, was a very satisfactory material for supporting the membrane and containing the liquid if the membrane leaked.

DEVELOPMENTS IN MACHINERY AND PIPING SYSTEMS FOR CHEMICAL AND LOW TEMPERATURE CARGOES

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Mr. Crook

This paper endeavours to illustrate the wide range of materials being used in the transportation of liquid gases and chemical cargoes by sea, with particular reference to those not directly associated with cargo tank construction, coatings and insulation which are the subject of other papers at this symposium.

Particular examples of early problems are cited with reference to the more uncommon materials used and, in some cases, specifically developed.

The author demonstrates that particularly in the case of chemical carriers, the choice of materials is not by any means based on an ideal, but rather on an economically acceptable compromise.

INTRODUCTION

In the majority of instances the machinery and systems components employed for special cargoes are identical to, or modifications of, conventional equipment used in other industries. It is generally in the area of materials that the differences occur, giving rise to the problems discussed.

The choice of material for any application is arrived at after due consideration of:

1) service loading;
2) compatability with product carried;
3) suitability for marine application;
4) past experience of satisfactory operation or failures in similar application;
5) availability in quantities and form required;
6) cost;
7) delivery dates;
8) expertise available for manipulation and operation;
9) acceptance by classification societies and other Regulatory bodies.

The result of this automatic method of selection in many cases produces a compromise solution mainly governed by cost and degree of sophistication. In the case of low temperature cargoes this philosophy ensues with particular regard to insulation and low pressure piping.

Products carriers deviate even more from the "ideal", the shipowner having to accept the best all-round system available within his budget which gives optimum flexibility on types of cargo.

In the following sections of the paper it is convenient to consider low temperature cargoes separate from what are commonly termed "chemicals".

LOW TEMPERATURE CARGOES

The title of this section refers to the carriage of liquid gases at temperatures approximating to their individual boiling points at atmospheric pressure.

Referring back to the introduction, the parameters which in most cases determine the choice of materials are compatability with the cargo carried (and its inhibitors or other dosed products) and low temperature suitability.

Liquid gas cargoes can be segregated into three basic groups regarding carriage temperatures:

i) butane, propane, anhydrous ammonia, vinyl chloride, propylene, chlorine, butadiene, at temperatures down to −45°C (−49°F);
ii) ethylene, −104°C (−155°F);
iii) methane (L.N.G.), −165°C (−265°F).

Each vessel is classed to carry one or more of these products and an L.P.G. vessel will normally be designed for propane, butane and anhydrous ammonia. This latter product necessarily restricts materials to those not containing copper or zinc. There is one exception to this rule which is mentioned later.

Likewise, an ethylene vessel will also normally be classed for propane and anhydrous ammonia.

It is possible that in future, methane carriers will have flexibility of cargo, but currently it is practice to limit them to methane, whilst consuming boil-off vapour in the main boiler or main engine. Capital cost of reliquefaction plant does not, in this case, justify an alternative.

Piping

Considering group (i), ferrous materials will normally be used, and for this temperature range, it is general in this country to use close grain carbon steel to B.S. 3603 (modified). However, 2 per cent Ni of continental manufacture has been used satisfactorily although small wall thickness did not help welding.

Groups (ii) and (iii) normally employ stainless steels of the A.1.S.1. 321, 316, 304 types or equivalent.

There are exceptions to the rule and, for example, 9 per cent Ni or aluminium could be used where the availability as pipe and the related costs are suitable.

Copper is very often used for liquid nitrogen systems, with bronze or similar flanging, being considerably cheaper than a vacuum insulated line of other suitable material. These pipelines would normally be in sizes up to 4 in bore and heavily insulated with polyurethane or similar insulant.

For the larger sizes, as with cargo systems, the cost of copper of sufficient wall thickness would be prohibitive.

The welding of pipelines has presented few problems with low temperature piping and can be compared with the methods employed for corresponding cargo tank materials.

Piping is bought in to the following basic standards, or manufactured on site where required, to the alternative standards indicated.

−50°C (−58°F):	BS 3603. 27LT50 or from material to BS 1501 — 161B LT50,
−100°C (−148°F):	BS 3603. 27LT100 or from material to BS 1501 — 503 LT100,
−190°C (−310°F):	BS 3605 (austenitic stainless steel) or from material to BS 1501 — 821 LT190.

Very often it is prudent to purchase materials to a higher

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standard than required in order to obtain better deliveries and lower costs by using "off the shelf" products.

Colour coding is an essential quality and production control requirement and adequate means of identification are needed from the point of dispatch at the steel mills through manipulation to final erection.

Classification societies exercise control over the quality of base material and finished product and, in general, this takes the following form, assuming that one of the foregoing standards is adopted.

Base Material

LT50 or LT100: apart from the usual tensile and bend tests, impact tests are also required and, depending on specimen size, minimum values will be required at a temperature 6°C (10°F) below minimum service temperature.

For approved austenitic stainless steel piping impact properties are not required although spot radiography can be called for on longitudinal welds.

The next step towards production is to develop an approved procedure which covers preparation, fit-up, electrodes and so on.

Test pieces are then prepared and tested together with macros of each procedure for butts, fillets etc. Having proven the ability to obtain the necessary results with regard to procedure, individual welders will be required to produce test runs which are generally visually inspected and radiographed.

Production may then continue, throughout which 100 per cent radiography obtains. However, providing that satisfactory quality is achieved, this may be relaxed, at the discretion of the surveyor, to some lesser frequency.

The incidence of *in situ* butt welds is kept to a minimum to avoid the possibility of a low quality weld sometimes produced by working under open air conditions. All finished piping is hydraulically tested to twice working pressure. If conditions demand completion welding on site, pneumatic pressure testing may be permitted, as hydraulic test, and resultant pipe cleaning and drying, is an embarrassment. The procedure is to raise the pressure gradually to something in excess of maximum working pressure with the area cleared of personnel. The pressure is then reduced to maximum working pressure and leak testing carried out.

Where stainless steels are used, insulation may be applied direct to untreated piping. In the case of carbon steel or other non-stainless materials, the insulated pipe must be suitably prepared to prevent corrosion from condensation. It is not deemed to be sufficient for the insulation to be air and watertight. Normally these pipe-lengths will be shot-blasted and primed prior to insulation. An example of a suitable priming material is zinc silicate.

Piping insulation is invariably based on polyurethane, or similar foamed material. Generally this will be applied as preformed sections in two layers and with staggered butts to prevent breakdown and icing as a result of cold "fingers". Whilst the insulation integrity depends on well fitting sections, the outer surface or vapour seal is of utmost importance. Whichever form this seal takes, whether g.r.p., mastic or metallic cladding, close attention to detail is rewarded by long life.

An alternative to pre-formed rigid sections is *in situ* foamed polyurethane, whereby gaps may be avoided, using the outer metallic cladding, mounted concentrically with the piping, as a former. However, this method does not make allowance for relative axial movement between hot and cold faces. In the more common two layer system, this is automatically compensated for, to some degree, by reducing the effective thickness to be considered. Another method is to have a thin flexible medium, such as glass wool, interposed between the main insulation and pipe wall.

If the foregoing principles are adopted, fissuring of insulation is not to be expected. Unlike early polyurethane and other foams the materials obtainable today are not only more uniform with regard to cell structure, but are also more flexible at low temperature. However, most "users" have had to learn the hard way and, in some cases, development and experimentation has had to be jointly undertaken by shipbuilder and insulation manufacturer. This has been particularly so in the case of cargo tank insulation, several expensive failures having been experienced.

Where adhesives are required, adequate preparation of mating surfaces is essential and chemically curing adhesives are generally to be preferred.

Plastics of one type or another are being used increasingly at sea, but for low temperature flammable cargoes, they are forbidden as main pipeline material.

Nylon piping is approved for limited application to instrumentation control and sensing pipework, providing it is protected from mechanical damage.

An objection to plastic piping of small bore, currently being raised, is that it is to a limited extent hygroscopic which has led to "freezing" troubles in low temperature applications. The author does not see any reason why this should present further restrictions.

Valves

Basically three main types of valve are used for low temperature systems, being of the ball, gate or globe type.

Ball Valves

Generally valve bodies will be in cast stainless steel or cast carbon steel and, whichever type, impact tests are required with inter-crystalline tests for stainless steel. There is however, some hope of a relaxation of this requirement in the case of stainless steel castings, on the grounds that impact properties are improved at low temperature.

The author's company has, of late, experienced a high incidence of casting failures due to porosity in stainless steels, giving rise to an embarrassing delivery situation. In the case of some suppliers, failure rate has been as high as 75 per cent. Very little information regarding the reasons for these failures has been made available to the author, but it is significant that a run of satisfactory castings can be succeeded by one faulty batch.

P.t.f.e. is used extensively for gland packing and ball seals, being a material with reasonable low temperature properties.

Below −104°C (−155°F) some doubt as to its suitability exists, and in the absence of an alternative, the ball is very often drilled in order to permit release of pressure in ball cavities, thereby avoiding reliance on the ability of the p.t.f.e. to flex. As far as the author is aware, no accidents have occurred at down to −165°C (−265°F) with undrilled balls. However, some operators, unsure of the safety of this approach, have even suggested that body cavities should be fitted with an external relieving device. All valves require to be "fire-safe" and this is achieved in various ways by different valve manufacturers. In each case, however, a secondary seating comes into effect if the p.t.f.e. is destroyed.

As will be seen p.t.f.e. has rapidly become of universal application both at low temperatures and with corrosive products. Nevertheless, there is a requirement for an equally inert material which can maintain resilience at cryogenic temperatures.

The moving parts of ball valves for low temperature are invariably of stainless steel and considerable problems have arisen as a result of galling. One remedy has been to chromium plate spindles, although the most usual method is to centralize the spindle using p.t.f.e. gland rings, thus preventing contact between fixed and moving parts. Where practicable, dissimilar grades of stainless steel are used, as is the case with centrifugal and reciprocating pumps.

Gate valves and globe valves are subject to the same considerations as have already been mentioned. Again, p.t.f.e. has been extensively used as a seating material although "flaking" has been experienced in the case of large actuated gate valves. Where valve cavity relief is not catered for by alternative devices, it is necessary to provide a connexion between the cavity and one side of the valve, thus making the valve effectively single seating and unidirectional.

Materials for valve bodies and fittings conform to the British Standards already referred to for piping where fabricated from plate, bar or sections.

In the case of forgings the standards adopted are basically:

−50°C (−58°F): BS 1503 — 161B LT50,

−100°C (−148°F): BS 1503 — 503 LT100,
−190°C (−310°F): BS 1503 — 821 LT190.

Castings:

−50°C (−58°F): BS 1506 — 621B LT50,
−100°C (−148°F): BS 1506 — 621 B Condition T. LT100,
−190°C (−310°F): BS 1506 — 821 LT190.

Impact testing and intercrystalline inspection is required for austenitic stainless steel castings, but not for plate, bar, section or forgings manufactured to approved standards.

Flanging and Jointing Materials

No particular problems have presented themselves in the choice of jointing materials for low temperature service and compressed asbestos fibre material will suffice. Tightness of joints has been obtained by shipyard labour without the use of torque wrenches or other special tools. However, as the size of vessels for the carriage of liquefied gases increases so will the diameters of pipelines. The author considers that, as with shore low temperature flanging, the fitting of low expansion coefficient spool pieces to flange bolts will be necessary.

The principle of this is to have extended flange bolts with a spool of 36½ per cent Ni interposed between the flange and the nut of the flange bolt. As the flange and bolts contract on cooling, the spool piece, which has negligible contraction, causes increased tension to be applied through the bolt to the flange joint. Thus the joint tightness is maintained with decreasing temperature.

As the discussion progresses, it becomes apparent that the designer's biggest headache is the interpretation of Rule requirements and the various "standards" being used. Not only is it necessary to consider the specific requirements of classification societies whose rules are, in general, interchangeable, but with the passage of time, national, international and governmental bodies, in increasing numbers, are introducing their own controls.

Materials for low temperature bolting are no exception and are governed by the same considerations as pipework and tank structure. It is usually preferable to identify low temperature bolts and studs by using thread types differing from that for conventional shipboard equipment. For example, where BS 3603 material is employed, U.N.C. threads are generally used instead of Whitworth. In the temperature ranges requiring austenitic stainless steel, the appearance is usually sufficient means of identification. However, it is preferable, as an added safeguard, that the philosophy is adopted that all low temperature attachments are made with studs rather than with bolts.

Where materials are machined from plate, bar or section, the same British Standards are adopted as for piping material. If forging is the source, the following apply:

−50°C (−58°F): BS 1503 — 161B LT50,
−100°C (−148°F): BS 1503 — 503 LT100,
−190°C (−310°F): BS 1503 — 821 LT190.

Heat Exchangers

Condensers, evaporators, heaters and vaporizers are all governed by the same considerations of low temperature operation as already mentioned and basic materials will be the same as for pipework or tank structure at corresponding operating temperatures.

To obtain increased efficiencies, finned tubes are being used increasingly and, with the added advantage of corrosion resistance, bi-metal tubing is now quite common.

One example is the salt water cooled ammonia condenser of a compound reliquefaction plant where the salt water side (inside) is aluminium brass with a finned sleeving of aluminium. The tubes are expanded into grooved tube plate holes. Operationally this type of tube arrangement has performed well, although the author has experience of failures resulting from maloperation. In this instance the plant was operated for a period without cooling water, resulting in overheating and yield of the aluminium, permitting ammonia to penetrate to the aluminium brass.

Tube plates are also manufactured in "clad" form and have presented no operational difficulties.

Costs are higher in some cases but generally low incidence of maintenance will justify the more sophisticated construction.

Coatings have also been applied to low temperature heaters with extremely good results and epoxy coatings for salt water side protection of tubes and tube plates have been particularly successful. However, specialized composite materials are less sturdy than conventional types and are more sensitive to operating conditions.

It is essential that plant operators are fully aware of the limitations as well as the advantages of such new innovations. Of paramount importance is the provision of comprehensive operating instructions.

Pumps and Compressors

Cargo pumps for the discharge of liquid gas cargoes are invariably of the centrifugal type.

The requirement that cargo tank penetrations must all be in the vapour phase has dictated the use of either deepwell or submerged electric pumps.

The main difficulties with deepwell pumps have been in the sphere of mechanical seals and intermediate shaft bearings.

Several variations of seal arrangement have been tried, the most successful being the double mechanical type with oil pressurization. "O" rings are generally of p.t.f.e. for low temperature service although down to about −80°C (−112°F) silicon rubber is still used. Failures have very often been attributed to bad fitting, emphasizing the inherent stiffness of p.t.f.e. at ambient temperatures. The same problem has been experienced in the mechanical seal of a Roots-type blower, where the interference fit of p.t.f.e. "O" rings made it impossible to close the seal faces, despite considerable spring tension.

Carbon continues to be favoured for static seal faces, in the absence of an alternative material less susceptible to the effects of "flashing" when low temperature boiling liquids are being handled.

Intermediate shaft bearings of deepwell pumps have presented considerable difficulties to the author's company in the past. The consideration of compatability with ammonia has dictated the use of copper-free materials and the next consideration is lubrication by the product pumped.

Different types have been tried ranging from carbon-cast iron composites, white metal, p.t.f.e. — carbon, to p.t.f.e. tape.

Tape bearings have operated extremely well, are cheap, simple to fit and dissipate heat well. With shafting lengths of anything up to 50 ft whirling characteristics are of prime importance in the design stage.

Many of the materials tried, suffered from pick-up, extrusion or general break-up from this phenomenon.

P.t.f.e. tape bearings however performed well and pick-up is, in fact, an advantage. Shaft journals are deliberately machined with specified roughness in order to promote transfer of p.t.f.e.

The submerged electric centrifugal pump has been in service for a considerable time and material considerations have presented few difficulties other than in ammonia service.

Motor conductors are generally copper, although aluminium is now being offered on the Continent where ammonia is specified. The motor windings are invariably "canned" in stainless steel for this application, the power leads being mineral insulated copper with copper and finally stainless outer sheaths.

It is in way of the cable connexions to the motor that ammonia has been able to penetrate and digest the copper windings. As a result, strict quality and erection control is exercised and where practicable, cable connexions are vacuum proven, prior to entering into service.

Reliquefaction plant compressors follow the same trends as other refrigeration machinery with regard to materials. Copper based components however have given satisfactory service with ammonia as bearing materials, although it is a prerequisite that the ammonia be dry. It would appear that oil films have to date adequately protected bronzes in this application.

Oil-free compressor pistons will normally be in aluminium, except where vinyl chloride cargoes are handled. In this case, cast iron pistons are fitted and all copper based materials replaced by suitable alternatives in order to obviate the risk of explosive acetylide formation.

With Rule requirements dictating that electric prime movers and cargo compressors are in separate compartments, gas tight bulkhead seals are required. Unlike shore installations, ships are highly flexible and in some cases considerable misalignment has to be accommodated. Early installations depended on stiff, through-bulkhead seating in an attempt to prevent this with some degree of success.

More recent designs incorporate a bellows unit permitting as much as 15° of axial misalignment. Another possibility is the use of magnetic fluids which have been a fall-out from the U.S. space programme. Little information is available at present and this type of product is not yet marketed in the U.K. However, there are distinct possibilities of such a development in the future.

This section would not be complete without mention of p.t.f.e. thread tape which is so effective a means of sealing small bore threaded connexions. No longer are compounds used which drip into valves and fittings with consequent blockages.

CHEMICALS OR PRODUCTS CARRIERS

The very title of this section covers a vast range of products now transported in bulk. Whenever a shipowner negotiates for a newbuilding, he will have a fair idea of the types of cargo for which he is likely to obtain a charter. Nevertheless, during the design stage, further lists of potential cargoes will probably be supplied to the shipbuilder and generally these cover several pages of foolscap. From this stage onwards, the "compromise" can be established.

Basically there are four degrees of sophistication available and the shipowner will choose a variation on one of these types. It is well to remember that the addition of one cargo to the products list may put costs up by several thousand pounds and equally the deletion of some can give commensurate savings.

The four basic types of products carrier have storage and handling facilities as follows:

1) oil tanker type construction with uncoated tanks and pipelines; no special materials;
2) some or all tanks coated or lined, pipelines similarly coated and some special fittings;
3) some or all tanks stainless steel clad or lined; stainless steel pipelines and special fittings;
4) some or all tanks in stainless steel with pipelines and all fittings similarly in stainless steel.

There are an infinite number of variations and compounds of these four types and the end product is invariably only as flexible as the shipowner's budget will allow.

For the purpose of this paper it can be assumed that the philosophy behind the ultimate choice of system is understood and it is necessary only to confine comment to the materials in current use, the particular difficulties obtaining, and ways of simplifying or avoiding these difficulties. Type (1) can be ignored as being conventional tanker practice.

However much work is sub-contracted, the shipyard approach to this type of vessel must be from a position of knowledge rather than ignorance. Detailed programming, quality control and general organization are essential if goodwill is to be maintained, losses are not to be incurred and realistic guarantees are to be given. The author makes no excuses for emphasizing what at first seems to be the most fundamental of principles.

Pipework

Coated

In this instance internal coatings are applied prior to final installation. Providing that the specified system is sufficiently durable, the pipe sections are also fully coated externally, care being taken to protect against mechanical damage in transit and during erection.

If epoxy, rubber or similar readily destroyed coatings are to be applied, the only external coating prior to erection will be in way of pipe supports and other flanges. These external areas require adequate masking and protection against damage prior to, and during, installation.

Pipe supports themselves warrant considerable thought regarding design, bearing in mind that in order to maintain high system integrity, faying surfaces should be avoided. Where practicable, pipe supports will be welded to the pipe to form an integral arrangement capable of accommodating thermal and ship movements. In this way relative movement between pipe and pipe support, which would destroy coatings, is avoided.

An alternative is to line the support with strip p.t.f.e. or other suitable material which is chemically compatible.

If pipe supports are to be coated before installation, the same care is required to prevent mechanical damage as with pipe lengths. One method of reducing the breakdown of coatings due to mechanical damage, with resultant cargo contamination or corrosion, is to use a relatively durable and compatible primer coating having a good bond strength. Limited breakdown is then of less consequence.

The incidence of flanges in a coated piping system will be kept to a minimum and depending on the degree of integrity required, flange bolts will be either mild steel or cadmium plated with an over-coat of the system specified for tank and pipework.

If costs permit, stainless steel bolting will be used; but over-coating is advisable to maintain the integrity of the flange coating.

Jointing materials vary considerably, but conventional compressed asbestos fibre will be suitable in many cases. P.t.f.e. is also widely used, generally in pre-cut envelope forms with C.A.F. filler gasket.

P.t.f.e. is stable at 20°C (68°F) above which point the volume increases. A corresponding shrinkage occurs on cooling. For this reason, solid p.t.f.e. is not normally used for flange or other jointing materials unless special provision is made to retain it. Recessed spigot or grooved flange faces are suitable methods of achieving this.

Most coating systems have restriction on temperature maxima and preclude the use of coated heating coils, which in consequence, are normally of stainless steel. Cone seal couplings are generally the method of joining pipe lengths, very often with p.t.f.e. or other suitable inserts. Threads are avoided where possible and these coupling tails are welded to the piping.

Heating coil supports require attention to detail in order to prevent chaffing or heat transmission to adjacent coated steelwork. These supports can be entirely of stainless steel, in which case they will be welded to tank structure prior to tank coating. The coating will be carried over the stainless/mild steel junction, but masked to terminate the coating clear of the hot region.

Alternatively the pipe supports may be of coated mild steel, insulated from the heated region by stainless steel and/or some other material such as one of the many man-made fibres available in block form.

Un-Coated, High Integrity Systems

Where stainless steel tank material obtains, the main consideration will be to obviate corrosion and cargo contamination. Therefore cargo and ancillary piping requires to be in stainless steel, AISI 304, 316 and 316 L types have all been used satisfactorily.

Heating coils are generally stainless steel, although aluminium, where compatible, may be an alternative.

Some cargoes react with heating coil materials, thus limiting surface temperature. The temperature at which reaction occurs varies for different coil materials and products. This must be considered when designing the heating coil arrangement and conventional steam heating is not necessarily employed, nor is it as easy to control skin temperatures. Systems are being used increasingly which circulate hot water or special heat transfer media, which throughout their cycle remain in the fluid state.

The final decision regarding materials in this instance will depend firstly upon technical suitability and finally upon cost.

Pipe supports for a high integrity system will be in stainless steel throughout and jointing materials may be C.A.F. or p.t.f.e. envelope type.

Valves and Fittings

Where a coating or lining system is used, valves and other fittings may be in stainless steel. However, the "compromise" will be to have stainless steel spindle and valve internals, the valve body being coated either internally, externally, or both. Sometimes it may be considered justifiable to allow for replacement as necessitated by corrosion, by using conventional tanker type equipment.

The ultimate in protection is to use all-stainless valves, but care must be exercised, particularly in the case of tanks used for ballast, to prevent galvanic action between carbon steel piping and austenitic stainless steel valves.

Valve extended spindles can be of stainless steel, but may also be in carbon steel which will be coated in the same way as tank structure and piping. In the latter case, spindle guide bushes are designed to prevent abrasion of the protective coating. This may be achieved in a variety of ways, by using p.t.f.e. guide bushes. In addition, the spindle may carry a stainless steel bush in way of the guides.

Straight runs of extended spindles are used where practicable, in order to obviate the need for non-corrosive universal couplings.

Pumps

Pumps for products carriers can be of centrifugal (pump-room located or deepwell) screw or reciprocating types. In each case, corrosive cargoes will demand that stainless steels are used, or that suitable coatings are applied to pump casings etc. As with any application where stainless steel moving parts are used, galling must be avoided as referred to in the liquid gas section.

Sometimes, as in the case with certain applications of reciprocating pumps, bucket liners will be of stainless steel with cast iron buckets.

Pump end bucket rings can be made from any suitably compatible material, which will generally have a p.t.f.e. base. Gland packing also may be of p.t.f.e. based material such as impregnated asbestos.

Suction and delivery valve integrity is important to pump efficiency and they will generally be constructed in stainless steels. The valve discs however are sometimes of suitable composite material to obviate galling. Such materials will normally be resin laminates.

Pump cover joints can be p.t.f.e. or other suitable material.

In the case of centrifugal pumps the difficulties of galling have been approached in a similar manner. Grades of stainless steel are chosen which give a difference of hardness between running components. Impeller neck bushes have been successfully lined with p.t.f.e. based tape which solved the deepwell pump problems cited earlier. Clearances are smaller in this case than that between impeller and wear rings, permitting 18/8 stainless steel or an alternative to be used throughout for all moving and stationary parts.

The chemical carriers referred to have all been capable of carrying a multitude of cargoes, but occasionally a vessel is designed around one cargo. At first sight, this would appear to simplify the designer's problem, whereas, in fact, they are usually the problem children of the chemical industry. Examples of such cargoes are liquid sulphur, liquid chlorine, phosphoric acid, ortho-phosphoric acid, phosphorous and ethylene oxide.

Each of these cargoes presents hazards, corrosion difficulties and temperature or other limitations which may tax the ingenuity of the designer, who in turn will look to the scientist and metallurgist to provide new materials.

Recent development has provided ethylene oxide polymers to make water more "slippery"; cryogenic polyimide resin lip seals capable of holding 5000 lb/in^2 at up to 12 000 rev/min; carbon fibres for a host of applications; explosive techniques to produce clad steels; and many more such innovations.

It is the duty of the designer to use the national, international and governmental information services to the utmost so that the "compromise" of today may become into the "ideal" for tomorrow.

Discussion

Mr. M. Z. Navaz, B.Sc., A.M.I.Mar.E., said it was possible that the problem of training and education of the ship's crew, in relation to the cargo carried, might in the future become the responsibility of the builder.

The grouping of low temperature cargoes in the temperature ranges stated in the paper generally complied with most national material standards. Chlorine in group 1 should be considered a special case: it was evident that special requirements would be called for, as this cargo was not compatible with others listed in this group.

The author had not made clear how the use of copper piping for liquid nitrogen systems could be cheaper than double wall vacuum insulated pipes. Did he agree, that in this case, heat transfer economics must also be considered in relation to the life of the ship? Failure to vapour seal the ends of the insulation could lead to corrosion, due to moisture migration. For this reason vapour sealings should be carried over the ends on pipe lengths and firmly landed on the bare pipework.

Regarding the use of nylon piping for signal transmission, care was required in its use on low temperature circuits. Nylon tubing could be hydroscopic to some extent and thus promote moisture migration: eventually solid particles could form. In connexion with the problems associated with p.t.f.e., were 'galling' problems really those associated with clearance tolerances and re-designing of sealing arrangements in relation to peripheral speeds of moving parts, associated with vibration?

The author considered aluminium incompatible with vinyl chloride, although this was not yet universally accepted. Mr. Navaz agreed with the author that cast iron pistons were the most suitable for this cargo.

Regarding problems associated with ammonia and copper rich materials, it was thought that recent cooler failures in the engine room of a ship had been caused by the cooling water services drawing in ammonia rich cooling sea water possibly from cargo service discharges located amidship. Care was required in handling cargo service sludge and contaminated discharge.

He sympathized with the author regarding the difficulties he had experienced in obtaining formal approval for the use of sheathed piping, particularly with plastic material. Regulating bodies had varying attitudes to their use for shipboard service. Future years would certainly see a pressing need for the use of both portable and fixed, rigid and plyable sheathing arrangements for piping and various other equipment as protective skins. This would come about with advances in non-desctructive testing equipment, being provided as a part of the ships equipment for use by ships staff. It was hoped that this testing equipment would also consist of intrinsically safe non-pressurized leak detection systems and simplified chemical qualitative testing equipment.

However efficient the ships cargo handling, conditioning and containment system might be, the ultimate responsibility for the safe and efficient transport of cargoes must be with the ship's staff alone.

Mr. R. K. Roberts, B.Sc., M.I.Mar.E., commented on coated pipe lines and their relation to aggressive cargoes. More and more work was being carried out in the field of tank coatings and increasing pressure was being brought to bear to find such coatings suitable for aggressive cargoes. Whereas at the present time most such bulk cargoes were contained in corrosion-resistant tanks, (stainless steel of suitable quality) it would obviously be more economic to find suitable coatings for use with mild steel. In the borderline aggressive chemicals (acetic and propionic acids), suitable or almost suitable coatings were on the point of being developed. In the event of coatings being accepted for tanks containing corrosive products, such coatings should not be carried on into the pressure pipeline system, mainly because of the impossibility of proper examination and testing to ensure the integrity of those lines in the pipework system. Local failure of the coating could result in rapid local corrosion of the pipe and subject personnel to contamination from subsequent cargo spray. Did the author know of any system of testing and inspection of a pipeline coating that could prove beyond doubt that there was no failure in that coating? In his opinion there was no such method at present and until there was, the safest and wisest course of action would be to see that the pressure side of such a pipeline system for an aggressive cargo was in a corrosion-resistant material.

He endorsed the author's remarks concerning his disapproval of a purging system by a cargo gas.

The Chairman of the meeting, DR. P. T. GILBERT, Ph.O., B.Sc., M.I.Mar.E., raised the point of the possible ill-effects of discharge of cargoes overboard. It was apparent that any large discharge of ammonia, if taken into the sea-water cooling systems of a vessel, could have disastrous effects. He understood that many tons of ammonia were liable to be discharged from time to time from vessels carrying such cargoes, and the effects on sea-water cooling systems, including the main condensers of vessels driven by steam turbines, could indeed be very serious. He had encountered an instance of this sort with tankers conveying spent caustic liquid for discharge at sea. On occasions this liquid found its way back into the main condensers of vessels, causing serious condenser tube corrosion that necessitated re-tubing after a short period of service. The effects of ammonia could be even more severe in a simular situation.

MR. R. C. FFOOKS, B.Sc., said the author had mentioned that part of the success of the balsa system was due to the money spent in developing it. He endorsed this, but added that on certain man-made insulation materials vast amounts of money had been spent without very satisfactory results. Some materials that at present looked promising, had had money invested in them by shipowners, designers, and by the manufacturers themselves, and much effort had been spent in looking for a material easier and cheaper to instal and also effective and perhaps one that would eventually become a primary and secondary barrier combined (this, he thought, was everyone's dream).

It seemed somewhat unfair to expect a shipbuilder to understand all the complications of chemical carriers,—L.N.G., L.P.G. and various other specialized ships—that he was expected to tender for competitively, and also to expect him to train his welders to weld invar 9 per cent nickel aluminium, all to a very high degree of competance. He therefore much appreciated Mr. Crook's comments on the extent to which he forsaw shipyards might opt out of this responsibility and rely on specialist contractors not only to supply items of equipment, but also, possibly to send in workers to do the welding, or even provide the shipyard with a complete package, leaving him to concentrate on the more conventional parts, i.e. propulsion, accommodation and so on.

MR. H. J. MILLER, B.Sc., M.I.Mar.E., commented on the statement in the paper: "It is essential that plant operators are fully aware of the limitations as well as the advantages of such new innovations. Of paramount importance is the provision of comprehensive operating instructions". From the operational point of view, he was of the opinion that insufficient clear instructions were given to the owner when buying a ship. He knew Mr. Crook would point out the numbers of pamphlets and plans distributed, but these were often sketchy and poorly presented. He cited a recent case concerning the delivery of a set of valves that arrived without clear instructions for fitting or adequate explanation of the basic design concept. The person responsible for inspecting the valves at the manufacturers was abroad and the valves did not fit. Finally, a representative of the manufacturers was urgently called for and the problem was cleared up within an hour or so of his arrival. This example reiterated his first point: information to the owner was imprecise. Many times this might be the fault of the owner who did not discover until two, three, or even four years later that the plans he had were not adequate. In other words, one did not find out if plans/instructions were satisfactory until something went wrong and they were needed. It was up to the shipbuilders (particularly in this dangerous field) to make sure that instructions were not just general pamphlets which might apply to a range of units, but pamphlets which dealt with that particular unit on that particular ship. He entered a plea to Mr. Crook —did his yard do all it could in this respect?

On the question of the heating of the cargo, the author had said: "Some cargoes react with heating coil materials, thus limiting surface temperature". He went on: "Systems are being used increasingly which circulate hot water or special heat transfer media". What, in the authors view, was the best way to treat a chemical cargo?

MR. P. J. CARR said with regard to pump design he had been involved some years ago with bearing problems associated with deep well pumps on an L.P.G. carrier. At that time, the particular carrier concerned was not likely to be used for ammonia and fortunately the problem was overcome by using 20 per cent lead bronze for intermediate shaft bearings. He was particularly interested to hear that in recent years there had been a move to the use of p.t.f.e. tape bearings, and that these seemed to have given satisfactory service. Had there been a tendency to increase the use of fully submerged pumps to avoid the problem with intermediate bearings? What was the reliability of these fully submerged pumps and how many spare units should one instal per tank these days?

DR. P. T. GILBERT, B.Sc., M.I.Mar.E., said the author had referred to the use of bi-metal tubes for water cooled ammonia condensers and stated that these normally performed well but could give trouble. There were, of course, circumstances when failure could occur, and if one component of the bi-metal tube was perforated for any reason it was evident that a complete failure would follow very quickly. Would the author comment on the heat transfer data used when designing heat exchangers incorporating such tubes? It was necessary to make some assumption about the bond between the two components; one might assume the bi-metal tube was equivalent to a solid metal tube or that there was a complete air gap between the two components. The effect on the overall heat transfer co-efficient, depending which extreme assumption was made, was obviously very large but in practice some intermediate value was probably used. To his knowledge there were not many data available about the heat transfer behaviour of bi-metal tubes, and Mr. Crooks observations would be welcome.

Author's Reply

The author, in reply to Mr. Navaz, agreed that training and education must be considered very seriously, by both the shipbuilder and the shipowner. When implementing a marine venture involving a ship worth up to £20 million to £30 million, it would be foolish not to carefully select officers and crew and provide all the training possible to prepare for service conditions. Failure to do this could put the whole project at risk.

Shipbuilders had the responsibility to ensure that their own management was suitably trained and that the shipowner was adequately prepared to take a vessel into service. The incentive was certainly there, when one considered that a ship was normally under guarantee for 12 months after delivery. Due attention to education must be rewarded by a low incidence of mal-operational failures.

The author had first-hand experience of this important aspect of producing sophisticated ships, and had sometimes found it necessary to organize university courses for the officers of vessels, with a view to acquainting them firstly with the chemistry of the cargoes that were to be handled and secondly to make them aware of the potential hazards of these cargoes.

The author accepted Mr. Navaz's comments on chlorine and by way of an explanation would confirm that this gas was put into group 1 solely because it was a liquefied gas in the relevant temperature range. However, the author was certainly aware of the peculiar hazards of marine transport of chlorine, and the specific restrictions attached to its carriage.

Mr. Navaz had queried the reasons for using foam insulated copper pipe for liquid nitrogen transfer lines as opposed to the vacuum insulated alternative. In this instance pure economics far outweighed the marginal reduction in heat gain obtained by using the more expensive vacuum insulated piping. Nitrogen was invariably used as super-heated vapour which required no insulation, and was stored in vacuum insulated storage vessels. Filling of these storage vessels was the only time that liquid nitrogen passed through the ship's lines, the operation being of short duration.

For the same reasons, all cargo pipe flanges and valves were normally left uninsulated except for condensate return lines. Leaks at flanges were thus more readily detected and did not damage the insulation. The heat gain during the relatively short periods of loading and discharging was minimal compared to the constant heat gain by way of cargo tank insulation.

The carrying of vapour sealing over the ends of insulation and firmly anchoring it to the pipe was essential and this was inferred in the paragraph of the paper dealing with piping insulation and the need to pay close attention to detail.

Moisture migration through nylon piping was a known fact, but providing near ambient temperature operating conditions obtained, freezing was not a significant problem. The author had no knowledge of such an occurrence.

Problems with p.t.f.e. had been mentioned by Mr. Navaz in relation to galling. It would be better to consider galling problems and how they had been overcome by the use of p.t.f.e. based materials as discussed in the paper. Basically, where stainless steels were used, galling of running components could be prevented by the use of materials of significantly different hardness values. Where bearing failures had been judged to be caused by poor lubrication, low heat removal and whirling, p.t.f.e. based tape bearings had been used with considerable success.

There was a lack of knowledge regarding vinyl chloride and its main contaminant, acetylene, and their respective reactions with aluminium and copper bearing materials. The author had experienced two minor explosions when running in oil-free reciprocating compressors drawing in air at the suction. It was well known that under certain conditions, finely divided aluminium particles were explosive and these conditions existed in the two incidents cited. It was for this reason that the author recommended the changing of aluminium pistons for cast iron and in order to prevent the formation of explosive acetylides, the replacement of copper based bearings for vinyl chloride service.

The author was aware of the suggestion that ammonia discharged overboard might have a damaging effect on coolers and copper based piping. There was no proof, as yet, of this effect, although the author recommended that the small quantities drained off loading arms etc. were discharged on the opposite side of the ship to the engine room sea inlets then in use. The author agreed that the discharge overboard of any material should be the subject of serious consideration.

Regarding the benefits to be obtained from preventive maintenance, it went without saying that anticipation of trouble would reward the operator by a low incidence of failure. A ship at any stage in its life cycle, whether during construction, or in service, would only be as good as its supervision.

The author shared the fears of Mr. Roberts in respect of coated pressure piping. Certainly coating integrity, which was almost impossible to monitor, must be considered. The best that could be done was to implement rigid quality control during pipe production and coating operations. The absence of weld spatter and other sharp edges, together with the number of bends per pipe length being kept to one, reduced the possibility of built-in defects. Shot blasting in itself provided a uniform surface preparation and where possible spray coating would provide more uniform coating thicknesses than brush application.

Dry film thickness determination was the final guarantee on coating integrity, and the author's company was now using instruments that permitted an extension lead to be used with the probe, thus enabling otherwise inaccessible areas to be checked.

In the case of highly aggressive cargoes, it was prudent to increase pipe wall thicknesses on pressure piping on deck and in pump rooms to provide a corrosion allowance. This was already being done by the author's company in the case of non-portable piping such as bulkhead pieces.

However, the only 100 per cent method of guaranteeing corrosion resistance was to use a suitably inert pipe material.

Mr. Ffooks had agreed that balsa was at present the favoured insulation for methane tanks and for the simple reason that developments to date had produced no suitable alternative system. The author, however, was of the opinion that very soon, alternative systems using man-made materials would become available at lower cost and with greater ease of manipulation and installation. Several organizations, including the author's, had shown promising results from researches. The question was posed by Mr. Ffooks, suggesting that it was too much to expect a shipyard to understand all of the complications of a sophisticated ship.

The author was of the opinion that, as the main contractor, the shipbuilder would be well advised to understand all details possible and shipyard management had a long way to go before becoming saturated with experience. So frequently in the past, shipyards have lost large sums of money through ignorance, lack of preparation and ill-founded faith in a sub-contractor who was also starting on a new venture.

At one time, with traditional ships, it was enough to order a piece of "bread and butter" equipment and expect it to work reasonably. Not so now, in the age of innovation and new sciences; it was essential to have a working knowledge of design and operational details of every piece of equipment. This necessarily entailed the provision of capable and dedicated management which was increasingly difficult to obtain in the present social environment.

Having educated the shipbuilding management, it was then time to decide upon the degree of sub-contracting which was partly dictated by the degree of home bred expertise available and partly by a desire to maintain labour loadings as stable as possible.

One company's philosophy regarding sub-contractors, might vary considerably from another's, but it was true to say that, having proven the ability to "produce the goods", it was sometimes desirable to patronize one contractor and allow him to grow with the shipyard. This, however, only applied in the case of the less readily obtainable service.

Mr. Miller commented on the lack of adequate operating instructions and the author sympathized with this all-too-common situation. Nevertheless, the author was conscious of this deficiency and had for some time been exerting pressure on suppliers in this respect. For a specalized ship such as an L.P.G. carrier, the author produced a comprehensive operating manual which encompassed the full range of cargo handling equipment and systems.

The basic format of such a publication followed the general pattern of:

1) products to be carried, their chemistry and hazards;
2) instrumentation and controls with emphasis on "function";
3) operations for which the vessel was designed;
4) emergency operations;
5) sample log sheets, useful conversion tables and other information such as Mollier charts.

This operating manual was intended as a means of expanding upon individual suppliers handbooks, whilst obviating the need to search through the many pamphlets and plans referred to by Mr. Miller.

Equally, the shipowner must not shed his responsibility to his sea-going staff and must be able to advise when required. Some shipowners were aware of this and had suitably staffed their superintendents' departments. Sadly there were exceptions.

The heating of chemical cargoes could never be a simple answer to Mr. Millers "maiden's prayer". Every cargo, or at best, each group of cargoes, presented different problems and no one system could be universally acceptable in every case.

Of the systems quoted in the paper, the circulated heat transfer medium was the most flexible with regard to temperature control. So much depended on what a shipowner was prepared to pay and his being able to produce, at the design stage, a realistic products list.

In reply to Mr. Carr, the author repeated his faith in tape bearings and other pump components such as throttle bushes. All the deepwell pump problems referred to in the paper had long ago been solved, the pumps having since given excellent service for more than two years. Submerged pumps were now with us, the latest generation of which were reliable. This statement was made with some reserve regarding ammonia which had been responsible for all the problems. It was hoped that the pumps recently put into service would prove that another hurdle had been crossed. With this reliability and lower initial cost, it would appear that, for liquid gas cargoes, the submerged pump would entirely replace the deepwell pump, however reliable the latter.

Invariably two pumps were fitted per tank to cover for failure, and any additions to this were an owners particular fancy. Sometimes a removable submerged pump was provided which would serve to discharge any one cargo—or containment-space as required. However, it must be remembered that, even with deepwell pumps, it was common practice to fit two pumps per tank.

The author would agree with the chairman, Dr. Gilbert, regarding the lack of information available on bi-metal tubing for heat exchangers. One must use manufacturers claims unless other experience enabled a direct comparison to be made with conventionally tubed heat exchangers of equal capacity. The author was unaware of any study which might have highlighted the effect of "bond" integrity between the two elements of a bi-metal tube, although it naturally followed that the more intimate the contact, the better the heat transfer coefficient.

The advantage of finned bi-metal tubing depended on many factors, two of which were the number and size of fins/unit length of tube, and the heat transfer coefficients on the inside and outside of the tube. Obviously the gains in efficiency were most pronounced when the external medium gave a low heat transfer coefficient compared with that of the medium circulating through the tubes. It was claimed that with the ratio of *inside film coefficient* ranging between 1 and 10, it was possible to reduce the number of tubes by between 5–40 per cent.

NICKEL-CONTAINING MATERIALS FOR SPECIAL CARGO TANKS

B. Todd[*] M.Eng., C.Eng. (Member) and G. L. Swales[†]


Mr. Todd


Mr. Swales

In recent years there has been a rapid growth in the shipment of chemicals and liquefied gases by sea. The former has been stimulated by the growth in chemical (particularly petrochemical) production and the latter by an upsurge in demand for gas principally as a fuel but also as a petrochemical feedstock especially in countries such as Japan and the U.S. eastern seaboard where there is insufficient indigeneous supply.

It is convenient to discuss the material requirements for the tanks in these ships under the heading of chemical tankers and refrigerated liquefied gas tankers.

CHEMICAL TANKERS

The nickel containing materials of most interest in the transport of chemicals are the austenitic stainless steels although some use has been made of pure nickel for the carriage of 73 per cent caustic soda—S.S. *Marine Dow Chem* built in 1954.

Whilst stainless steel is an obvious choice for a wide range of corrosive chemicals, its capability of avoiding product contamination and its ease of cleaning make it attractive for cargoes such as wine, edible oils and latex and also for relatively non-corrosive chemicals such as ethylene oxide, styrene, phenol etc. where there are stringent product purity requirements.

Increasing concern by port authorities about the carriage of hazardous cargo is accelerating the trend towards double skin vessels which makes it more feasible to consider more functional materials, such as stainless steels, for cargo tanks.

Many enquiries for new chemical tankers stipulate suitability for handling mineral acids such as nitric, sulphuric and phosphoric acids and caustic alkalis. Most tank coatings are restricted to handling chemicals in the PH range 4-9 and outside this range corrosion resistant materials such as stainless steel are essential.

Versatility and flexibility are the main factors in the field of chemical transportation and it is in these respects that the use of appropriate grades of stainless steel offer outstanding advantages. Versatility stems from the ability of stainless steel to accommodate an exceptionally wide range of cargoes allowing maximum scope for increasing revenue by accepting turn-around cargoes; flexibility results from the ease with which properly designed tanks can be cleaned, so reducing cleaning time and costs.

CHOICE OF GRADE OF STAINLESS STEEL

Although there are many grades of stainless steel for chemical tanker applications, economic factors, marine and chemical corrosion considerations and range of cargoes which can be handled, narrow down the choice to relatively few grades, i.e. those containing molybdenum such as A.I.S.I. Type 316. Examples of cargoes where the molybdenum containing grade is desirable are phosphoric acid, organic acids and wine containing high SO_2 contents.

Table I gives the composition and typical properties of the gardes of wrought stainless steel likely to be considered for the construction of chemical cargo tanks. Whilst the molybdenum-free grades such as Types 304, 304L and 321 will be satisfactory for handling most chemicals, for maximum flexibility it is generally advisable to use the molybdenum-containing grades—Types 316, 316L, 317 or 317L. The choice of these grades is also dictated by marine corrosion considerations as the addition of molybdenum improves resistance to pitting in seawater.

For most cargoes unstabilized grades will be satisfactory, but for phosphoric and other mineral acids it is advisable to use stabilized or low-carbon grades (nowadays usually the latter) to avoid the possibility of intergranular corrosion adjacent to welds. Grade 316 with closer control of carbon content (0·04 per cent or 0·05 per cent maximum) has been used for a number of ships with some saving in cost. However, for ships in tramping service where there is uncertainty about cargoes to be carried, it is worthwhile specifying 316L in which the carbon is stringently limited to 0·03 per cent maximum.

Consideration of the behaviour of austenitic stainless steels in a few of the more aggressive chemicals will illustrate these points and substantiate the suggestion that 316L is the best all-round choice for general purpose vessels with 317L, meriting consideration in special cases. An earlier paper(1) gives a more detailed treatment of this subject but to indicate some of the considerations phosphoric acid and wine are exemplified as typical of a corrosive acid and of a non-corrosive cargo, where maintenance of product purity is the main consideration.

a) *Phosphoric Acid*

There is considerable interest in the transport of phosphoric acid—a business which could increase with the desire of the lesser developed countries with large phosphate rock resources, to produce phosphoric acid at the source of the rock rather than export the rock.

There are two basic types of phosphoric acid:

i) Wet-process acid produced by digestion of rock with sulphuric acid and evaporating to give 42–54 per cent P_2O_5 acid;

ii) Furnace-grade acid made by oxidation of phosphorus to P_2O_5 and hydration to give 54 per cent P_2O_3 acid.

Wet process acid generally contains appreciable quantities of fluoride (from the rock) and chloride (from the rock, process water or seawater contamination during carriage). Whilst much published data may suggest that Type 304 stainless steel is adequate for handling phosphoric acid such data often refer to pure acid, and grades 316L or 317L should be used for commercial acid—see Table II.

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TABLE I—COMPOSITION AND TYPICAL MECHANICAL PROPERTIES OF AUSTENITIC STEELS USED IN BULK LIQUID TRANSPORT

Type of Steel	AISI Type Designation		Composition							Mechanical Properties		
			C per cent	Cr per cent	Ni per cent	Mo per cent	Ti per cent	Si per cent	Mn per cent	UTS kgf/mm²	0.2 per cent proof kgf/mm² minimum	Elongation per cent minimum
18/10	Type 304	minimum	—	18·0	9	—	—	0·2	0·5	—	—	—
		maximum	0·06	20·0	12	—	—	1·0	2·0	52	21·0	30
Low C 18/10	Type 304L	minimum	—	18·0	9	—	—	0·2	0·5	—	—	—
		maximum	0·03	20·0	12	—	—	1·0	2·0	50	19·0	30
18/10/Ti	Type 321	minimum	—	17	9	—	5×C	0·2	0·5	—	—	—
		maximum	0·08	19	12	—	0·07	1·0	2·0	52	24	30
18/12/2·5Mo	Type 316	minimum	—	16·0	10	2·25	—	0·2	0·5	—	—	—
		maximum	0·08	18·0	14	3	—	1·0	2·0	52	22·5	30
Low C 18/12/2·5	Type 316L	minimum	—	16·0	10	2·25	—	0·2	0·5	—	—	—
		maximum	0·03	18·0	14	3	—	1·0	2·0	50	21·0	30
18/12/3·5Mo	Type 317	minimum	—	18·0	11	3·0	—	0·2	0·5	—	—	—
		maximum	0·08	20·0	15	4·0	—	1·0	2·0	52	22·5	30
Low C 18/12/3·5Mo	Type 317L	minimum	—	18·0	11	3·0	—	0·2	0·5	—	—	—
		maximum	0·3	20·0	15	4·0	—	1·0	2·0	50	21·0	30
18/12/Mo/Ti		minimum	—	16·0	10	2·25	5×C	0·2	0·5	—	—	—
		maximum	0·08	18·0	14	3	0·7	1·0	2·0	52	24·0	30

For equivalent grades there may be a slight variation in maximum and minimum values for composition and properties between various standards such as ASTM, BS, DIN, etc. This table is only intended as a general summary and appropriate specifications should be consulted.

TABLE II—EFFECT OF CHLORIDE ON CORROSION BY PHOSPHORIC ACID

Temperature range 86°F–100°F (30°–38°C)

Stainless Steel Type	ppm Cl added	Corrosion rate mm/year
304	0	Nil
304	8	0·036
304	15	0·2
304	23	12·7*
304	39	23·1*
304	117	24·7*
304	156	23·0*
304	196	27·4*
304	274	18·6*
304	391	23·1*
316	196	0·016

* Hydrogen evolved and acid coloured green

Table II is based on laboratory tests in 75 per cent reagent grade phosphoric acid containing specified concentrations of added chloride. Specimens were submerged in glass flasks.

It shows the effect of chloride content in phosphoric acid and the importance of using the molybdenum containing grades. Other impurities affecting the corrosivity of phosphoric acid are fluorides, sulphuric acid, ferric iron and hydrofluosilicic acid.

Corrosion tests in typical wet process acids containing fluoride and chlorides at temperatures up to 104°F (40°C) showed corrosion rates of the order of 0·1 mm/year. Laboratory tests on phosphoric acid to which varying amounts of chlorides and fluorides have been added often show higher corrosion rates than commercial acids with similar impurity at storage and transport temperature. This has been attributed to the inhibitive effects of ferric iron, alumina, calcium, magnesium and silica in commercial acids. Fluoride and chloride exert a synergistic effect in increasing the corrosivity of the acid but chloride seems to be the more potent in this respect. Under shipping conditions, the main effect of high fluoride content appears to be to increase corrosion in the vapour space whilst higher chloride content appears to increase the tendency to pitting under deposits on the tank bottom. In the wet process of making phosphoric acid, calcium sulphate is formed and although mainly removed by filtration, further settling out may occur during shipment.

Surface deposits on stainless steel are undesirable and it is advisable to regularly inspect and clean tanks used for wet-process phosphoric acid. To overcome this problem some designers have proposed the fitting of mechanical or hydraulic stirring systems to keep the calcium sulphate in suspension. Whilst this would certainly be beneficial, the difficulties of avoiding dead spaces in the corners of the tanks where deposits could accumulate and the costs (both initial and maintenance) of a stirring system would have to be considered. The use of more highly-alloyed material, e.g. Type 317L stainless steel or alloys such as 25 Ni, 20 Cr, 4 Mo, 2 Cu, Alloy 20, or Alloy 825 for the tank bottom is likely to be a simpler solution and may be justified where especially aggressive phosphoric acid cargoes are to be carried regularly.

For the majority of phosphoric-acid carriers, 316L is being used. However, for several German ships, e.g. *Lizzi Terkol*, 317L clad steel has been used. In this ship, which has been in service for over three years, the tanks are in excellent condition. More recently *Onabi* with 317L clad steel tanks has entered service.

Other German ships have incorporated both 317L and 316L, the former being used in the vapour space and the tank bottom and 316L for the remainder.

b) *Wine*

There is growing interest in bulk wine shipment; one wine tanker with stainless steel tanks, *Angelo Petri* has been in service for many years and another is under construction in France. There have been many years' experience of using stainless steel in the storage and transport of wine(2).

Some white wines contain appreciable quantities of sulphur dioxide as a biological suppressant, the quantities being limited to a maxima of 40–70 ppm dependent on the country concerned. Long-term tests in wines containing excessive amounts of SO_2 (e.g. 500–600 ppm) have shown that both Type 304 and 316 are not affected under totally immersed conditions. In the vapour space some corrosion may occur with Type 304 due to SO_2 concentration in this space, when the SO_2 content of the wine exceeds about 30 ppm, whereas Type 316 is not affected even under artificial conditions of excessive SO_2 content, for example 500 ppm. However, many white wines have an SO_2 content of less than 30 ppm and experience with Type 304 stainless steel has been satisfactory.

A few parts per million of iron is found in many white wines. If this is allowed to build up beyond about 9–10 ppm then in some wines the taste is impaired, and they may become cloudy. Long-term experience backed by controlled tests(3) indicates that in long period storage in stainless steel there is no increased iron content even with SO_2 content well in excess of normal statutory limits. With resin coated tanks, pinholes in the coating can give contamination by iron from the base material.

CLAD STEEL VERSUS SOLID STAINLESS STEEL FOR CARGO TANKS

Until recently, carbon steel clad with 1½–2½ mm of stainless steel has been used for most shipboard tanks with solid stainless steel used mainly for transverse and centre line bulkheads. Clad steel has generally given good service but recently there has been a tendency to use solid stainless steel introducing a number of advantages and perhaps a potential problem.

A plate clad with 1½ to 2½ mm of stainless steel becomes cheaper than solid steel, in terms of plate cost, at a certain thickness (the breakeven thickness) which can vary from about 7 to 10 mm.* This variation depends on factors such as production methods, the grade of stainless steel used, the country of origin etc. The breakeven thickness decreases as the more costly grades are considered—that for 317 being less than for 316, for example. Also, depending on the welding methods used and contingencies allowed for by the fabricators, the breakeven thickness for completed fabrications may be considerably higher than the plate cost breakeven point. Since in most cases tank thicknesses are below 10 mm, the use of solid stainless steel may result in cheaper tanks or at worst tanks of similar cost. Also in exceptional circumstances (e.g. handling a very corrosive acid contaminated by seawater, or carrying seawater ballast for prolonged periods) which might lead to serious localized pitting, say 1–1½ mm deep, this pitting would not seriously affect the safety of a solid stainless steel tank but might cause concern in a clad one. The solid stainless steel tank could continue in service until local repair was feasible whereas similar pits in the clad steel would be close to penetrating the alloy layer putting the tank at some risk and necessitating immediate attention.

If, however, wing tanks are to be used for seawater ballast the following possibilities have to be considered if solid stainless steel is used:

a) If there are local bare areas of carbon steel in contact with bare stainless steel immersed in seawater accelerated corrosion of the carbon steel could occur there. The large cathodic area provided by the stainless steel and the small anodic area of carbon steel could give rise to fairly rapid corrosion of the bare steel areas. Obviously reduction of the cathodic area, for example by painting the exterior of the stainless steel will circumvent this problem;

b) If the stainless steel is not in contact with appreciable areas of bare carbon steel in the seawater, pitting of the external surface of the stainless steel might occur under the predominantly stagnant conditions. Painting of the stainless steel will eliminate corrosion at the bare areas of the carbon steel. Various paint systems for this application are now being evaluated. Furthermore, it is known that stainless steel can be prevented from pitting in seawater if it is in contact with appreciable areas of bare carbon steel (a carbon steel: stainless steel area ration of 1:9 has been suggested as sufficient). Zinc anodes have also been used successfully for this purpose.

Although experience is still limited there are ships in service with solid stainless steel painted on the ballast side and experience tends to suggest that this problem is less severe than once anticipated. The ballast spaces of one such ship which were coated with a coal-tar epoxy paint, were examined by the authors after three and a half years' service and were found to be in excellent condition even though the ballast tanks had been regularly filled with seawater ballast.

It seems that the ballast tank problem can be avoided by relatively simple and inexpensive techniques. Therefore, the economic and technical advantages of solid stainless steel referred to earlier can be utilized.

High Proof Strength Stainless Steel

An important development in the last few years has been the introduction of high proof strength variants of the standard grades of stainless steels.

Most modern design practices for storage tanks and pressure vessels in Europe are based on yield strength or proof-strength criteria rather than the formerly used ultimate tensile strength criterion. The minimum proof strength of the conventional grades of stainless steel is relatively low, e.g. 20 kg/mm² compared with 25 kg/mm² for mild steel. Improvements in proof strength of the order of 50 per cent or more, with more moderate improvements in ultimate tensile strength may be obtained by:

1) The addition of 01·5–0·25 per cent nitrogen to conventional grades of austenitic stainless steel, e.g. 304, 304L, 347, 316, 316L. (This method is not applicable to titanium-containing grades since the titanium reacts with the nitrogen).
2) Warm working involving finishing rolling temperatures below 1470°F (800°C) with final annealing at 1562°F–1652°F (850°–900°C) rather than the full softening treatment at 1922°F (1050°C) normally given to conventional grades.

Nitrogen-containing High Proof Stress Steels

The effect of nitrogen content on proof strength is illustrated by comparison in Table III of normal 316L and nitrogen-containing 316L, the grades of most interest for chemical ships. This comparison is on the basis of typical producers' minimum guaranteed values.

TABLE III—COMPARISON OF PROPERTIES OF NORMAL AND HIGH PROOF STRENGTH STAINLESS STEEL TYPE 316L

	0·2 per cent proof strength at 68°F (20°C) kgf/mm²	0·2 per cent proof strength at 212°F (100°C) kgf/mm²	UTS at 68°F (20°C) kgf/mm²
316L	21	16	52
Nitrogen-containing 316L	32	24	65
Warm-worked 316L	41	36	63

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* Based on cost comparisons obtained March 1969.

The cost relative to standard grades varies from country to country, but in the case of steel from the U.K. producers, the premium for high proof strength nitrogen-containing grades is from 0–5 per cent. (March 1970).

TIG, MIG, metal arc and submerged arc welding using appropriate standard stainless steel welding consumables can be applied. It can readily be demonstrated that the longitudinal and transverse properties of welds are always higher than the minimum guaranteed proof strength values of plate material. The corrosion behaviour of nitrogen-containing grades is for all practical purposes identical to that of the corresponding normal grades.

Warm-Worked Stainless Steel

High proof strength stainless steel produced by warm-working is at present limited to plate in the 3–18 mm thickness range. Table III shows the minimum guaranteed properties for warm-worked 316L from one producer.

A slight reduction in strength properties occurs at the weld zone. For design purposes a 15 per cent reduction in the minimum guaranteed value is sufficient compensation. Care must be taken with high heat input processes such as submerged arc welding to control the heat input to limit the reduction in properties. By taking account of these considerations, submerged arc welding has been satisfactorily used on warm-worked steel for chemical tankers.

Within the U.K., there is no cost premium for warm-worked high proof strength steels over corresponding standard grades.

Use of High Proof Stress Stainless Steel in Chemical Tankers

Particularly where the thickness of bulk heads is governed by stress calculations rather than by the minimum set by Classification Societies advantage can often be taken of high proof strength steels for chemical ships. These steels are incorporated in Lloyds Rules which stipulate a minimum thickness of 6½ mm for high proof strength steels, compared with 7 mm for conventional grades. Broadly, subject to these limitations on minimum thickness, and other detailed design considerations, a 15 per cent reduction in thickness is allowed for high proof strength steels compared with conventional grades. (Examples are given in the section dealing with design considerations). Consequently, high proof strength steels can advantageously be considered for tanks handling high-density cargoes.

Warm-worked high proof strength steels have been incorporated in some chemical ships constructed in the U.K. and the nitrogen-containing steels in chemical tankers recently built in Holland, Belgium and Spain.

TABLE IV—CORROSION ALLOWANCES AS GIVEN BY LLOYDS' RULES

	Deductions from normal 3 mm corrosion allowance	
	solid stainless steel	clad stainless steel c)
Exposed to cargo on both sides	½ mm	not applicable
Exposed to cargo on one side and dry on the other	1½ mm	1 mm
Exposed to cargo and water ballast on the other	1½ mm a)	½ mm
Tank bottom—underside accessible and dry	1 mm	½ mm
Tank bottom—underside accessible but in contact with water ballast	1 mm a)	0 d)
Tank bottom—underside inaccessible due to presence of heating ducts (which normally contain fresh water)	1 mm b)	add ½ mm e)

Total corrosion allowance for carbon steel deep tank bulkhead plate is 3 mm.

DESIGN AND FABRICATION ASPECTS

a) *Basic Design Considerations*

The general basis for the design of stainless steel and stainless clad steel is to use the criteria for the minimum thickness of a mild steel bulkhead making appropriate reductions in the corrosion allowance, depending on the corrosion conditions existing on either side of the bulkhead as indicated in Table IV. Appropriate corrections are made for high density cargoes, and for the thickness and section modulus of stiffeners. The Classification Societies usually stipulate overriding thickness minima which, in the case of Lloyds Rules, are 7 mm for normal austenitic steels and 6½ mm for approved high-proof strength stainless steel. In the case of clad steel a 1½ mm minimum of stainless steel layer is specified for the tank sides with 2 mm for the bottom.

The effect of these considerations on bulkhead thickness is shown in Table IV where appropriate deductions have been made from the normal 3 mm corrosion allowance for rules based on carbon steel.

Notes:

a) Solid stainless steel may require coating on the "outer" surface if exposed to areas of mild steel in seawater in order to avoid accelerated corrosion of bare carbon steel.

b) The heating ducts may be of mild steel but only fresh water or oil is to be used for the heating element. If fresh water is used then means of monitoring for the presence of rust should be provided.

c) The thickness of clad steel includes the cladding and the thickness of the cladding itself is to be at least 1½ mm (0·06 in) at the sides and top and 2 mm (0·08 in) at the bottom.

d) If the mild steel side in the ballast tanks is coated, the deduction may be increased to 1 mm (0·04 in) which is equivalent to reducing the corrosion margin on the outer surface by ½ mm (0·02 in).

e) It is considered advisable to *increase* the thickness of tank bottom plating in way of inaccessible heating ducts.

If we consider a bulkhead exposed to cargo on one side and water ballast on the other and assuming this bulkhead is required to be a 10 mm thick in carbon steel, then the comparative thicknesses for stainless steel, stainless-clad steel and high proof-stress stainless steel are as follows:

	Clad steel	Solid stainless steel	High proof stress stainless steel
Thickness	9½ mm	8½ mm	7½ mm

Note: These relative thicknesses may be altered where the tanks are heated to a temperature exceeding 176°F (80°C) as the proof strength of stainless steel is slightly lower at these temperatures and as thermal stresses are generated in the ship's structure due to the higher coefficient of expansion of stainless steel.

Since the breakeven point for solid stainless steel and clad steel on the basis of plate cost is of the order of 7–10 mm and perhaps higher when fabrication costs and contingencies are included, it is evident that substantial materials cost saving may accrue from the use of solid rather than clad steel. Further savings can be obtained with high proof stress stainless steel, the amount depending on the cost premium over conventional steel which varies from country to country.

b) *Ballasting*

The ballasting arrangements of chemical tanker are of particular importance because of the possibility of cargo contamination and tank corrosion if normal seawater ballast is used. For this reason the trend in chemical tankers is towards the provision of dedicated ballast space and double bottom tanks can be used for this purpose.

Ballast space corrosion considerations when solid stainless tanks are used have been referred to earlier but in some ships the problem has been completely avoided by using special ballasting arrangements which prevent contact of the stainless steel and seawater ballast. One means of achieving this is to use a continuous system of carbon steel heating ducts on the bottom of the tank precluding contact of the stainless steel with seawater in the double bottom tank. If, under exceptional circumstances double bottom capacity is insufficient, it may be necessary to use cofferdam space for ballast. If fresh water is available and can be used economically for ballast this would circumvent any problem in these spaces. If not, and the tanks are uncoated, then the time factor is important and if the space can be washed out with fresh water after ballasting, then short occasional exposure to seawater is unlikely to create serious problems.

From consideration of cargo contamination and tank corrosion, the use of cargo tanks for ballast should be rigorously avoided. However, if, for reasons of safety this is unavoidable, then thorough washing with fresh water is essential and the tank should be inspected to ensure that any deposits have been removed completely.

c) *Tank Finishing*

Since the corrosion resistance of stainless steel is mainly dependent on the presence of a passive film on its surface any interference with this film will reduce corrosion resistance. In fabricating tanks care should therefore be exercised to avoid embedding foreign matter, particularly iron, rust and welding slag in the metal surface. Another potential cause of pitting is weld spatter adhering to the metal surface. Proprietary products are available for coating the steel surface near the weld to prevent spatter adhesion and these are easily removed when the welding operation is completed.

Depending on the welding process used, the weld surface may be smooth or heavily rippled. In the latter case, it is advisable to smooth the surface by light grinding. In the case of clad steel, care must be taken in grinding in the weld zone as this can reduce the thickness of the clad layer and this is not easy to detect. Even where considerable care is taken in fabrication, it is necessary to apply a final cleaning procedure which generally involves acid pickling and final washing. This procedure is intended to remove embedded iron particles and any oxide films that may be formed around the welds. Broad guidelines for this procedure are given in ASTM Standard A380. A pickling solution or paste based on nitric acid and nitric/HF mixtures is used for pickling and this procedure is often described, perhaps dubiously, as "passivation". Some proprietary pickling pastes offered for this purpose contain ferric chloride and these should be avoided because even a trace of ferric chloride left on the tank will induce rapid pitting.

Since manually applied pickling procedures can be unpleasant, there is scope for adapting tank cleaning equipment for this purpose.

OPERATING FACTORS

Table V summarizes procedures which have been found satisfactory over many years for road and rail tankers and gives general guidance which may be adapted for shipboard use for cleaning tanks between cargoes.

The increasing stringency specifications for some chemical products (particularly as far as chlorides are concerned) and the desire to obviate possible corrosion problems, make it highly advisable to use fresh water in all tank cleaning operations, and many specialized chemical ships are designed to do this.

Workmen entering tanks for any purpose should be equipped with appropriate soft footwear, and care should be taken to ensure tank cleanliness. If modifications or repair involving welding are carried out on a tank, the same procedure as in initial tank finishing should be applied to affected areas.

CONCLUSION

Whilst stainless steel is a relatively expensive material, its versatility and flexibility enable it to be used to advantage. That stainless steel can be used profitably in this industry to meet technical and economic requirements is evident from its rapidly growing usage.

REFRIGERATED LIQUEFIED GASES

The last decade has seen rapid technological advance in the shipment of refrigerated liquefied gases particularly anhydrous ammonia −27°F (−33·4°C) liquefied petroleum gas (LPG) −41°F (−42°C), liquid ethylene −157°F (−103·8°C) and liquefied natural gas (LNG) −256°F (−162°C). Special attention has to be paid to the materials in the tanks for these cargoes as normal shipbuilding steels tend to become brittle as the temperature is lowered.

Steel is the obvious first choice for cargo tanks as shipyards are geared to handling this material. Progressive additions of nickel to steels depress the temperature at which good toughness is obtained as shown in Fig. 1. Appropriate grades of stainless steel also have excellent properties down to very low temperatures and stainless steel barges have been built to carry liquid hydrogen −418°F (−253°C). Another alloy of interest is the 36 per cent nickel-iron alloy which, in addition to excellent low temperature toughness, has a very low coefficient of expansion. This has been made use of in some membrane designs for liquid methane and propane tanks.

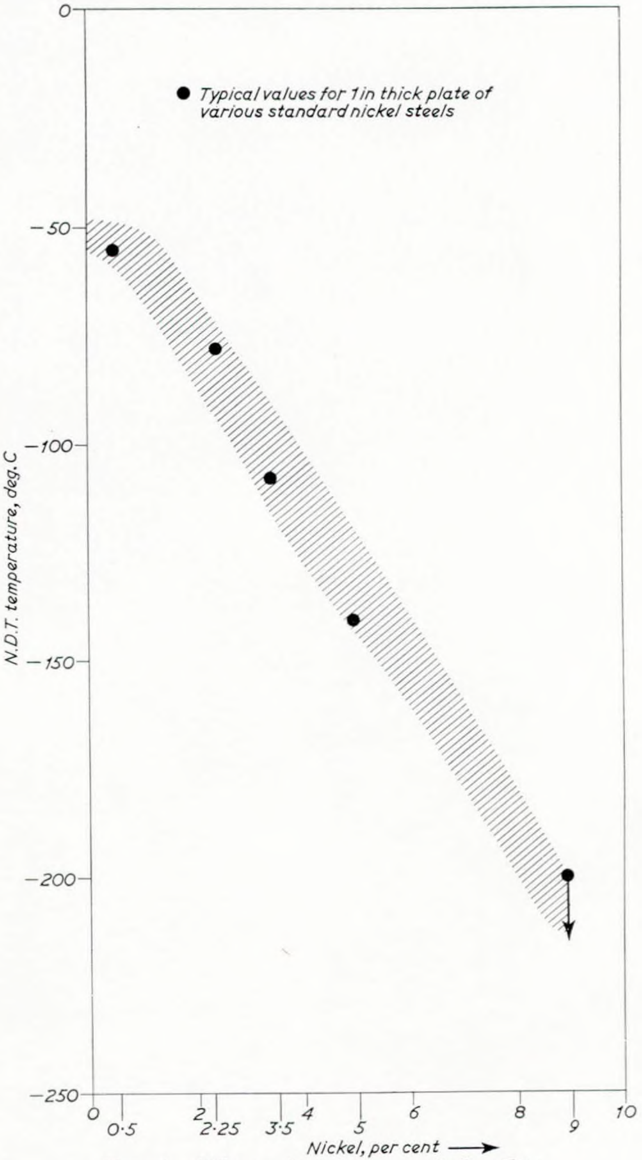

FIG. 1—*Effect of nickel on nil ductility transition of steel plate*

TABLE V—CLEANING PROCEDURE FOR STAINLESS STEEL TANKS

Commodity	Preparation	Cleaning	Rinse	Precautions
Petroleum products, gasoline, jet fuels, kerosene, Diesel, lube, white oils, etc.	Baffled tanks should be constructed with 3-in nipples in each area between baffles for cleaning accessibility.	Recirculatory system using non-caustic alkaline detergent with flood or impingement type rotary spinners. Clean from 2 to 15 min for each spinner position depending on cargo.	Hot water for one or more minutes	Stainless tanks eliminate need to pre-test detergent or to choose less efficient cleaning media to accommodate tanks.
Vegetable oils, china wood, tung, blown castor oil and similar oils.	If clean bore—use high impact spinner through dome opening.	If air-dried, use heavy duty caustic cleaner; otherwise use recirculatory system with non-caustic detergent with impingement or impact spinners.	Hot water rinse	
Tallows, waxes, heavy lubes and paratones.	Tanks should have 3-in nipples between baffles for cleaning accessibility. If clean bore—use high impact spinner through dome opening.	Recycling system using alkaline detergent preferably applied with impingement type spinner.	Hot water rinse	Drain carefully at unloading point; if melting point of commodity is very high, use steam first. If not properly drained, commodity will clog tanks.
Detergents, wetting agents, soaps, etc.	If baffled—tanks should have 3-in nipples between baffles for cleaning accessibility. If clean bore—use high impact spinner through dome opening.	Use steam or spin on a hot water rinse. Do not recycle.		Avoid recycling since it will fill tank with foam.
Nitro-benzol, phenol, aniline oils, oil of mirbane, etc.	If baffled—tanks should have 3-in nipples between baffles for cleaning accessibility. If clean bore—use high impact spinner through dome opening.	Steam clean, do not recycle.	No rinse necessary after lengthy steaming. Avoid quick temperature drop, unless dome is open to eliminate possibility of sucking in tank from vacuum.	Some of these commodities are highly toxic. Do not allow cleaning residues to enter sewer or regular cleaning system. Drain into a French Drain and cover with earth. It is sometimes advisable to keep the same tanks in this service.
Insecticides, herbicides, fertilizers and related liquids.	If commodity is not oil base, pre-rinse with cold water.	If not oil base, use recycled detergent. If oil base, spin detergent solution long enough to emulsify but do not recycle.	Hot water rinse.	Some of these commodities are very toxic.
Caustics, acids, etc.	Tanks should have 3-in nipples between baffles for cleaning accessibility. If clean bore—use high impact spinner through dome opening.	Cold water wash through spinner and drain. If reactive to water drain off properly leaving very little product in tank.		Make certain whether or not commodity is reactive with water. Some acids—especially inorganic types such as sulphuric—react violently with water.
Latex, PVA emulsions, acrylic emulsions, etc.	Load tank with about 200 gallons of cold water immediately after unloading product. Close dome covers until tank can be cleaned.	Open valves and wash with cold water through high impact spinner. If product has set-up and requires scraping, use sonic unit with strippers especially developed for hardened latex such as Astro-Strip No. 2. Follow with hot caustic wash.	Hot water rinse.	Keep dome opening tightly closed; avoid possibility of air drying.
Asphalts, bitumals.	Steam for ½ hour or more to get tank hot. If followed with sonic unit, better and faster cleaning will result.	Lengthy cleaning time can be cut considerably with sonic equipment using prescribed safety solvent (such as Astro-Sol No. 2). Apply through each vessel opening for 15 minutes. Follow with alkaline wash or use vapour degreasing system employing chlorinated solvent such as trichlorethylene or perchlorethylene.	Alkaline rinse first to remove coke and odour, then hot rinse.	
Resins, paints, lacquers, varnishes.	If solvent soluble add several gallons of xylene, M.E.K. or similar solvents in same family to tank after unloading. (If not available, use water).	If water soluble, use alkaline detergent recirculatory system; apply with spinner. If solvent soluble, pre-clean with sonic equipment using a safety solvent recommended by supplier; otherwise use vapour degreasing with chlorinated solvents. While sonic approach is very new, it has proved extremely quick, effective, and reduces the amount of solvent needed per tank cleaning.	Hot water rinse.	Keep dome openings tightly closed. Do not use hot pre-washes. Clean thoroughly.

* Chart prepared by Grady Watts, Chemical Detergents Co. Inc.

TABLE VI—COMPOSITION AND PROPERTIES OF NICKEL-CONTAINING STEELS FOR LOW TEMPERATURE SERVICE

		Composition per cent							Mechanical Propetries			
Steel	Specifications*	C	Mn	P	S	Si	Ni	Heat Treatment	Yield Point kgf/mm^2 ($tons/in^2$)	U.T.S. kgf/mm^2 ($tonf/mm^2$)	Elongation per cent minimum	Charpy V-Notch kgf m minimum
½ per cent Ni	AFNOR NFA 36·208 0·5 Ni A	0·14 maximum	1·3 maximum	0·030 maximum	0·035 maximum	0·30 maximum	0·3/0·7	Normalized	27·0 (minimum) (17·1)	42·50 (26·7–31·7)	25(5D)	5 at −58°F (−50°C)
3½ per cent Ni	ASTM 203 Grade D	0·17 maximum	0·80 maximum	0·035 maximum	0·040 maximum	0·15/0·30	3·25/3·75	Normalized and Tempered Grade D	26·0 (minimum) (16·5)	47·5–54·1 (29·0–34·4)	23	5 at −148°F (−101°C)
5 per cent Ni	VDEH Werkstoff Blatt 680 12 Ni 9	0·20 maximum	0·30/0·60	0·035 maximum	0·035 maximum	0·15/0·35	4·5/5·0	Quenched and Tempered	45·0 (minimum)	60·75 (38·1–47·60)	20(5D)	9 at −184°F (−120°C) (DVM $kgf\ m/cm^2$ 45 ft/lb)
9 per cent Ni	ASTM A353 and	0·13 maximum	0·9 maximum	0·035 maximum	0·040 maximum	0·15/0·30	8·5/9·5	Double Normalized and Tempered	52·7 minimum (33·5)	70·3–84·4 (44·6–53·6)	22	3·5 at −319°F (−196°C) (25 ft/lb)
	A553	do						Quenched and Tempered	59·8 minimum (37·9)	70·3–84·4 (44·6–53·6)	22	3·5 at −319°F (−196°C) (25 ft/lb)

* Other relevant specifications
3½ per cent Ni—BSS 1501—503 (Indraft)
VDEH—Werkstoff Blatt 680
5 per cent Ni—AFNOR
36—208—5 Ni

9 per cent Ni—BSS 1501—509 (Indraft)
AFNOR NFA 36—208
VDEH—Werkstoff Blatt 680
Norske Veritas—NV 20—2

Note: Gauge length 2 in except where indicated.

LPG AND AMMONIA

Ships are usually designed for carrying both these liquids as the material requirements are approximately the same. The lowest temperature encountered is about −41°F (−42°C) (propane) and suitable toughness can be obtained in fine grain carbon manganese and carbon manganese niobium steels. Particularly on the continent, however, steels with a small nickel addition—0·5 per cent—are widely used. The main reason for this appears to be the relative ease of achieving consistent results and in particular to meet requirements on transverse properties in some continental codes.

Table VI gives details of the steels under consideration together with some national specifications (where applicable) and an example of composition heat treatment and properties as laid down in one of those specifications.

Much of the early usage of these steels at low temperature was in land-based applications and design codes for pressure vessels etc. were developed e.g. ASME, TUV, British Standards. Whilst the Classification Societies have developed their own requirements for ships these incorporate much of the established practice.

There has been some history of cracking of high strength structural steels in road and rail transport of anhydrous ammonia and whilst there have been no reports of failures in ships, cognizance must be taken of this in specifying materials for tanks for this cargo. The presence of CO_2 and O_2 seem to be necessary for promotion of cracking whilst moisture has an inhibitive effect.

One LPG tanker, *Hippolyte Worms* has used the membrane design for LPG. The membranes were made from Invar*—a 36 per cent Nickel-iron alloy—which is considered later.

Welding

As it is more difficult to achieve toughness with cast structure of weld metals than in wrought materials, particularly when deposited in certain positions it is usually necessary to use a weld metal with a higher nickel content than the base plate. For example the carbon manganese, carbon manganese niobium and ½ per cent nickel steels are often welded with weld metals containing 1–3 per cent nickel. Manual electrodes are extensively used and generally contain about 1½ per cent nickel. Submerged arc welding has also been used with 3 per cent nickel wire and basic fluxes.

ETHYLENE −157°F (−103·8°C)

3½ per cent Ni steel has been used in land based plants for the production of ethylene but with the more severe requirements on board ship the tendency has been to use 5 per cent and 9 per cent Ni steels. The 5 per cent Ni steel meets most code requirements down to −220°F (−140°C) but until recently its availability has been confined to Germany and 9 per cent nickel steel has been used in Britain and France because of its wider availability. Table VI indicates general requirements for these steels.

Lincoln Ellsworth and *Thales* are two ethylene tankers with 5 per cent Ni steel tanks—Table VII gives details of some ethylene tankers.

Dual purpose liquid ethylene/chemical tankers with stainless steel tanks are now being built.

In welding 5 per cent and 9 per cent nickel steel it has not been found possible to obtain the required properties in welds of compositions matching the base plate and it is necessary to use nickel base or special austenitic steel electrodes. This will be dealt with in detail under LNG.

LIQUEFIED NATURAL GAS (METHANE −256°F (−162°C)

The greatest potential growth in the future for liquefied gases is undoubtedly for LNG. Apart from the early development ships such as *Methane Pioneer*, *Pythagore*, *Beauvius* and *Findon*, ten ships have been built or are nearing completion at the time of writing with fifteen on order. With new projects in the offing, for transporting LNG from Venezeula, North Africa and Nigeria to the U.S., Middle East, Brunei to Japan, many more ships are likely to be built in the next few years.

The earlier ships used free standing tanks in aluminium alloys or 9 per cent nickel steel but the trend in recent years has been towards membrane designs. At present, however, there is a resurgence of interest in self-supporting tanks of spherical and cylindrical design. (See Table VIII). 9 per cent nickel steel was used for the cylindrical tanks of *Jules Verne*—Fig. 2 and is to be used for at least three 87 000 m^3 ships with spherical tanks. Apart from this however, it has been used for supporting structures in some membrane ships and tank supports in ships with aluminium alloy tanks built in Italy and Spain.

Detailed properties of 9 per cent nickel steel are given in Table VI.

Table VII—Ethylene tankers

Name	Cargo capacity		Owner	Year built	Builder	Cargo tank material	Minimum temperature	Remarks
	m^3	metric tonnage						
Emiliano Zapata	3344	1915	Petroleos Mexicanos	1970	Swan-Hunter	9 per cent Ni steel	−157°F (−104°C)	
Euclides	4000	2230	Antarctic Gas Incorporated	1970	Chantiers Du Havre	9 per cent Ni steel	−256°F (−162°C)	Ethylene and Methane
Lincoln Ellsworth	830	450	Einar Bakkevig	1966	A.G. Weser	5 per cent Ni steel	−157°F (−104°C)	Can load from pressure storage up to 90 lb/in^2
Thales	1800	1000	Gazocean Armenent	1967	Chantiers Du Havre	5 per cent Ni steel	−157°F (−104°C)	
Yard No. 165	4100	2300	Einar Bakkevig	1970	Moss Vaerft	5 per cent Ni steel	−157°F (−104°C)	
Yard No. 171	12000	6690	Smedrigs	1971	Moss Vaerft	5 per cent Ni steel	−157°F (−104°C)	

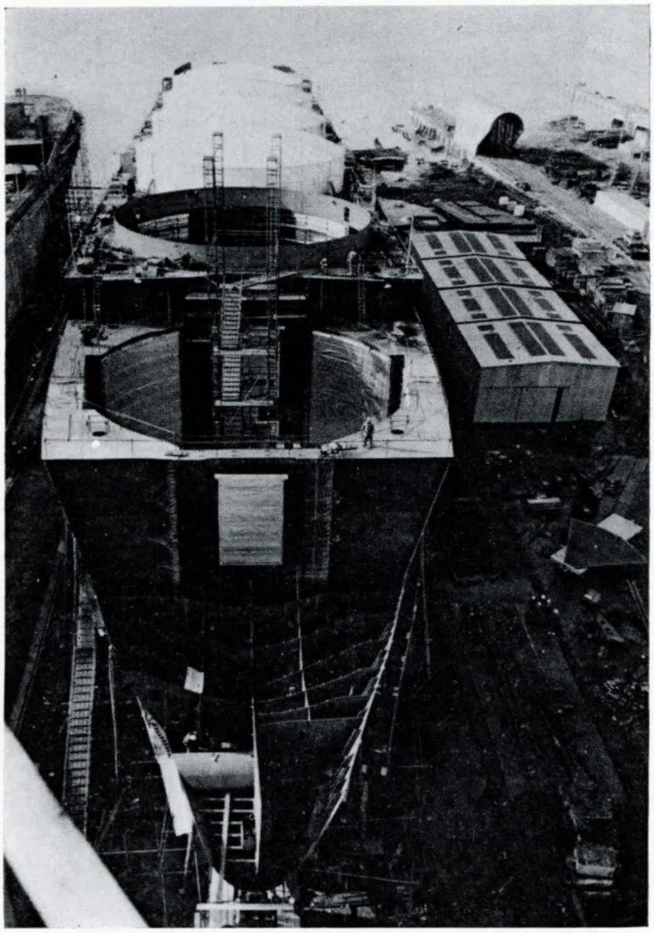

Fig. 2—*Methane tanker* Jules Verne *during construction showing cylindrical 9 per cent nickel steel tanks*

9 per cent nickel steel is used in two grades depending on the heat treatment, namely, double normalized and tempered, and quenched and tempered. Both grades are acceptable and property requirements are given in Table VI. It will be seen that the main difference between the two grades is in their yield strengths.

Welding of 9 per cent Nickel Steel

9 per cent nickel steel can be welded by most of the major welding processes (4, 5) including metal arc, MIG (spray, short arc, pulsed-arc) and submerged arc. Welding consumables fall into two broad categories:

i) Ni-Cr or Ni-Cr-Fe base
ii) strengthened austenitic steels e.g. 16Cr/13Ni/8Mn/3·5W or 18/13/8/8 Cr/Ni/W/Co.

The coefficient of expansion of the Ni-Cr base weld metal is much closer to 9 per cent nickel steel than the austenitic weld metals and this may be considered a significant factor in some designs. The nickel chromium and austenitic steel weld metals for welding 9 per cent nickel steel all exhibit outstanding notch toughness down to −328°F (−200°C) and choice is largely on the basis of proof or UTS strength depending on the design code and overall economics.

In the U.S.A. most 9 per cent nickel steel has been fabricated to ASME Section 8 for pressure vessels or API 620 for large storage tanks.

ASME Section 8—Design criteria is $\frac{\text{UTS}}{4}$ therefore the design strength of unwelded steel ASTM 353 and 553 is 25 000 lb f/in^2. However, the strength of the weld is a limiting factor. Nickel chromium base coated electrodes (e.g. Inco-Weld A, Inconel* 182 etc.) and bare wires (Inconel 82, 92) in general meet a 95 000 lb f/in^2 minimum. UTS across the joint (95 per cent weld efficiency) thus giving a design strength of 23 750 lb f/in^2. Newly developed consumables (Inconel Alloy 625 wire and Inconel 112 coated electrodes) will give a 100 per cent joint efficiency but, as these are considerably more expensive, savings in plate cost have to be balanced against increased welding consumable cost for each specific design.

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TABLE VIII—METHANE TANKERS WITH NICKEL-CONTAINING ALLOY TANKS

Ship	Cargo capacity		Owner	Year built	Builder	Cargo tank material	Remarks
	m^3	metric tonnage					
Pythagore	630	265	Gazocean Armenent	1964	Chantiers De Havre	Stainless Steel	Membrane
Jules Verne	25 500	11 500	Gaz Marine	1965	Chantiers de La Seine	9 per cent Ni Steel	Cylindrical Tanks
Arctic Tokyo	71 500	30 400	Arctic LNG Transportation Co.	1969	Kockums A.B.	36 per cent Ni-Fe Alloy Invar	Membrane
Polar Alaska	71 500	30 400	Polar LNG Shipping Corpn.	1969	Kockums A.B.	36 per cent Ni-Fe Alloy Invar	Membrane
Descartes	50 000	29 400	Gazocean Armenent	1971	Chantiers de l'Atlantique	Stainless Steel	Membrane
Yard No. 1388	40 000		Sonatrach	1971	CNIM La Seyne		Membrane
Yard No. G.25, H.25, I.25	75 000		Shell Tankers	1972/3	Chantiers de l'Atlantique	Stainless Steel	Membrane
Yard No. 257	40 000		Messageries Maritimes	1973	La Ciotat	Stainless Steel	Membrane
2 Ships	75 000		Shell Tankers	1974	CNIM La Seyne	Invar	Membrane
1 Ship	75 000		Shell Tankers	1974	Chantiers de l'Atlantique	Stainless Steel	Membrane
1 Ship	75 000		Shell Tankers	1974	La Ciotat	Stainless Steel	Membrane
3 Ships	88 000		1) Lief Hoegh L. Dreyfus and Saga 2) P & O, A. P. Moller Fearnley and Eger 3) Norwegian Consortium	1973/5 " "	Kvaerner-Moss Rossenberg Verft " "	9 per cent Ni Steel " "	Spherical Tanks " "
2 Ships	120 000		El Paso Natural Gas Co.	1974/5	Chantiers de Dunkerque	Invar	Membrane
1 Ship	120 000 *Benjamin Franklin*		Gazocean		La Ciotat	Stainless Steel	Membrane
1 Ship	120 000		Trans Oceangas S.A.		La Ciotat	Stainless Steel	Membrane
1 Ship	25 000		P. Smedvik Norway	1973	Kvaerner Moss Moss Yard	Not Finalised	Spherical Tanks Methane/ ethylene Carrier
2 ships	35 000 17 000		Lofoten Maritime Enterprises	1974/5	CNIM	Invar	Membrane

API 620—Design criteria is 0·3 × UTS or $\frac{2}{3}$ yield strength which ever is lower.
For 9 per cent nickel steel 0·3 × UTS is the controlling factor
Design strength of unwelded plate is 30 000 lb f/in^2
Design strength 95 per cent joint efficiency 28 500 lb f/in^2
Design strength 100 per cent joint efficiency 30 000 lb f/in^2

European Codes

The majority of European design codes and Classification Societies requirements for pressure vessels and tanks are based on yield or proof strength, generally YS × $\frac{2}{3}$, with safeguards for materials with a high YS/UTS ratio. There is some variation depending on whether welded joint properties or all-weld metal properties are used in computing allowable design stresses for welded structures. Higher values are generally possible when joint strength, rather than all-weld metal properties are used. An example of TUV requirements, given below, illustrates significant differences with the American codes referred to earlier.

Based on extensive qualification procedures TUV assign minimum 0·2 per cent proof strength values on all-weld metal tests for use in computing design strength e.g.

Ni Cr base electrodes wires	minimum 0·2 per cent proof strength
e.g. (Inco-Weld A, Inconel 182 *Nicrex 9, NCF 9, UTP 66 Inconel 92, Inconel 82)	38–42 kgf/mm^2 (54 000–60 000 lb f/in^2) according to type
Austenitic steel electrodes e.g. ESAB (184) 16Cr/13Ni/8Mn/3·5W Grinox 41 "Skola"	45–50 kgf/mm^2 (64 000 lb f/in^2) according to make of electrode
Minimum YS of 9 per cent nickel for design purposes	50 kg/mm (71 000 lb f/in^2)
Design strength of unwelded plate	33·33 kg/mm (47 000 lb f/in^2)
Design strength with 38 kg f/mm^2 weld metal	25·33 kgf/mm^2 (36 000 lb f/in^2)
42	28 kgf/mm^2 (39 000 lb f/in^2)
45	30 kgf/mm^2 (43 000 lb f/in^2)
50	33·33 kgf/mm^2 (47 000 lb f/in^2)

It will be noted that whilst the joint efficiency on this basis is generally much lower the overall design values of welded structures are significantly higher than corresponding U.S. codes. This indicates that there is considerable scope for taking further advantage of the high strength of 9 per cent nickel in the Codes based on the $\frac{2}{3}$ proof strength criterion, such as TUV, by the development of stronger nickel base welds with higher all-weld proof strength than that of existing welding consumables.

Relatively inexpensive high carbon nickel chromium welding wires are available which give minimum 0·2 per cent proof in all-weld metal tests approaching the yield strength of 9 per cent nickel steel. Currently they can only be deposited by low heat input welding processes (short-arc MIG), which are not universally accepted for major site welding projects. Modifications of this wire are under development which should permit its use in high heat input welding processes such as submerged arc and spray transfer MIG.

Submerged arc welding fluxes using Inconel 82 and Inconel alloy 625 wires have been developed in the last few years and used successfully on large land-based LNG tanks and ethylene ships.

Arc-Blow

9 per cent nickel steel has higher magnetic retentivity than normal ship plate steels and this may, in unfavourable circumstances, lead to instability of the arc during welding. This problem has been encountered occasionally and is usually associated with welds in corners where there are large amounts of metal in close proximity to the arc.

Attempts to reproduce the effect in the laboratory have proved unsuccessful and its occurrence in practice has been fairly rare and can be avoided if suitable care is taken. Techniques which have have proved effective are as follows:

1) Avoid magnetic handling of the plates;
2) Demagnetize the plates, or the edges of the plates which are to be welded, with electromagnetic coils;
3) Use A.C. welding processes and consumables.

Post Weld Heat Treatment

As 9 per cent nickel steel retains its toughness after welding, post weld heat treatment is not necessary and indeed is impracticable for the large structures used in ships. ASME Boiler and Pressure Vessel Code Committee has accepted this in a special ruling (Code Case 1308) and provided that pieces individually cold formed have not exceeded a fibre strain of 3 per cent no stress relief treatment is required. Where this strain is exceeded the parts should be stress relieved at as low a temperature as possible in the range 1040°F–1112°F (560–600°C) and the time of treatment should not be unnecessarily prolonged. This is to prevent excessive austenite formation. A minimum cooling rate of 329°F (166°C)/minimum down to 608°F (320°C) is also advisable to circumvent temper brittleness.

New Material Developments

9 per cent Nickel steel has temperature capabilities down to at least −319°F (−196°C) and there is interest in cheaper steels with somewhat lower nickel content, which would, however, be satisfactory at LNG temperatures −256°F (−162°C). An 8 per cent nickel steel has already been developed in the U.S.A.(6) although to the authors' knowledge, this has not yet been used commercially.

More recently, in Japan and the U.S.A. steels with 5–6 per cent nickel with small additions of molybdenum and with special heat treatments and presumably controlled rolling have been suggested(7).

MEMBRANE TANKS

Three basic types of cargo tanks are used as follows:

1) Gas carried under pressure at ambient temperatures;
2) Semi-refrigerated gas in pressure type tanks at somewhat reduced temperature and correspondingly reduced pressure;
3) Fully refrigerated gas carried at low temperature and at approximately atmospheric pressure.

The present paper is mainly concerned with fully refrigerated cargo tanks and these can be classified as follows:

a) Free standing tanks which can be parallelopipedic or cylindrical;
b) Pressure vessel type e.g., cylindrical or spherical-design

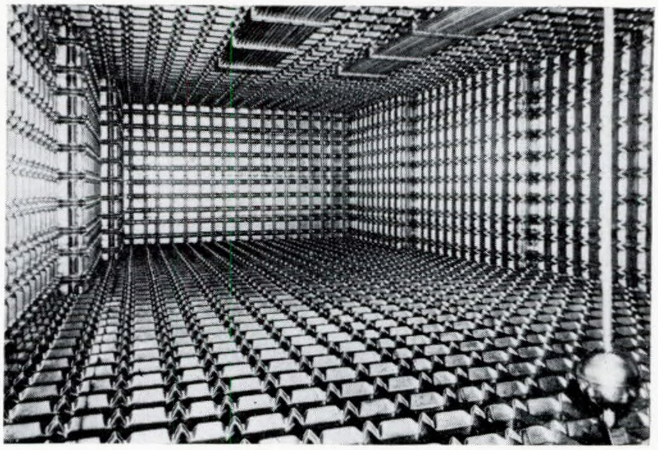

FIG. 3—*Internal view of a stainless steel membrane design tank on* Pythagore

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TABLE IX—TYPICAL COMPOSITION AND PROPERTIES OF STAINLESS STEEL AND 36 PER CENT NICKEL-IRON ALLOYS FOR LOW TEMPERATURE APPLICATIONS

	Composition per cent							Mechanical properties			
Alloy	C	Si	Mn	S	P	Cr	Ni	0·2 per cent proof strength (tonf/in^2)	U.T.S. kgf/mm^2 (tonf/in^2)	Elongation per cent	Charpy V-notch kgf m
Stainless steel AISI Type 304	0·03	0·75	1·2	0·02	0·02	18·5	10·7	24·0 (15·2)	57·0 (36·2)	50 (5D)	10·5 at −319°F (−196°C) (75 ft lb)
36 per cent iron alloy	0·09	0·2	0·3	0·01	0·02	—	35·8	28·0 (17·8)	49·0 (31·1)	40 (2 in)	15 at −319°F (−196°C) (109 ft lb)

FIG. 4—*Internal view of Invar membrane tank on* Polar Alaska

to avoid the need for a secondary barrier;

c) Membrane tanks—in this type cargo containment and load carrying functions are separate. The former is fulfilled by a thin membrane (usually of metal) whilst the latter is achieved by transmitting the load through the insulation to the ship's structure. Tank material considerations for types a) and b) have already been discussed and grades of steel appropriate to the temperature requirements of the cargo are used.

There are two basic types of membrane design currently being used for LNG ships: one using stainless steel (Type 304L) and the other 36 per cent Ni-Fe low expansion alloy. In the case of stainless steel, thermal dilation is accommodated by forming a corrugated pattern in two directions in the sheet—see Fig. 3. This problem does not arise with 36 per cent Ni-Fe alloy as the coefficient of expansion is so small that the stresses generated are low and can be accommodated by the material. Fig. 4 shows a membrane tank built with 36 per cent Ni-Fe alloy Invar. Tanks of this type require much less material than free standing tanks, e.g. stainless steel membranes are approximately 1·25 mm thick and 36 per cent Ni-Fe alloy about 0·5 mm thick. Table VIII gives details of composition and properties of stainless steel and 36 per cent Ni-Fe alloy. A third type of membrane design has been used on LPG ships, e.g. Bridgestone Maru No. 5 and on a Japanese ethylene tanker. This is a plain membrane design using relatively thick material, i.e. about 6 mm and is receiving consideration for LNG ships, where the membrane would be in 9 per cent nickel steel.

Welding of Membrane Tanks

Stainless steel is welded by the TIG process generally without filler wire using normal stainless steel sheet metal practice.

Continuous resistance seam welding techniques using specially designed machines have been used extensively on 36 per cent Ni-Fe alloy in LNG ships.

TIG welding with and without filler wire has also been used for 36 per cent Ni-Fe-alloy(8). Closely controlled techniques have to be adopted, when no filler wire is used, in order to obtain high integrity welds. Such techniques have been successfully used on LNG ships. Special filler wires have been developed for this material and have been used for thicker sheets at the corners of membrane tanks.

CONCLUSIONS

The shipment of fully refrigerated liquefied gases is still at a relatively early stage of development and there is, as yet, no clear cut trend towards any single design of tank or choice of material. However, within the next few years experience will be gained with several types of free standing and membrane tanks after which some definite trend may emerge. Whatever design is chosen it is likely that nickel containing steel will continue to play an important role in liquefied gas tank construction.

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Discussion

MR. E. B. BUDD, M.I.Mar.E., took up a point that was made by an earlier contributor on the system design of cargo tanks. Clearly the design had to take account of the material, but the ramifications of the design on the ship system should also be examined.

Fig. 3 showed a tremendously deep waffle pattern in stainless steel, which was to take up the thermal dilation. A 90° angle corrugation would increase the surface area by root 2, and also the amount of metal by root 2, which could be why the authors had suggested deep corrugation. The heat transfer was proportional to the square root of the external containment area and the internal containment area, so the boil off was roughly 20 per cent more with a corrugation than with a plain inner tank. This in Mr. Budd's opinion should have quite a big effect. What had the authors done with this boil off? How easy was manoeuvring? What was the cost of the reliquification plant, and how often was it used?

Finally, Mr. Budd asked if these optimization studies had already been done or were they in the process of being done? And was there any data on the overall cost per ton of nickel-containing cargo tanks?

MR. P. JEAL said that often, excessive safety margins were incorporated because of ignorance of the true properties of certain materials. If more was known about the materials, shipbuilders could possibly reduce the safety margins and improve the costing without adding to the risks. This being the case, there was a tremendous amount to be done in trying to get together corrosion information.

Mr. Jeal's company, as suppliers of stainless steel, were quite often asked by the shipping lines and by shipyards, if his company's steel would withstand certain specified chemicals. Originally these specified chemicals numbered between 30 and 40. But the last request his company received (from a foreign shipowner) listed 280 and these included chemicals with trade names his company had never heard of, as well as many exotic organic chemicals.

Mr. Jeal thought that many people did not appreciate that such things as temperature impurities were vital factors. His company were supplied recently with two samples of phosphoric acid for testing. Tests showed that 304 would be perfectly satisfactory. However, when the two acids, which were supposed to be typical samples, were analyzed they were found to be without chlorides and the fluorides content was fairly low. Had the chlorides and fluorides contents been high, 304 would have been completely unsatisfactory, and possibly 316C would have been necessary.

With this sort of problem Mr. Jeal thought that it was in the common interest of the shipowners, the shipyards and the materials' suppliers to pool together corrosion information. Whether it could be done through the Institute of Marine Engineers or some other such body, he did not know. Mr. Jeal added that because a pooling of information would be to the benefit of all concerned, secrecy ought not to be an argument for obstruction.

MR. NORRIS, M.I.Mar.E., said that both in this paper and in at least one other the authors had refused to look into the future. Taking Table VIII for example under "Remarks", it went "Membrane, Cylinder Tanks, Membrane, Membrane, Membrane" and so on till "Spherical Tanks".

He would have liked them to have given some reasonable predictions. He thought they would have been in a good position to do this, because they were not associated with one particular shipbuilding or shipowning company and because they were involved directly with materials.

He was optimistic about spherical tanks since he had seen such tanks operating successfully in refineries.

Mr. Norris added the final point that shipowners now had to work out a compromise involving three factors—technical standards, cost, and ship delivery dates in the purchase of a new ship.

MR. S. J. FREDERICK, at the risk of being accused of not having studied the paper said he could find no reference to the problems involved in welding clad steels. Mr. Todd did mention in his presentation that the welding of clad steels was more expensive than the welding of solid stainless, but if one had a tank fabricated from clad steel and, as a result of the inexperience of the welder, ended up with a certain measure of dilution, when that tank was used for ballast with seawater very serious corrosion of the welds could result.

It might be said that avoiding dilution was simply a matter of using an appropriate welding technique; but one was entirely dependent on the skill of the welder, who very often did not fully appreciate the problem.

Mr. Frederick was pleased to hear Mr. Todd state that, particularly with regard to the high proof stress stainless steels, one could end up with a tank which, if not cheaper, was at least no dearer than the tank made from clad steel.

MR. O. M. CLEMMETSEN noted that one item in the equation concerning the break-even thickness for clad and solid stainless steel plates was the production method. This term presumably included the difficulty of inspection of the clad plate as it left the mill. It was not unknown for the cladding to come away from the backing plate and for this to become apparent only at the final cleaning of the ship. What methods were used for checking that there was overall adhesion, or what kind of percentage adhesion was considered reasonable?

On the question of stainless steel and mild steel plates in the same ballast tank the problem could be divided into two aspects: excessive corrosion of the mild steel in the absence of relatively large areas of stainless steel; and corrosion of the stainless steel due to rust deposits from the mild steel. Both could be cured by pointing the stainless steel, as was suggested, but Mr. Clemmetsen found it difficult to accept that pitting of stainless steel could be prevented by the presence of bare carbon steel. There was a case a few years ago, he said, when a clad steel deep tank was severely damaged in a short time due to mild steel heating coils being fitted, and rust from these being deposited all over the stainless steel surface.

Mr. Clemmetsen pointed out that in case anyone looked for Table IV in the current Lloyds' Rules, this table was derived from guidance notes issued to the surveyors regarding scantling determination when clad and stainless steel bulkheads were fitted. In Lloyds' Register's Provisional Rules for Chemical Tankers which were now before the Technical Committee, a somewhat different presentation had been adopted from that shown in this paper, but with the same final results. In this connexion reference was made to a normal corrosion margin of 3 mm. This was a reasonable assumption in the guidance notes for the purpose of a logical approach to such a table. It did not necessarily mean that 3 mm was in fact, the corrosion allowance on all thicknesses of carbon steel plate. On stainless steel one was usually concerned more with pitting rather than overall corrosion and one could get a pit going practically through the plate without really impairing the total strength, although the safety margin against possible leakage would be small. One had therefore in assessing corrosion margins to consider the type of corrosion to be expected.

It was suggested that the occasional use of seawater ballast in a tank containing both stainless and mild steel was acceptable but Mr. Clemmetsen would not like to recommend this in the case of heating ducts which formed cofferdams such as shown in the photograph, since it was impossible to inspect the interior of such ducts after completion. Perhaps there was a possibility of introducing an inhibitor which would render this operation safer.

Finally to estimate the relative importance of stainless steel in shipbuilding in relation to other industries, could the authors give some idea of the tonnages involved?

Mr. R. F. Ffooks, B.Sc., M.R.I.N.A., asked if the authors could say whether there was any work being done on a lower percentage alloy than nine per cent nickel for LNG self-supporting tanks. The suppliers of tank aluminium were working on a higher strength alloy to improve their competitive position and it would seem that perhaps there might be similar work being done in the nickel camp. One of the disadvantages of nine per cent nickel for self-supporting tanks was the lack of availability of rolled sections having the same mechanical properties as the plate. Was there any improvement in this situation?

Mr. Ffooks added that he hoped Mr. Todd and Mr. Swales were not trying to introduce into the English language the dreadful word "parallelapipedic" which was practically unpronounceable—it was the first time he had seen it used in English and it was possibly a French translation of something simple like trapizoidal or box shaped.

Authors' Reply

Mr. Swales, in reply to Mr. Ffook's question regarding the development of a lower cost nickel steel for LNG service, said there were several different steels being developed—one for example was a modification of 9 per cent nickel steel to 8 per cent nickel steel—purely an economic saving. There were also other developments aimed at the mid-nickel range—the 5 per cent nickel steel for example which had been used down to about −120°C; there were also a number of developments in Japan and in the U.S. to improve this steel to make it satisfactory for −162° service and a 6 per cent nickel was under development in Italy. So the answer to Mr. Ffooks' question was yes, there was a lot of effort in the steel industry to keep these steels competitive in the context of LNG tanks.

In reply to the question about availability of rolled sections, Mr. Swales thought it was fair to say that the position had improved somewhat since Mr. Ffooks looked at it a few years ago. Mr. Swales was thinking particularly of Germany where rolled and extruded sections had been available in the past; furthermore, rolled sections were now available in Sweden.

With regard to Mr. Frederick's view of clad versus solid steel, particularly in the context of weld metal dilution, the authors could not agree more. This was one of the reasons why fabricators tended to put on contingency allowances for any trouble they might run into in welding clad steels, and this was one of the factors inherent in the higher price over and above break-even point for plate costs. Of course, a lot could be done to avoid this. One method that had been adopted was to use stainless steel weld metal throughout to cut down the amount of dilution, and in particular, choosing specific electrodes with higher nickel chromium and molybdenum contents so that when diluted they still reasonably matched 316 stainless steel. This type of electrode was 25/12 with molybdenum, which had been widely used on the Continent for welding clad steel. Of course, if the weld was very badly diluted and if for example ballast water was carried in the tanks, one could expect some corrosion—or at least rust staining in the first instance, and perhaps pitting. It depended really on getting a good number of layers and proper procedure on the clad side, or the use of stainless steel weld metal throughout, to reduce weld dilution. But it was not only in the case of weld metal dilution on clad steel that one might get this rust staining. It could occur on solid stainless steel if the welds were not clean, in which case rust staining arose largely due to inadequate cleaning of the oxide films caused during welding. The point was strongly made in the paper that the authors did not recommend carrying seawater ballast in the tanks; they had simply intended mentioning that on occasions if, for the safety of the ship such water had to be carried certain precautions had to be taken.

Mr. Clemmetsen had mentioned not using ballast water in the heating duct compartments. Of course, said Mr. Swales, fresh water heating or oil heating, and not seawater were specified in the paper.

Another question by Mr. Clemmetsen related to the amount of stainless steel used in chemical tankers in relation to total U.K. production. The amount of stainless steel going into chemical tankers in Europe last year was somewhere in the region of 7000 to 8000 tons. This compared with a total European consumption of about 185 000 tons.

The break-even thickness, as Mr. Clemmetsen had pointed out, did depend very much on the production methods and the amount of inspection that was applied. Of course, explosive methods of making clad steel had been considered in the last few years, and Mr. Swales thought it was too early to say whether they were really better from the bond point of view than the traditional methods of rolled cladding. Generally speaking, ultrasonic inspection was used quite widely for checking the bond but varied in stringency depending on the inspection grid. There were specifications for the percentage of bond, but he thought these were rather dangerous, and that every plate should be interpreted in relation to the area, how it was distributed and its ultimate application. A very small local area of poor bonding or even several of them in one plate, was probably not serious, but a fairly large single area could be very much more important, and Mr. Swales did not think it was sound to talk in terms of percentages. This had to be interpreted on the basis of the actual inspection. Virtually 100 per cent bonding could be guaranteed using ultrasonic inspection with a very small inspection grid size, but this would be expensive.

A question was raised by Mr. Clemmetsen about the dangers and benefits accruing from having carbon steel and stainless steel together . One could imagine rust being washed off the carbon steel heating coil onto the stainless steel and of course, deposits were a bad thing for stainless steel. On the other hand, one could imagine other configurations where the stainless steel was not likely to be coated by deposits from carbon steel, for example, in ballast tanks where carbon steel could help protect stainless steel at holidays in the paint coating. Mr. Swales thought the figures referred to, were based on U.S. Navy work which showed that pitting could be suppressed by cathodic protection using carbon steel anodes, and an area of 1:9 was suggested. Plenty of cases where carbon steel had protected stainless steel could be seen but if rust washed onto stainless steel then it was a deposit as Mr. Clemmetsen had suggested, and deposits had to be avoided like the plague for maximum corrosion resistance.

Mr. Todd, taking Mr. Budd's remarks first, said that the authors were not systems designers but were materials specialists and could not therefore offer any views on the subject he had raised. The designs which were illustrated in the paper were in all cases proprietary designs. One would have assumed if they were at all able to sell them the designers must have studied them in some detail.

On the question of extra boil-off from the extra area, Mr. Todd did not know how valid this was. The heat had still to travel through the installation, and as there was no flow past these ripples, Mr. Todd did not think it would too much influence the heat transfer. As regards the actual material with the ripples involved, Mr. Todd thought it was hardly significant in the cost of the ship; something like 400 tons of stainless steel would be required in a large vessel of the design illustrated at a cost, maybe of £150 000. As the ship's price was mentioned at £20m, he did not think the variation in ripple size would have much effect on total cost.

In answer to Mr. Norris's questions on future trends, again the authors could not really offer much information, but what they would suggest in this context was that different designs for different sizes of ship might be preferred. For example, in relation to the design for the convoluted stainless steel membrane, one company had produced a spherical tank design which they claimed could be cheaper in smaller sizes. But they did not really offer any very exact economic break-even point related to different sizes.

Mr. Todd therefore thought that there would probably be more than one design used, depending on the size of ship; but quite what that would be he couldn't say. Certainly the shipowners, as Mr. Norris had said, seemed to favour the heavy steel plate designs of spherical tanks or trapizodial tanks. This was more in keeping with what they were familiar with, and furthermore the shipyards were used to handling heavy steel plate. But the authors would not like to hazard a guess on the final designs.


Mr. Durham


Mr. Ferguson

ALUMINIUM ALLOYS FOR CHEMICAL AND LOW TEMPERATURE CARGOES

by R. J. Durham* and W. Ferguson*

INTRODUCTION

Although the range of commercially available aluminium alloys is extensive, the list of characteristics desirable in a ship tank or container narrows the choice of alloy to a fairly short list for most applications. The features looked for are principally:

1) compatibility of the metal with the intended contents, i.e. good resistance to corrosion;
2) a satisfactory combination of strength and ductility for the avoidance of notch brittleness and to allow forming operations to be carried out if necessary;
3) good weldability and minimal mismatch between weld and parent metal strengths;
4) resistance to stress corrosion.

When a cargo has to be carried at a temperature much different from room temperature, an additional consideration arises; the material properties may vary markedly over the temperature range of interest and the usual practice is to design for the worst possible combination of strength and service conditions. In the case of low temperature tanks, for example, the room temperature strength governs the design. Most applications of aluminium are at room or sub-zero temperatures so this paper concentrates to a large extent on these material properties appropriate to such applications.

PROPERTIES

With the foregoing requirements in mind the properties of suitable alloys can be described. Table I gives the specified tensile properties of selected materials. Where there is a range of thicknesses the figures appropriate to a thickness of 25 mm are given. As the gauge of metal will commonly exceed 2·6 mm (0·125 in) just one or two examples of cold worked tempers are given as plates would most commonly be used in the annealed (O) or as hot rolled (M) conditions. Information about a more extended range of materials may be obtained from British Standards 1470–1476. Although thicknesses given are those quoted in the standards, greater thicknesses are available in some instances. In addition to the tensile properties, shear and bearing ultimate stresses are given. The expected minimum values are obtained by the method adopted to give the figures quoted in B.S. C.P. 118(1). Where a self-supporting tank is designed with extruded stiffening members the guaranteed material properties can be obtained from B.S. 1476 and from C.P. 118.

In addition to the standard materials named in Table I, the alloy group consisting of aluminium alloyed with zinc and magnesium, characterized by the improvement in strength which occurs as a result of spontaneous aging after welding, has been studied intensively in recent years. For room and low temperature applications this group may prove to be an alternative to N8 in the future. Aluminium-zinc-magnesium alloys have already been used for off-highway dump truck bodies, military bridges and underground railway cars to give just three examples. Those selected as examples are basically Al-4Zn-2Mg alloys of U.S. and Canadian origin though similar British and other European materials are available.

Compatibility and Corrosion Resistance

The alloys listed in Table I have without exception a high resistance to the action of most chemicals. The circumstances of individual applications can vary widely, however, so each case should be given careful consideration. Several publications exist which give extensive information about the action of a wide range of substances on aluminium (2,3). The alloy N51 is designed for applications where the service temperature is moderately elevated (up to 200°C) and is much used on that account for containing hot ammonium compounds especially ammonium nitrate. All the alloys are unaffected by contact with low temperature cargoes such as liquefied natural gas and ethylene. It is to be noted that many reactions with aluminium tend to be self-stifling and attack is limited by build-up of a protective layer. In general it is true to say that unalloyed aluminium has the best corrosion resistance followed by alloys containing manganese(N3), magnesium (N4, N51 and N8), and magnesium and silicon (H30) in that order, even the last named having very good corrosion resistance. In addition to the effects of the cargo, the materials must resist the marine environments. All the alloys named in Table I have excellent resistance both as parent plate and after welding. Aluminium alloys like many other metals are subject to galvanic corrosion when dissimilar metals are coupled together in the presence of moisture acting as an electrolyte. Contact with heavy metals must be avoided. Aluminium can, however, safely be coupled with zinc, cadmium, chromium or stainless steels.

Stress Corrosion

In general there are no stress corrosion problems associated with any of the standard materials. N8 is not recommended (4) for applications where temperatures exceed 65°C for long periods, because the metal may then become susceptible to stress corrosion, otherwise there is no problem.

The Al-Zn-Mg alloys when made and heat treated in accordance with the latest manufacturing practices should also be adequately resistant though it is as yet too soon for any great amount of accrued service experience to be available on the subject.

Strength and Ductility

Although aluminium alloys can be employed in applications at moderately elevated temperatures they find their

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* Alcan Ltd.

TABLE I—MECHANICAL PROPERTIES OF SHEET AND PLATE

Specn B.S.	Alloy Alcan	Temper or condition	Minima			Expected minima		Thickness
			0·2% P.S. hbar (ton/in²)	U.T.S. hbar (ton/in²)	Elongation %	Ultimate shear stress hbar (ton/in²)	Ultimate bearing stress hbar (ton/in²)	
1470 1C	GB 2S	M	—	(7·0 (4·5)	—	4 (2·6)	14 (9·0)	≯ 25 mm
		H4	—	11·0–14·0 (7·1–9·0)	6	6·5 (4·2)	22 (14·2)	≯ 12·5 mm
N3	GB 3S	O	—	9·0–13·0 (5·8–8·4)	24	5 (3·2)	18 (11·6)	≯ 2·6 mm
		H4	—	14·0–17·0 (9·0–11·0)	6	8 (5·2)	28 (18·1)	≯ 2·6 mm
N4	GB M57S	M	—	18·0 (11·6)	14	10·5 (6·8)	36 (23·3)	≯ 25 mm
		O	6 (3·9)	16·0–20·0 (10·4–13·0)	20	9·5 (6·2)	32 (20·7)	≯ 25 mm
N51	GB B53S	O	8	21·5–28·5 (13·9–18·4)	12	1·3 (8·4)	43 (27·8)	≯ 25 mm
		M	12·5 (8·1)	21·5 (13·9)	8	1·3 (8·4)	43 (27·8)	≯ 12·5 mm
N8	GB D54S	O	12·5 (8·1)	27·5–35·0 (17·8–22·7)	14	16 (10·4)	55 (35·6)	≯ 25 mm
		M	13·0 (8·4)	28·0 (18·1)	10	16·5 (10·6)	56 (36·2)	≯ 25 mm
H30	GB B51S	TB	11·5 (7·4)	20·0 (13·0)	15	12 (7·8)	40 (25·9)	≯ 25 mm
		TF	24·0 (15·5)	29·5 (19·2)	8	17·5 (11·3)	59 (38·2)	≯ 25 mm

O = annealed
M = hot-rolled
TB = solution heat-treated
TF = solution heat-treated and aged

Notes: Tensile properties of material in the M temper are "for information only".
Shear and bearing stresses are "for information only".

greatest use at ordinary ambient temperatures and below. Because of its good strength and ductility and the stability of its characteristics at temperatures down to at least −200°C N8, Al-Mg4-Mn-Cr alloy, has been widely used not only at room temperature but also for land and ship tanks and for piping for liquefied methane. Thus a considerable amount of data has been generated giving the tensile properties and notch ductility at temperatures down to −200°C and below.

The modulus of elasticity of several aluminium alloys has been found to be about 12 per cent higher at −195°C than at ambient temperature and to decrease progressively as temperature rises (see Fig. 1).

The tensile strengths and elongations of a number of alloys have been described in considerable detail by others (5, 6, 12). Figs 2a, b, and c show the variation with temperature of proof stress, ultimate stress and elongation respectively, of seven alloys. It is especially noteworthy that the ductility as shown by the elongation shows an increase as temperature falls in nearly every case, proof and ultimate strength also increasing.

Past service failures at low temperatures in other materials have brought about an awareness of the need for good notch ductility at all temperatures in the service range. Many tests have been devised to measure notch ductility ranging from tensile tests on very large and thick plates containing weld seams with built-in flaws (11) to Charpy tests on pre-cracked pieces of 10 mm square cross-section. The features examined included comparisons of the maximum stress developed with the yield stress of the material at the same temperature, the energies absorbed in the fracture process

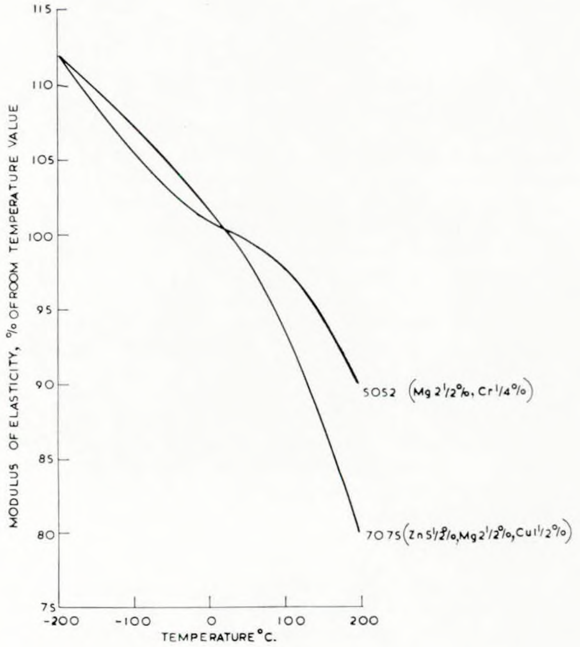

Fig. 1

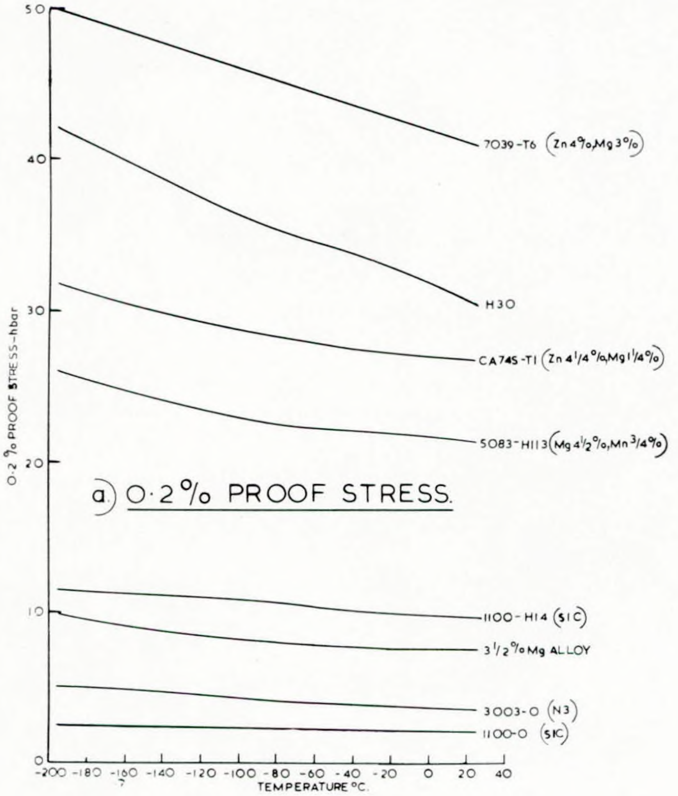

Fig. 2a

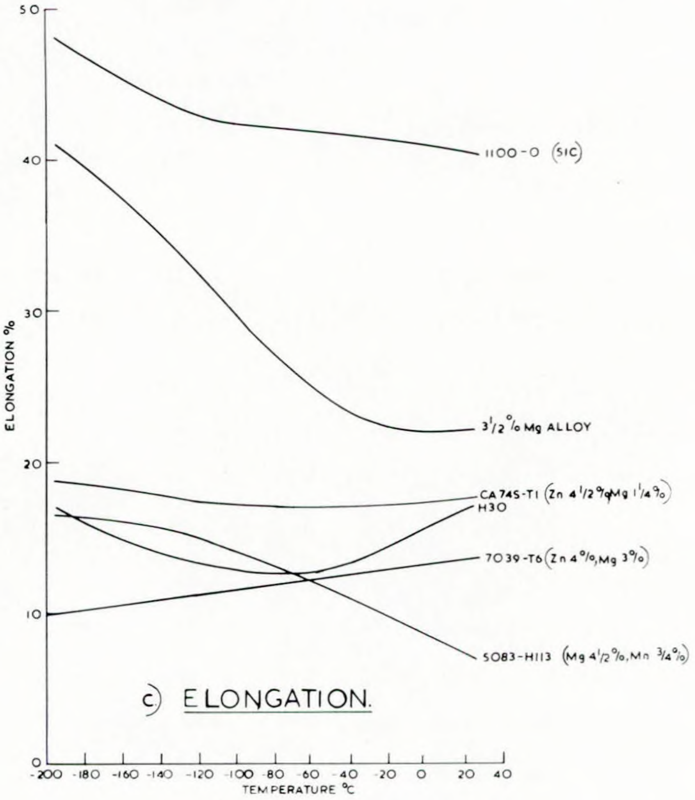

Fig. 2c

Fig. 2b

at different temperatures, and the extent of ductile shearing as evidenced by looking at fracture surfaces. Generally, tensile stresses are developed either directly or by bending. All tests have the common object of showing the stability of the material properties to temperature variation. Figs 3 and 4 show the notch yield efficiency of several alloys at 25 and −196°C. The efficiency is measured by the ratio, notched U.T.S. divided by 0·2 per cent proof stress at the same temperature. If the value exceeds 1 the conclusion can be drawn that similar material stressed in much the same way in a practical situation would yield before fracture occured. The data are taken from references (6) and (8). Neither at 25 nor −196°C did the notch yield efficiency fall below 1 and the figures for individual materials did not vary much with temperature. The Charpy test provides a simple method for checking the toughness variations in the regions of welds. Table II gives the energies absorbed in Charpy tests on 12·5 mm and 44 mm plates of N8-O material. The thinner plate was butt-welded in two passes, one from each side, and the thicker one in 32 passes using Al-Mg5 filler wire, and the metal arc—shielded inert gas—consumable electrode (MIG process). Viewed overall the joints showed very good stability; the weld metal was most affected by cooling but its Charpy value never fell below 2·2 m kg/cm^2 (between 10 and 11 ft lb). The thinner plate had the greater toughness. The influence of thickness of toughness is illustrated in Fig. 5 showing the propagation energy values measured (15) in N8-M plates at room temperature and −196°C using tear test pieces, whose other dimensions were proportional to their thicknesses. It will be seen that temperature had no marked effect on the results. The slope of the propagating energy/thickness relationship is between 2 and 3. This suggests that the energy values were roughly proportional to the volume of metal yielded ahead of the crack tip and hence that similar unit propagating energies were absorbed in fracturing thin

TABLE II—RESULTS OF CHARPY TESTS ON D.V.M. SPECIMENS FOR N8-0

Position of notch base	Charpy value mkg/cm²		
	20°C	—70°C	—196°C
12 mm plate: Parent material	3·76	4·34	3·81
Centre of weld	3·85	3·62	2·66
Touching weld transition	3·90	3·71	4·10
1·5 mm from weld transition	5·28	5·05	4·14
3·0 mm from weld transition	6·34	6·18	5·47
44 mm plate: Parent material	3·81	3·31	3·05
Butt welded seam centre of weld	3·90	4·00	2·23
Touching transition zone	3·52	3·38	2·61
1·5 mm from transition zone	4·18	4·14	3·43
3·0 mm from transition zone	4·37	4·18	3·52

Test piece: 10 mm sq. section.
Notch 1 mm radius, 3 mm deep.
See DIN 50 115.

and thick plates. Resistance to fatigue is to some extent dependant on tensile strength if the influences of surface condition and shape are eliminated. Fig. 6 gives the stress for a life of 50 million cycles of stress plotted against U.T.S. for several alloys using smooth polished test pieces under zero mean stress conditions. The effect of a tensile mean stress is illustrated in Table II where the results are for butt-welded joints in 6 mm plate. It will be noted that the welded joint strength for zero mean stress is $\frac{1}{3}$ to $\frac{1}{4}$ of the polished bar values appropriate to the same materials and the cause is the presence of surface imperfections (not machined), stress concentrations (the weld bead to plate transition), and residual stress (the welding process). Attachments which involve fillet welded joints provided a more tortuous load path and the fatigue strengths are even lower. At low temperatures fatigue is improved; at −196°C the improvement is 50 per cent or more as illustrated for N8M fillet welded joints in Fig. 7 (10).

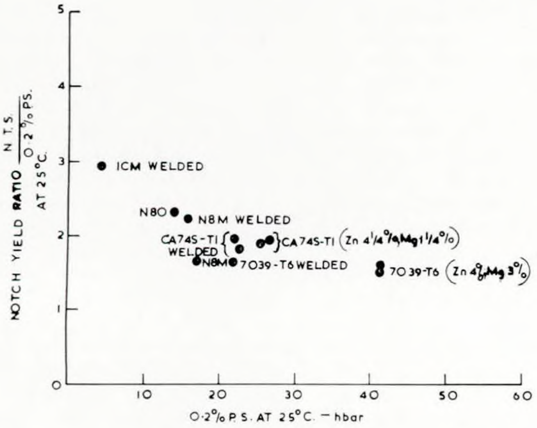

Fig. 3

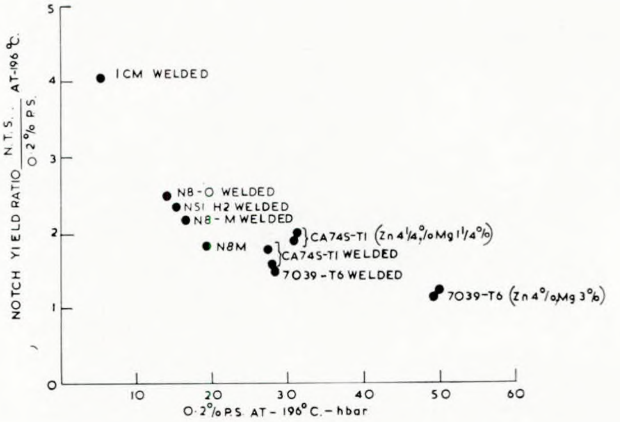

Fig. 4

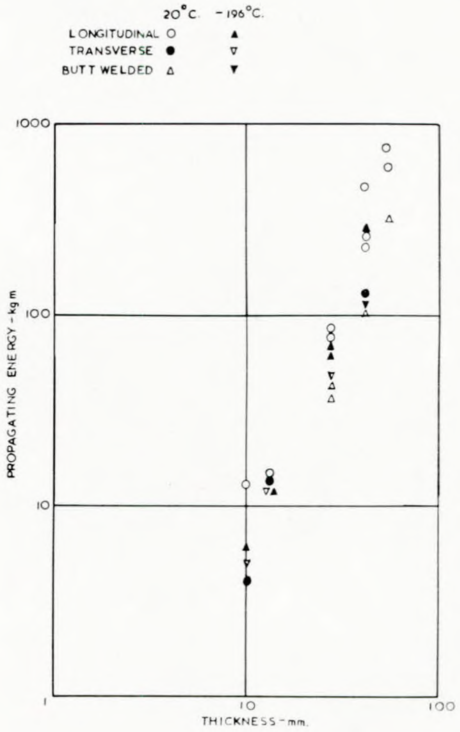

Fig. 5

DESIGN OF CARGO CONTAINERS

The suitability of aluminium alloys is accepted for containing chemical or low temperature cargoes in ships because of the resistance of the various alloys to chemical attack or

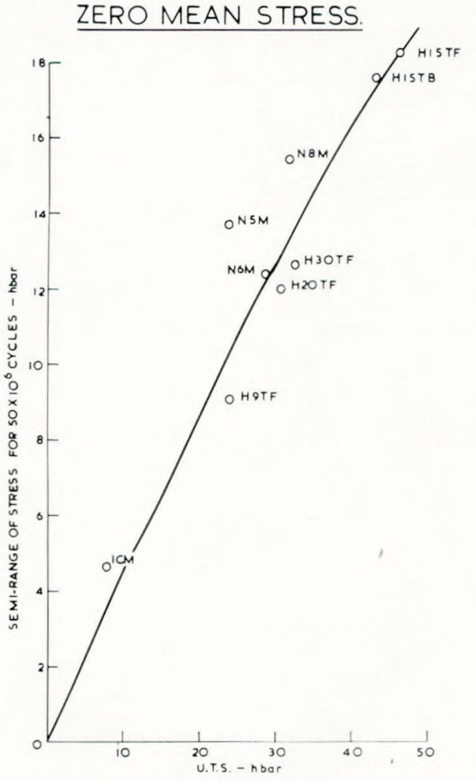

Fig. 6

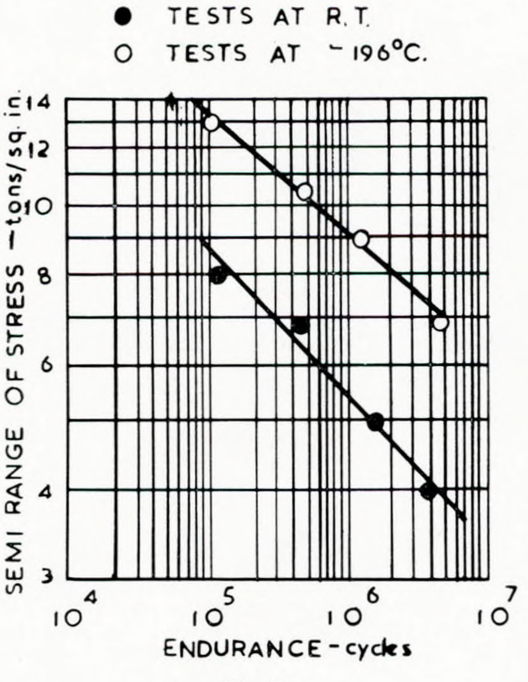

Fig. 7

the retention of the mechanical properties at low temperatures. At present the bulk transport of chemicals is limited, but drums or containers in aluminium alloy are used for this trade. In the low temperature field, aluminium alloys have excellent properties which have permitted them to be used as bulk containers for liquid methane and liquid ethylene within ship hulls, and as this is one of the most important uses of alluminium alloys in shipping, it is intended to discuss these in more detail.

Development of Low Temperature Tanks

Early studies of tanks for liquid methane considered cylindrical tanks having a vertical axis as this arrangement was simple to design and induced temperature stresses were comparatively low. Further, the fabrication cost would be low. However, this arrangement wasted considerable space (almost 30 per cent) so that attention was turned to rectangular tanks which more fully used the space available in the ship hold.

The first rectangular tanks fabricated in the United Kingdom were those for *Methane Princess* and *Methane Progress* which used the equivalent of the British alloy N8. The shell plating decreased in thickness from bottom to top and stiffening was by horizontal angles which were double braced at the corners The tanks were divided by a longitudinal bulkhead which had the effect of reducing the maximum pressure in the tank under dynamic loading. These tanks weighed approximately 130 tonnes each and had the following approximate dimensions:

Length = 10·7 m (35 ft)
Breadth = 21·3 m (70 ft)
Height = 14·0 m (46 ft)

This type of construction, although economical in material, requires a considerable amount of manual welding as the corner brackets and diagonals cannot be welded by an automatic system.

The alternative system, of vertical stiffeners with horizontal framing, although using slightly more material appears more attractive, as much more of this structure can be welded automatically in large elements and then assembled as a complete tank.

Fabrication

All the joints in the tanks for *Methane Princess* and *Methane Progress* are welded. For the butt welds in the main shell plating high current automatic MIG welding was used with one pass on each side of the joint. These welds were 100 per cent inspected by X-ray. Stiffeners were welded to the plating also by this welding system, but using fillet welds.

Loading Conditions

Although pure liquid methane has a density of 0·42, a density of 0·5 is possible in the commercial product because of impurities. However, for the figures of tank efficiencies quoted, the figure of 0·42 has been taken. A gas pressure of 13 790 N/m^2 (2–3 lb/in^2) is assumed to exist in the tank caused by boil-off. The effect of ship motion is defined by Lloyd's Register of Shipping as:

Roll — a complete roll of 30°, port to starboard in ten seconds;
Pitch — a pitch of 6° half amplitude in seven seconds;
Heave — a heave of L/24·3 m (L/80 ft) half amplitude in eight seconds.

Material

The material has already been considered earlier and a permissable stress for N8 alloy is found by following Lloyd's requirements, which allow the lower value of $\frac{3}{4}$ of the Proof Stress or $\frac{3}{8}$ of the Ultimate Stress. For this alloy a a permissible stress of 93 MN/m^2 (6 ton/in^2) is allowed.

Tank Efficiency

The efficiency of tanks may be measured in various ways, for instance, in cubic metres per ton of metal or in tons of liquid contained per ton of metal. In Fig. 8 the second method has been used. Here the capacity (in tons of methane) is plotted against the specific capacity (tons of liquid methane/ton of tank) for various tank cross-sections. The change in volume of a tank of given cross-section is made by increasing or decreasing the length. In Fig. 8, curve 1 refers to a tank

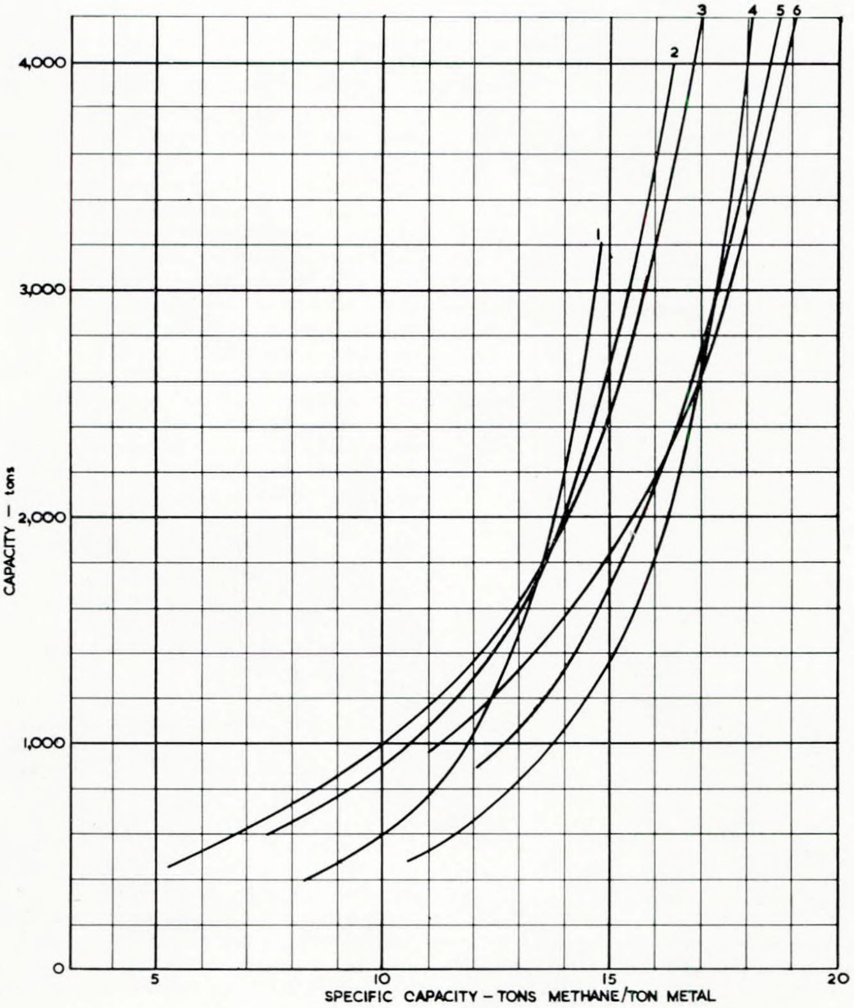

Fig. 8

with a width of 9·8 m (32 ft) and a depth of 14·0 m (46 ft). In this case two tanks of this width would be mounted side by side in the hold. A tank of 19·5 m (64 ft) width and 14·0 m (46 ft) depth with a longitudinal bulkhead is considered to obtain curve 2 and it will be noted that above a capacity of 1800 tonnes the wider tank is more efficient. Curve 3 is obtained with a tank 22·5 m (74 ft) wide and shows a greater efficiency than the two previous tanks at high capacities.

Effect of Higher Working Stress

It is obvious that a change in working stress will affect tank weight but the relationship is not linear. In the study to obtain the curves in Fig. 8, the effect of increasing the working stress by 25 per cent was examined and for tanks having the same cross-sections as those stated, but designed to a higher stress, curves 4, 5 and 6 were obtained. Curve 4 refers to a tank width of 9·8 m (32 ft), curve 5 to a width of 19·5 m (64 ft), curve 6 to a width of 22·5 m (74 ft). Using this higher stress, the point at which the 19·5 m (64 ft) wide tank becomes more efficient than the 9·8 m (32 ft) wide, is now about 2900 tonnes capacity.

For any working stress it is possible to derive the specific capacity of a tank 22·5 m × 14·0 m (74 ft × 46 ft) cross-section from Fig. 9. This diagram shows that in the case of a tank of 2000 tonnes capacity, the improvement in efficiency for a stress increase of 25 per cent is in the region of 11 per cent and for a stress of 50 per cent the efficiency only improves by 15 per cent.

Although the tanks built and operated in N8 aluminium alloy have behaved as predicted and given good service, it has been felt for some time that an improvement in working stress would help the competitive position of aluminium in this field. A large increase in working stress is not required as this would necessitate more expensive alloys, and the gain in efficiency would be lost in higher material price. If, however, an increase in working stress of 25 per cent was desired then an alloy having a proof stress of 154 MN/m^2 (10 ton/in^2) and an ultimate stress of 308 MN/m^2 (20 ton/in^2) is called for which could be supplied by an aluminium-zinc-magnesium alloy without difficulty.

In recent years, the replacement of free-standing tanks by membrane tanks has been considered. This arrangement does not preclude the use of aluminium, although the quantity per ship would decrease drastically. The inner hull of the ship carries the loads from the cargo and the membrane is purely a liquid barrier so formed that it can elastically deform to take dimensional changes caused by temperature change.

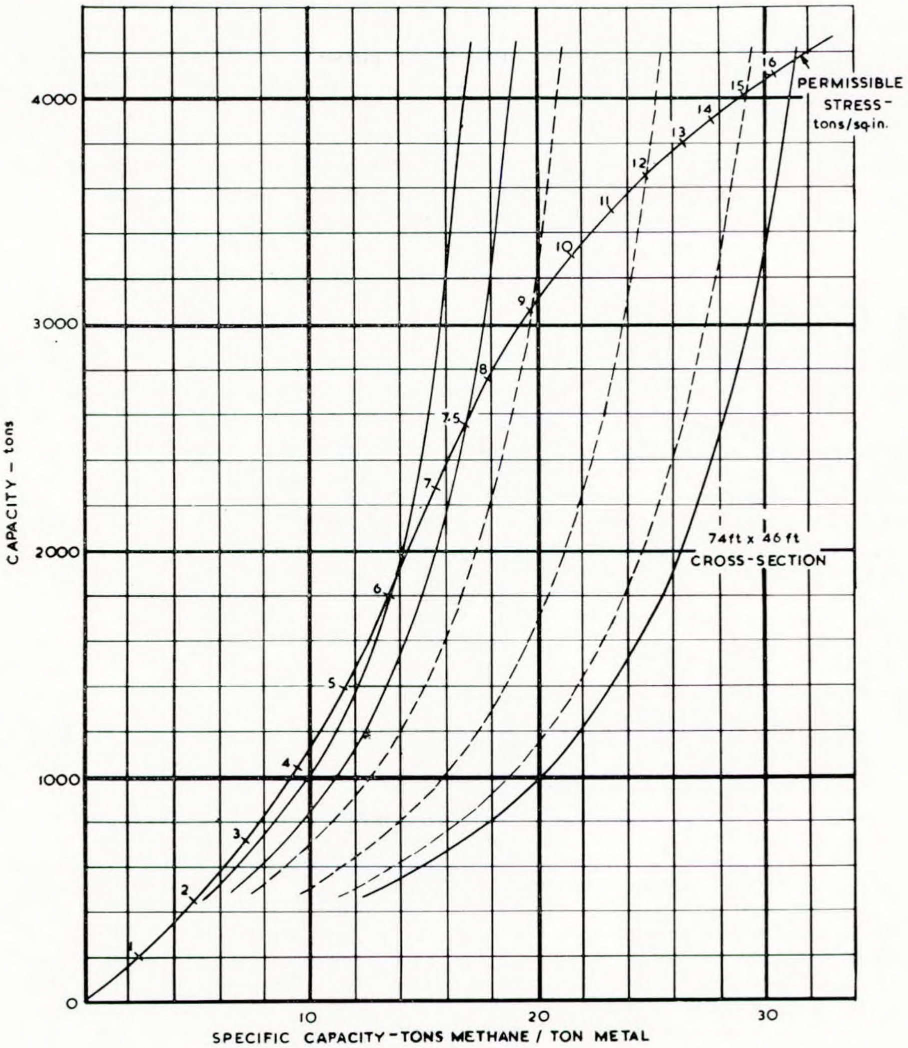

Fig. 9

TABLE III(A)—FATIGUE STRENGTH AT 50 x 10⁶ CYCLES OF BUTT WELDED JOINTS

	N8M					H30				
Tensile mean stress hbar (ton/in²)	0 (0)	2·3 (1·5)	4·6 (3)	7·7 (5)	10·8 (7)	0 (0)	2·3 (1·5)	4·6 (3)	7·7 (5)	10·8 (7)
Semi range of stress hbar (ton/in²)	5·28 (3·4)	3·7 (2·4)	2·9 (1·9)	2·5 (1·6)	2·5 (1·6)	3·9 (2·5)	3·6 (2·3)	2·9 (1·9)	2·6 (1·7)	2·2 (1·4)

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Discussion

Dr. P. T. Gilbert, M.I.Mar.E., said that in selecting materials for vessels which were to convey chemicals, including low temperature cargoes, aluminium alloys immediately spring to mind as potentially useful. Consideration of their properties suggested that their use could well be an economic proposition and it was no surprise to find that such was the case. Their favourable properties were: good corrosion resistance, lightness combined with reasonable strength, and ease of fabrication including welding. Some of these matters were discussed in considerable detail in the paper. The authors had, in particular, given much information on mechanical properties as determined in ordinary tensile tests and in impact and fatigue tests. They had, on the other hand, said comparatively little about corrosion resistance, and perhaps more could usefully have been included about problems encountered in fabrication.

Dr. Gilbert suggested that the paper could have been improved if it had contained a clear statement of the nominal compositions of the aluminium-base materials under consideration, preferably in tabular form. There were references in the text of the paper to the composition of some of the alloys but the information appeared to be incomplete. For those who were not as familiar with aluminium alloys as the authors it would have been helpful to have had a summary, to avoid the need to look up British Standards or other reference documents. On consulting the latest (metric) version of B.S. 1470, the standard referred to in Table 1, he was unable to find alloy N51 but understood this was a 2·75 per cent magnesium alloy with manganese and chromium additions and that it appeared only in the more recently issued B.S. 4300.

An attractive feature of aluminium alloys was that they were not embrittled at low temperatures, and, indeed, the strength and ductility, in general, tended to increase somewhat as the temperature was reduced, as the data in the paper showed. Their suitability for containing low temperature cargoes, from this viewpoint, was therefore obvious. In absolute terms the strength of these materials was moderate and this would necessitate the use of rather bulky components and thick sections. Dr. Gilbert saw no reason why this should introduce any particular problems, constructional or otherwise, but perhaps the authors could confirm that this was the position.

Aluminium had good resistance to many chemical environments and could be used where other materials might suffer undue attack, e.g. in the presence of sulphides or ammonia. In common with other materials, however, it had its limitations; for instance, it was rapidly attacked by solutions of strong alkalis. As mentioned in the paper, galvanic corrosion could occur when dissimilar metals were in contact in the presence of an electrolyte. Aluminium was at a disadvantage in this respect, since in practice other metals coupled to it would often be more noble and if any accelerated corrosion occurred the aluminium was likely to be the material to suffer. Dr. Gilbert asked the authors how serious a problem this was in the construction of ships' tanks or containers, since presumably contact with mild steel was unavoidable at some points. Was it sufficient to use jointing compounds containing inhibitors, or was it necessary to ensure complete electrical insulation? He had in mind that aluminium alloys were not very successful for heating coils in oil tankers, as they suffered severe corrosion, particularly in tanks that carried seawater ballast, if not insulated from the steel tanks. If they were insulated, on the other hand, difficulties were liable to occur due to build-up of static electricity. In the case of ships' tanks made of aluminium, the anode/cathode ratio would be much more favourable than with heating coils; nevertheless, the problem was ever-present in marine environments and he felt it was important to know what precautions had been found necessary to avoid trouble.

Mr. E. B. Budd, Chairman, thought it was odd that membrane tanks had been dismissed in the paper. He would have thought that these tanks would have been a major target of the aluminium manufacturing industry. Some American missiles had made use of chemical milling in order to reduce weight and in the case of a free-standing tank such a reduction would increase the volume with little loss of strength. He asked the authors to comment.

What were the fire hazards involved in using three or four per cent magnesium alloy because in the early days magnesium alloys were quite a fire hazard in some aeroplanes?

Mr. E. D. Dolan said that in considering aluminium and its alloys for general use in the petroleum industry, his company had been very much concerned with two particular aspects. (He had no doubt they were both hoary aspects to the authors.) One was the fall-off in tensile strength with rising temperature, which cast doubts on the stability of aluminium structures in fire situations. The other was that aluminium was subject to sparking on impact. If one dropped a rusty spanner into an aluminium tank, the spark produced could cause an explosion. Of course, said the speaker, the authors would argue that if an explosive atmosphere existed a spanner should never have found its way into a tank; but this sort of thing did happen. Finally, Mr. Dolan thought that none of the metallurgical experts had investigated thoroughly why certain metals had good impact properties at low temperatures.

Mr. B. Todd, M.I.Mar.E., said there were two questions he wished to ask. The authors had mentioned the thickness of aluminium in a large LNG ship. Could they specify how large this ship was? Secondly, expansion had to be accommodated in any design of tank. How was this to be done in a large free-standing tank?

Mr. G. L. Swales said that he would simply like to say that there was a membrane tank built in aluminium, with a view to its use in an LPG carrier—at least it was started in aluminium but it was finished in stainless steel.

Mr. H. J. Miller, B.Sc., M.I.Mar.E., although not working in the field of temperature cargoes said he looked to this paper to give him some guidance on aluminium alloys for chemical carriers. He could not find any, but perhaps he had missed it. He did, however, find this little note: "The suitability of aluminium alloys is accepted for containing chemical or low temperature cargoes in ships because of the resistance of the various alloys to chemical attack or the retention of the mechanical properties at low temperatures. At present the bulk transport of chemicals is limited, but drums or containers in aluminium alloy are used for this trade." Mr. Miller drew attention to this because, rightly or wrongly, he believed it to be quite a possibility that at some time in the future we might have to consider going away from carrying chemicals in bulk. He knew that most people would not accept this but he would invite them to look at present trends in pollution and anti-pollution laws. Recently for example *The Times* said that some 13 members of a German company were in court because of their alleged pollution of the Rhine.

This made one wonder whether the meeting was looking at the question in quite the right way; perhaps it hinged on what Mr. Ffooks had in mind when he had said that perhaps we should consider a completely new approach. It was a possibility that containers would be the answer for future transport of chemicals. If so the containers would have to be very solid because of the danger hazard of lifting one of these and lowering it onto the quay.

One of the main things against the normal type of container, quite apart from other obvious shortcomings (and it was only by considering all these that one came round to a new approach on design) was the weight of the container. Here aluminium would have the edge, but aluminium did not have the properties that were required. Had the authors, or any of their design departments, considered the possibility of, say, insulated aluminium containers with surface treatment? Were they working along these lines? Were they thinking along these lines? Finally Mr. Miller said that one of the biggest problems in the aircraft industry during the last war was age-hardening, and yet he did not see any reference to this in the paper. He would have thought that with the temperature variations which went on throughout the life of the vessel, this was a thing which should be considered, but perhaps a lot had happened in the intervening years.

Mr. H. S. Campbell, A.I.Mar.E., supported Dr. Gilbert's suggestion that compositions should have been included in the table of alloys. Mr. Campbell said he was fairly familiar with aluminium alloys, but even so, he said he had to look at the composition of some of them. He also found the paper rather difficult to follow because some of the figures referred to alloys that were not included in the table, while the information on some of the alloys that were included seemed rather sparse. Mr. Campbell would have particularly welcomed more information on the weldable medium strength aluminium-zinc-magnesium alloys. The $4\frac{1}{2}$ per cent zinc, $1\frac{1}{4}$ per cent magnesium alloy CA 74S, for example, was only referred to sporadically; he wondered in particular where it fitted into Fig. 6, which showed the relationship between fatigue strength and tensile strength for various alloys. The table did include on the other hand, some alloys such as H15 which he did not think were really relevant to marine applications because of their poor corrosion resistance. Could the authors say more about the medium strength aluminium-zinc-magnesium alloys?

Authors' Reply

Messrs. Durham and Ferguson wrote that the nominal compositions of the principle aluminium alloys of interest were as follows:

BS1470—	IC	99 per cent Al
	N3	Al Mn 1·2
	N4	Al Mg 2 Mn 0·3
BS4300/8—	N51	Al Mg 2·8 Mn 0·75
BS1470—	N8	Al Mg 4·5 Mn 0·8 Cr 0·1
	H30	Al Si 1·0 Mg 0·6 Mn 0·5
AA7004— (Alcan	CA 74S)	Al Zn 4·3 Mg 1·8 Mn

Dr. Gilbert could be assured that the thicknesses of aluminium plates and sections in self-supporting tanks gave rise to no constructional difficulties. In a tank 45·72 m long × 26·6 m wide × 19·5 m high (150 × 87·5 × 64 ft), thicknesses might vary from about 30 mm to about 12 mm for the shell plating, with stiffeners of flange thickness 12–25 mm and depth about 380 mm. The attachment of the stiffeners to the plate would be by a single pass fillet weld on each side.

Galvanic corrosion had been studied in depth and could be obviated by correct design. Complete electrical insulation was unnecessary, so that build-up of static electricity need not occur. The paper mentioned the use of compatible materials at points of contact. Other steps could be taken which were described in detail in "Corrosion of mechanical joints in aluminium and aluminium-steel structures" by F. F. Booth.[1] So far as low temperature cargoes were concerned, the electrolyte needed for galvanic corrosion was absent except when the tank was empty, and the tank was rarely allowed to be empty, so the problem ought not to be overemphasized.

In answer to Mr. Budd's question about membrane tanks the original membrane tank designs were Norwegian and the material considered was aluminium. The authors did not know why no one had been particularly interested in these aluminium alloy tanks. Perhaps one reason was that the co-efficient of expansion of aluminium was twice that of steel, but this was countered by the fact that the modulus of elasticity was one-third; hence only two-thirds of the stress generated in steel was generated in aluminium. The weight of material in a membrane tank was very much less than in a self-supporting tank. The aluminium industry was not so interested, therefore, in the former type of development.

Messrs. Durham and Ferguson went on to say that the possibilities of incendive sparking of aluminium alloys had been reviewed by Bartels.[2] The likelihood of incendive sparking increased with magnesium content, but alloys with magnesium contents up to about 5 per cent were unlikely to be more than one-third as dangerous as magnesium. The softer the temper of the aluminium, the less the likelihood of impact sparking. An impact energy of steel on aluminium or vice-versa of 200 ft lb, (271·2 J) gave rise to a low ignition probability of methane-air mixtures. The most easily ignited mixture was 6·4 per cent methane by volume. What risk did exist could be greatly restricted by careful cleaning of the inside of tanks during examination or refitting and by keeping hand tools, such as spanners, attached to lanyards. Steel on steel impacts also gave rise to incendive sparks but these

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[1] British Corrosion Journal, 1962, Volume 2, March.

[2] The use of light metals and their alloys in hazardous areas. ERA 70–32. Electrical Research Association, May 1970.

occurred less frequently than methane-induced sparks—the opportunities for fires to occur in this way were presumably few.

Aluminium alloys were relatively weak at elevated temperatures. A useful guide to the maximum temperature at which they could be used was half the melting point in absolute degrees. This meant that in effect aluminium could not be usefully employed for many applications at temperatures exceeding about 200°C. The melting temperature of pure aluminium was 660°C. Aluminium alloys could only have fire resistance of the order needed to resist the British Standard fire test if they were protected by temperature resistant coverings.

The authors were unable to explain why aluminium alloys had a good resistance to notch impact tests, but it was worth noting that almost all materials other than metals with a face-centred-cubic lattice structure had a nil-ductility-transition temperature or temperature range.

Mr. Campbell mentioned CA 74S, which the authors regarded as one of the most suitable Al-Zn-Mg alloys for low temperature tankage. Fig. 6 was intended to illustrate how alloys belonged to one family in respect of the relationship between their tensile strengths and their basic fatigue strengths at zero mean stress using polished specimens. Alloys of different strengths, from commercially pure aluminium to aircraft-strong alloy had been plotted to cover as wide a strength range as possible—hence the points for H15 alloy. The absence of CA 74S from Fig. 6 was not serious as the graph had no application to the design and performance of components having as-manufactured surfaces and which contained geometrical discontinuities such as welds, bolts and rivet holes. A few more words about the Al-Zn-Mg alloys were in order as these alloys were possible alternatives to the Al-Mg series. The composition could be varied to give a range of properties. The zinc content could range from about 3–5 per cent, and the magnesium content from about 1–3 per cent, but many alloys were close to a nominal composition of zinc 4 per cent, magnesium 2 per cent. The materials could be precipitation heat-treated and would then be stronger. They would usually be welded however. One of the most interesting properties of this alloy group was that after welding—which meant, in effect, re-solution heat-treatment of the material close to the weld because this material was not very quench sensitive and cooling in air would give a re-solution treatment—ageing at room temperature occurred, and the tensile strength increased with time. As a result, the strength improved after welding, though the improvement was small after the first thirty days. Yield strengths of 154–186 MN/mm^2 (10–12 ton/in^2) and ultimate strengths of 308 MN/mm^2 (20 ton/in^2) and more were attainable. Selection of an alloy included an element of chance. If one was prepared to use a material of higher strength but a little more likely to give trouble in service (perhaps by being slightly more liable to suffer some corrosion) a more highly alloyed higher strength example of the Al-Zn-Mg group could be used. If a material which had to be vice-free was chosen it should have as low an alloy content as possible, and CA 74S, which conformed to AA 7004, approached this desirable characteristic.

Mention had been made of age hardening. The speaker had, wrote the authors, been drawing on his experience in the aircraft industry, where Al-Cu-Mg alloys were widely used. In tanks, only Al-Mg alloys had been used hitherto. They did not age harden at room temperature, and certainly not at sub-zero temperatures.

On the question of the expansion of free-standing tanks, one method of permitting free expansion had been to anchor the tanks to cruciform attachments at the top and bottom; thus the tank could contract about its centre. In fact, when it was contracting, the weight of liquid on the base was small, so differential movement could be accommodated by sliding. Before the tank was full, the base contraction had already ceased and there was no further movement.

Regarding Mr. Miller's comments, the authors wrote that there was an ISO range of containers of 8 ft^2 cross-section, and of lengths 20, 30 or 40 ft. There was also a range specially designed for container ships and having end frames to make them suitable for this purpose.

TANK COATINGS FOR CHEMICAL CARGOES

J. Rogers M.A., M.Sc. Tech.*

Increased ocean transport of bulk chemicals has led to increasing demands for chemically resistant tank linings to prevent contamination or deterioration of the cargo and to reduce corrosion. At the same time such linings contribute to improved safety and lower costs resulting from easier tank cleaning and inspection.

Satisfactory performance of these linings depends not only on the correct selection of lining for any particular cargo—there is, as yet, no "universal" lining—but also on correct formulation and application. The latter includes suitable blast cleaning of the metal surface prior to applying properly prepared coating material and subsequently ensuring that the lining is fully cured to give the required mechanical and chemically resistant properties.

The main types of lining in current use are described, together with some recent developments in this field. Some indication is also given as to the suitability of these types of linings for certain cargoes, but emphasis is laid on the fact that in many cases factors other than a knowledge of the type of coating and intended cargo will determine whether any particular lined tank is acceptable for any given cargo.

Mr. Rogers

INTRODUCTION

During the past 10 to 15 years, the internal lining of ships' cargo and ballast tanks has become commonplace. In crude oil and refined oil tanks that may be used for ballast, various coatings are now acknowledged to be an effective means of reducing wastage of steel by corrosion, thereby increasing the working life of the ships. This has gained official recognition by classification authorities such as Lloyds and The American Bureau of Ships, reduced scantlings being permitted when suitable approved coating systems are adopted. This has led to increased payloads and other economic advantages.

However, an interesting point regarding cargo tank lining was made in The Nautical Magazine(1) of 1886 in an article describing the building on the Tyne of what was probably the first-ever craft for carrying petroleum products in bulk. "It also was suggested that, in order to prevent discoloration of the refined oil, the interior of the compartment intended to carry it should be coated with patent enamel". This early proposal to use a lining to prevent contamination of a cargo rather than to prevent structural deterioration by corrosion is particularly interesting in that it is very much in line with the main purpose of tank lining in today's bulk liquid chemical carriers.

In chemical tankers, cargo tanks are not generally used for salt water ballast, nor are coatings relied upon to contain products which are highly corrosive to steel, such as mineral acids. While some coatings do possess adequate chemical resistance, it would, in practice, be impossible to guarantee 100 per cent coverage of the steel by the relatively thin paint-type coatings in current use. Even in the unlikely event of a freshly applied coating being perfect, undetected mechanical damage to the coating during service could permit dangerous chemical/steel contact. For the carriage of such corrosive products, other methods of containment are necessary, e.g. stainless steel construction, stainless steel lining or heavy duty rubber sheet linings. These methods are of necessity applied by a few specialist concerns and in view of their cost are used to a limited extent only in service where complete product isolation is essential.

Some shore-based tanks have been rendered suitable for storing such corrosive chemicals by lining them with thick epoxy or polyester resins reinforced with glass fibre or glass flake. This method does not, however, appear to be used in ships' tanks, probably because of the greater difficulty—even with these thick films—of achieving and maintaining a complete barrier.

Prevention of cargo contamination is generally a more important function of the coating in chemical carriers, and because of operating conditions, structural deterioration by corrosion is unlikely to be as serious as in an oil tanker where the tankage alternates between refined oil and sea water.

In general, composition specifications for chemical products are very much more stringent than for oil products and the maximum permitted contamination is generally limited to a few parts per million.

Most oil products do not consist of a single component but a blend of different hydrocarbons giving an end-product with the required properties, and some slight degree of mixing of different grades during transport and storage of similar products may be tolerated, provided the final product is still within performance specifications. In the case of chemical products, however, which, more often than not, consist of a single pure chemical, it is essential to ensure that there is no mixing of traces of one chemical with another. In this connexion, the ease with which lined tanks may be cleaned free of a previously carried cargo is of considerable importance. An unlined tank which has become rusty or pitted absorbs and retains chemicals to a much greater extent than the smooth surface associated with a coated tank. Cargo residues are removed only with some difficulty from such rusty sur-

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* Corrosion Adviser, Shell International Petroleum Co. Ltd.

faces and this can lead not only to contamination of one product by another but can also give rise to explosion and toxicity hazards if the cleaning and gas freeing processes are inadequate.

Fresh water is frequently used in tank cleaning operations and it is found in practice that the reduced quantity of fresh water as well as time required for cleaning lined as opposed to unlined tanks results in significantly lower costs.(2)

Many chemicals are sensitive to iron pick-up, either from rust or from the steel tank itself. This is not only a question of contamination of cargo by rust particles—such contamination in, for example, hydrocarbon solvents, can generally be removed merely by allowing any rust particles to settle in the receiving tank after discharge. With many chemical cargoes, however, rust particles or contact with steel (rusty or otherwise) may catalyse chemical deterioration of the product, e.g. polymerization of some plastics raw materials, decomposition of chlorinated hydrocarbons, etc. While such chemical change is sometimes controlled by the use of inhibitors, a chemically resistant coating forming a barrier between product and tank surface is often an additional necessity in order to maintain product quality.

Most coatings used in chemical cargo tanks provide a white or light coloured finish and this greatly facilitates inspection of the tank whenever necessary.

Summarizing, therefore, the main purposes of lining bulk chemical carriers are to prevent cargo deterioration or contamination by rust, iron or previously carried cargo, and to a less extent to prevent structural deterioration due to corrosion. Other advantages arising from tank lining include improved operational safety in respect of flammable and toxic cargoes, as well as reduced costs, by facilitating tank cleaning, gas freeing and inspection.

SURFACE PRE-TREATMENT AND COATING APPLICATION

Before discussing in greater detail the main types of coating in use, some remarks on the application of tank coatings in general might be appropriate. It is not proposed to give a detailed description of the application processes for each type of coating but rather to point out some of the salient points relating to all of them.

Firstly, good pre-treatment of the metal before coating is essential. All sharp edges and welds must be ground to a smooth finish and all traces of rust, millscale, dirt, etc., removed. Nothing short of blast-cleaning of the steel surface is acceptable if the long term potential of the coating is to be realized. Quality of blast-cleaning can and does vary widely depending on types and particle size of abrasives, air pressure, distance and angle of nozzle from the surface, speed of blasting, etc. and, perhaps even more, on the standard of supervision. Standards of blast-cleaning are described in the various specifications laid down by different authorities, e.g. British Standards Institution,(3) Steel Structures Painting Council (U.S.A.),(4) and perhaps the best known photographic standard SIS 055 900 issued by the Swedish Standards Association.(5) Size of abrasive is particularly important since if this is too coarse, a very rough surface is produced with many "peaks" and "valleys". With such rough surfaces the peaks frequently protrude through the applied coating providing starting points for subsequent film breakdown—see Fig. 1. Obviously, film thickness of any coating is very important and application should be in accordance with the manufacturers' instructions to give the specified thickness, although if the blast pattern or "profile" is coarse, a thicker lining consisting of more coats may be necessary to provide adequate coverage of the peaks. Used abrasive particles must also be carefully removed from the tank before painting, generally by brushing followed by vacuum cleaning. Particles of abrasive embedded in the coating greatly detract from its durability and general performance.

8 BS mesh (2mm) grit—maximum profile amplitude about 250 microns (0·010 in)—metal peaks penetrating paint film

22 BS mesh (0·7mm) grit—maximum profile amplitude about 100 microns (0·004 in)—metal peaks adequately covered by paint film

FIG. 1—*Surface profile and paint coverage*

The effect of abrasive particle size and other factors on the speed and quality of blast-cleaning, together with field test methods for controlling this quality and cleanliness has been described in greater detail by Singleton and Wilson.(6) Although their paper deals largely with the blast-cleaning of ships' hulls externally, much of the data applies equally well to internal tank lining.

Coating conditions in ships' tanks are, of course, never ideal and generally far from it. The geometrical configuration of the tanks and scaffolding frequently forces blast-cleaning and spraying operators to work in awkward positions calling for extra care in achieving adequate coverage of edges and rough welds as well as overhead and recessed areas. In this respect, conditions are more difficult than exist in shore-based tanks. In addition, lighting may be poor, and temperature and humidity difficult if not impossible to control. Condensation of moisture on surfaces, which readily occurs when the temperature of the steel is below ambient under humid dockyard conditions is particularly troublesome and dehumidification equipment is generally necessary.

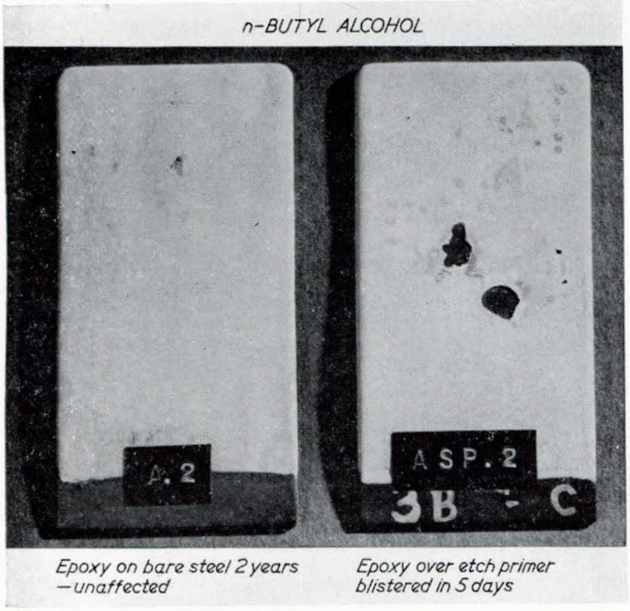
Obviously under such difficult application conditions tank lining is an operation requiring well trained and well equipped personnel, working under conscientious supervision and inspection.

In the case of new tankers, these applicational problems can be overcome to some extent by applying the lining during the construction period, although even so, blast-cleaning (e.g. of welds) and coating application can only be completed inside the tank after construction work has finished.

Many of the coatings used are so called "two-pack" coatings which cure or harden by chemical interaction of two components. These two components must be thoroughly mixed in the correct proportion before use, and after mixing must be used within the specified "pot life" laid down by the manufacturers. To avoid errors in mixing ratios, the two components are normally supplied in appropriately sized containers. Some of the more recently developed two component coatings are now applied by special mixing spray-guns, in which the two components are metered separately in the correct proportions into the gun and mixing takes place within the spray-gun head during application.

During and after application of the two-pack coatings, good ventilation is necessary to remove solvents in the paint film. Apart from very important safety considerations and possible effects on the health of the operators, failure to remove solvents from the film will delay and may even prevent full curing. Ample time must be allowed for the coatings to develop their full chemical resistance and this process can be accelerated by blowing warm air through the tank. In general, once the solvents have evaporated, the more heat supplied the better since higher temperature improves chemical resistance by increasing the degree of chemical cross-linking between the components.

Coatings are normally applied against a specification and it will be appreciated from the foregoing that good inspection to ensure that the specification is followed is most important, the inspector making use of various instruments such as wet/



Epoxy on bare steel 2 years —unaffected

Epoxy over etch primer blistered in 5 days

FIG. 2—*Effect of vinyl etch primer on resistance of epoxy lining to n.butyl alcohol*

dry bulb thermometers for relative humidity determination, film thickness meters for both wet and dry paint, "pinhole" detectors, etc.

One of the problems associated with applying epoxy and similar linings, especially in larger tanks, is that blast-cleaning is a relatively slow process and to avoid re-rusting of the surface it is common practice to apply a quick drying "holding primer" to protect freshly blast-cleaned steel while blast-cleaning continues until the whole tank is ready for lining. It is most important to use a "holding primer" which is compatible with, and equal in chemical resistance, to that of the lining as a whole. One of the most commonly used holding primers is a vinyl butyral etch primer or wash primer. Unfortunately, this has poor resistance to many solvents, especially alcohols and aromatic hydrocarbons, and epoxy and polyurethane linings applied over this type of primer will soon fail in contact with such solvents due to migration of the solvent through the top coats to the solvent-sensitive priming coat. This is illustrated in Figs 2 and 3. The mechanically damaged areas on these panels were caused after removal from the test liquids, in checking film adhesion. A two-pack epoxy primer with relatively high pigment loading and suitably blended thinners provides the necessary chemical resistance as well as protective and quick-drying properties.

TYPES OF LININGS

What are the requirements of a good lining?

Essentially the coating must be unaffected by the cargo and must equally cause no contamination of the cargo. Ideally, this should apply to any cargo carried. Unfortunately there is, as yet, no such "universal" tank lining, but obviously the more versatile the lining the better.

It must show good adhesion, flexibility and impact resistance to withstand the working of the ship and possible mechanical maltreatment.

To some extent it must withstand exposure to marine atmosphere, although this is probably less of a problem than its resistance to repeated cleaning, which may include hot water jets and/or steaming.

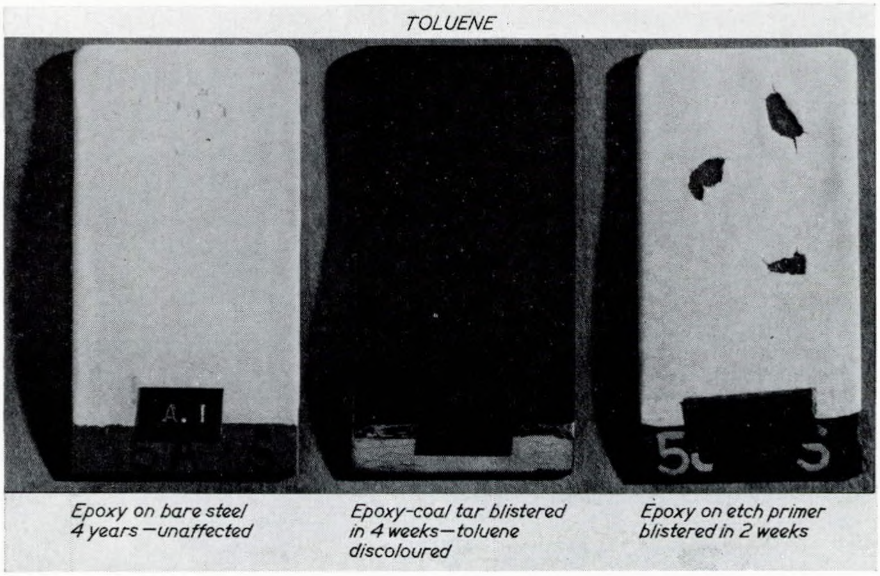
Ease of application and tolerance to poor application conditions are also very desirable characteristics in coatings.

Cost is, as always, a consideration but in view of the high potential cost of a lining failure, technical suitability and reliability will generally far outweigh lining cost considerations.

The three main groups of tank linings currently in use in bulk chemical carriers are the zinc silicates, epoxies and polyurethanes and it is proposed to outline briefly the chemical nature of these.

Zinc Silicates

Fundamentally, these coatings consist of zinc powder and silicate solution requiring to be mixed by the applicator before application. Various silicate solutions are used by different manufacturers, including water-based sodium or potassium silicate, or ethyl silicate in alcoholic solution. Curing or hardening of the coating takes place by hydrolysis of the soluble silicate followed by interaction with the zinc to form an insoluble zinc/zinc silicate complex. The hydrolysis may be brought about by spraying the applied coating with an acidic solution—generally known as "post-curing",



Epoxy on bare steel 4 years —unaffected

Epoxy-coal tar blistered in 4 weeks—toluene discoloured

Epoxy on etch primer blistered in 2 weeks

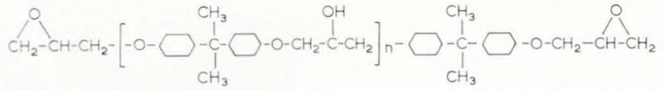
FIG. 3—*Effect of vinyl etch primer on resistance of epoxy lining to toluene*

or, especially in the case of the ethyl silicate, by relying on hydrolysis caused by naturally occurring atmospheric moisture —i.e. "self-curing". Although the physical properties of these different zinc silicate coatings may differ, e.g. in their resistance to mechanical damage, their chemical nature and therefore their resistance to chemical products is very similar. These coatings are normally applied as a single coat of about 75 microns to a blast-cleaned surface. Zinc silicate coatings are sensitive to quality of surface preparation, and blast-cleaning to a white metal finish (Swedish Standard SA3) is necessary.

Epoxy Coatings

Although many different epoxy resin formulations are available for coating applications, those used for chemically resistant tank linings are invariably of the two-component, catalysed type.

The uncured epoxy resin, shown diagrammatically as follows:



where n has a value between 0 and 3, is thermoplastic, but is cross-linked or cured to a chemically resistant, thermosetting film by means of a curing agent, interaction taking place between the amino groups of the latter and the epoxy and/or hydroxy groups in the resin.

In the early days of epoxy resin-based coatings, polyamines, such as diethylene triamine,

$$H_2N—CH_2CH_2—\overset{H}{N}—CH_2—CH_2NH_2$$

were the most commonly used curing agents.

This type of amine-cured epoxy still remains one of the most chemically resistant coatings curing at ambient temperatures, although in practice the polyamine curing agent has been largely replaced by an amine-adduct, i.e. a polyamine which is partially reacted with epoxy resin, the adduct curing agent being less volatile and possessing a number of applicational advantages. The cured film is, however, very similar chemically in both cases and both are usually referred to as amine-cured epoxies. Subsequently, polyamide resins, in which polyamines are combined with long chain dibasic acids, were introduced as curing agents. These also have some applicational advantages, as well as some claims towards better moisture resistance and flexibility, but since they do not possess such good all round chemical resistance as the amine-cured types, they are not normally used in chemical bulk carriers and will not therefore be considered further in this paper.

Once the two components have been mixed, chemical reaction takes place between them and the coating must then be applied within the usable "pot life". Most of the epoxy coatings so far used in lining chemical tanks have been based on solutions of solid epoxy resins, the presence of organic solvents providing a suitable spraying consistency and at the same time retarding the reaction in the mixed paint to give an adequately long pot life of up to one working day or even longer. Because of the presence of thinners in the paint it is necessary to apply the lining in a number of thin coats in order to ensure that the solvents evaporate and are not trapped in the dried film. Solvent retention in the film is known to affect chemical resistance adversely and may cause "tainting" of potable liquid cargoes—e.g. wines. Solventless epoxy linings which cure in thicker layers would obviously be of special interest in the chemical transport and storage field. In the absence of solvents, however, the pot life of suitable liquid, low molecular weight epoxy resins, when mixed with the curing agent, is so short and viscosities of many combinations so high, that application by conventional methods is impracticable. The obvious advantages of solventless epoxy coatings in chemical tank lining has, however, led to the important development in recent years of spray equipment suitable for the application of truly solventless epoxy coatings. The essential points of this equipment are its ability to heat the two components of the paint, to meter them accurately in the correct proportions, to mix them positively and to atomize the mixed paint adequately at the spray gun orifice. Heating of the two components not only lowers the viscosity, facilitating mixing and spraying but also accelerates the cure of the coating. Being solventless, the curing of the coating is, in any event, rapid and this in itself is an added advantage.

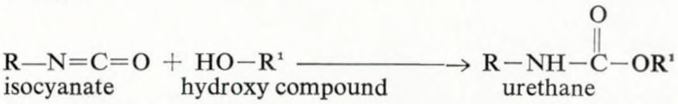
The rate of application with this equipment can be as high as one gallon per minute, giving a single coat system of approximately 8 to 12 mils (200–300 microns) thickness.

As indicated earlier, epoxy linings should be applied only to blast-cleaned surfaces. They are a little more tolerant than the zinc silicates to surface preparation and an SA 2·5 standard is normally adequate.

Before leaving the subject of epoxy coatings one should briefly mention the coal tar modified epoxy coatings which are widely used in crude oil carriers. While these coatings possess very good resistance to most aqueous chemicals, their solvent resistance is inadequate for many refined organic chemicals and would normally cause unacceptable contamination of such cargoes. They are rarely used therefore, in chemical carriers except in a few special cases.

Polyurethane Coatings

The urethane reaction leading to the development of polyurethane coatings may be shown in its simplest form as follows:



$$\underset{\text{isocyanate}}{R—N{=}C{=}O} + \underset{\text{hydroxy compound}}{HO—R^1} \longrightarrow \underset{\text{urethane}}{R—NH—\overset{\overset{O}{\|}}{C}—OR^1}$$

Chemically resistant polyurethane coatings are formed when polyisocyanates react with polyhydroxy compounds (polyols) to form cross-linked, long chain molecular structures. As with epoxy linings these coating materials are generally supplied as two separate components, a polyisocyanate component in one container and a pigmented polyol in the other, the two components being well mixed just prior to use. After mixing, the urethane chemical reaction takes place resulting in the formation of the hard, chemically resistant film.

This type of polyurethane should not be confused with the single pack polyurethane decorative paints. These are essentially conventional alkyd based paints in which a proportion of diisocyanate has been incorporated into the resin during manufacture, and the paint still dries by atmospheric oxidation. Although these modified alkyds show some improvements over unmodified alkyds in chemical resistance, hardness and abrasion resistance, their chemical resistance is still very much below that required for tank linings.

Single pack, moisture cured polyurethane systems which cure by absorbing moisture from the atmosphere are also available and these consist of polyol/isocyanate adducts which have terminal isocyanate groups. Curing involves reaction of these terminal isocyanate groups with moisture absorbed from the atmosphere. While these coatings possess good chemical resistance, they are generally only available as unpigmented varnishes because of storage stability problems when moisture cured polyurethanes contain pigments unless the latter are specially dried.

Polyurethane tank linings, for which pigmented systems are preferred are therefore invariably of the two component polyol/isocyanate type.

CHOICE OF COATING

Before assessing the suitability of available coatings for various chemicals, a number of assumptions, emphasizing the responsibility of all concerned with the manufacture and application of chemically resistant coatings, must be made.

Firstly it must be assumed that the coatings under con-

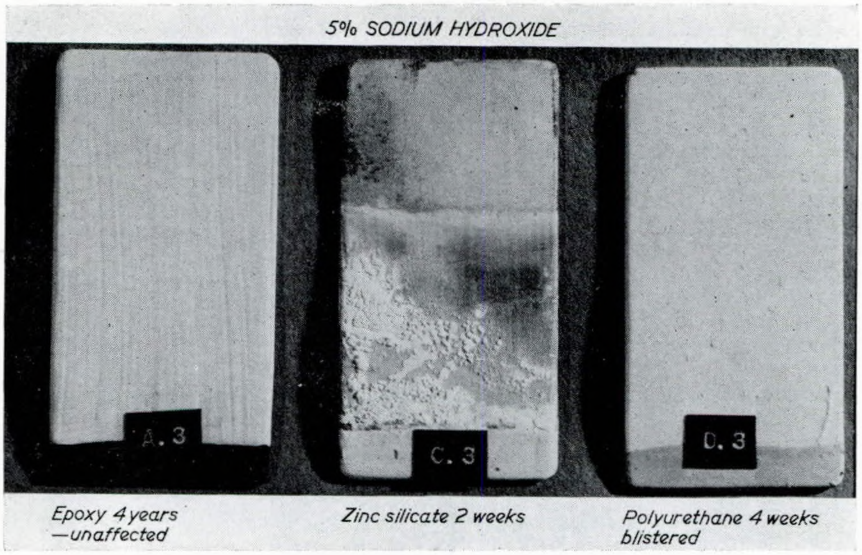


FIG. 4—*Resistance of linings to caustic soda*

sideration are formulated and manufactured to give optimum performance obtainable with that particular type.

Secondly, it must be assumed that application, including surface pre-treatment and subsequent curing of the coating, is correctly carried out.

Obviously, any shortcoming on the part of either paint manufacturer or applicator can render the selected lining completely unsuitable for the purpose envisaged and to avoid any evasion of responsibility by either, the adoption of a good overall inspection system is advisable. Some shipowners do in fact lay down specifications for both coating material and its application, and arrange for a full inspection service to control all aspects of the coating system, using either their own inspection personnel or an independent inspection organization.

Some paint companies manufacturing specialist linings undertake to supervize application to ensure that lining is carried out correctly. This practice is, however, not infallible since a paint supplier may, on occasion, be reluctant to take the strong line necessary to ensure good application with the painting contractor who may at the same time be his customer. Other paint manufacturers have subsidiary coating contracting companies within their own group and such groups are frequently prepared to undertake and guarantee the lining project on a 'supply and apply' basis.

Assuming available coatings are correctly formulated, manufactured and applied, selection may be based to some extent on a theoretical consideration of the chemical nature of the coating and cargo, and this coupled with experience will in many cases give a clear cut indication. Frequently, however, laboratory immersion tests are necessary and although not infallible, such tests are the next best thing to actual practical experience. Such laboratory tests must of course examine any deleterious effect on the cargo by the coating as well as *vice versa*.

On occasion, the suggestion has been put forward that it should be possible to assign to chemical cargoes a 'degree of aggressiveness' towards coatings in general. This is, of course, out of the question since a chemical which is highly destructive towards one type of coating may be completely harmless

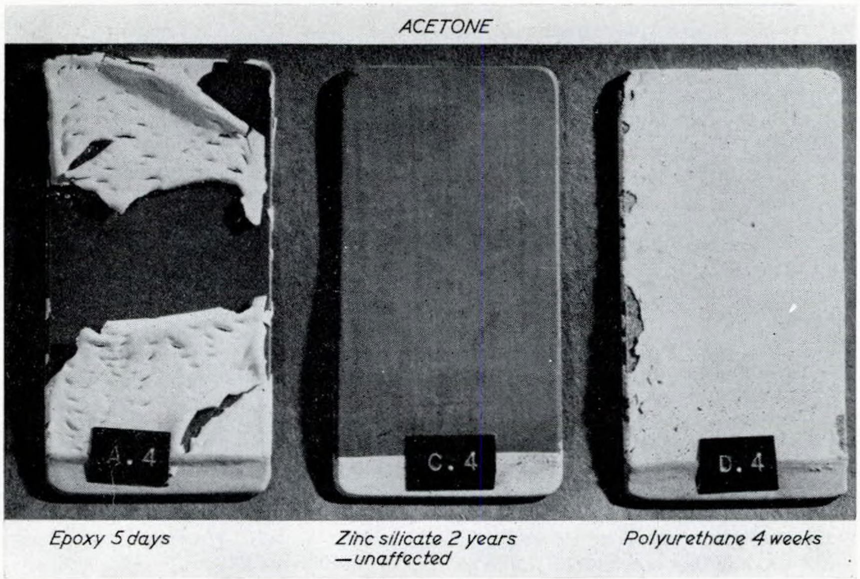


FIG. 5—*Resistance of linings to acetone*

to another, e.g. strong alkalis which immediately destroy zinc silicate coatings have no effect on epoxy linings, while acetone will soften and ultimately strip epoxies and polyurethanes but have no effect on zinc silicates. This is illustrated in Figs 4 and 5.

Fig. 5 illustrates also another aspect. All the coatings shown are commercially available materials and while neither epoxy nor polyurethane coatings would be recommended for acetone storage, the epoxy in this particular test showed rather lower acetone resistance than expected. Under the laboratory conditions of this test it is unlikely that this is due to application or inadequate curing, but is more probably due to formulation detail. Although the basic formulation for all these linings and their general properties are well established, minor modifications are frequently made to improve specific properties—perhaps resistance to a specific chemical. This can, however, have at the same time an adverse affect on other properties—perhaps resistance to other chemicals. Thus, addition of phenolic resin to epoxy linings will frequently improve acid resistance at the expense of alkali resistance. Again, increasing the proportion of amine curing agent in epoxy linings will increase their resistance to organic solvents at the expense of water resistance and *vice versa*. When therefore, consideration is being given to the carriage of a chemical where the lining resistance is border-line or doubtful, the technical department of the lining manufacturer is generally the best source of guidance.

Choice of lining for any particular ship will therefore depend on product or products to be carried and for general purpose multi-product carriers it is becoming normal to coat a number of tanks within one ship with different linings.

In Table I an attempt has been made to indicate compatibility of types of coatings with various chemical groups of products. However, this table serves less to indicate which coatings are suitable for which cargoes, than to emphasize the doubts existing regarding suitability of coatings for many products, since within each chemical group there are exceptions, especially in their effect on epoxies and polyurethanes. This coupled with lack of essential knowledge regarding application in any particular case makes it impossible to give anything other than a rough indication.

One of the main difficulties is that with most groups of organic chemicals, e.g. alcohols, ketones, esters, etc., individual chemicals differ in their effect on coatings, the lower members (i.e. lower molecular weight) generally being more aggressive than the higher homologues. Thus epoxy and polyurethane linings do not possess long term resistance to acetone and methyl ethyl ketone (lower ketones) or methyl acetate (a lower ester) but are satisfactory for higher homologues such as di-isobutyl ketone and dibutyl phthalate.

This largely explains the large number of ‡ indications in the table and emphasizes the need to consider each case on its merits.

CARE AND MAINTENANCE OF COATINGS

One of the main advantages of lined tanks is as mentioned earlier, the ease of cleaning, and frequently water washing is sufficient. However, detergent solutions and steaming may also be used without adversely affecting the coating. If, however, steaming is considered necessary, e.g. to remove toxic or other residues, this should not be continued longer than necessary and care should be taken to avoid direct impingement of steam jets on to the coating, since this can cause blistering of the coating. Steaming should not of course be commenced until explosimeter tests show the tank to be 'gas-free'. In the case of zinc silicate coatings any detergents used should be essentially neutral since alkalis readily attack zinc.

The most serious damage to coatings occurs of course in the event of an unsuitable combination of product and coating. In such cases, the damaged coating is generally irreparable and complete stripping by blast cleaning followed by recoating as from new is the only solution. Particular care

TABLE I—CHEMICAL RESISTANCE OF COATINGS

Type of Product	Amine cured	Polyamide cured	Coal tar	Poly-urethane	Zinc silicate
Aliphatic hydrocarbons	†	†	† a)	†	†
Aromatic hydrocarbons	†	‡	*	†	†
Alcohols	†	‡	*	†	†
Alkalis	†	‡	‡	*	*
Acids, inorganic	*	*	*	*	*
Acids, organic	‡	*	*	‡	*
Acids, fatty ex vegetable, animal oils	‡	‡	*	†	*
Vegetable oils	†	*	*	†	† b)
Animal/fish oils	†	†	*	†	† b)
Esters	‡	*	*	‡	†
Ketones	‡	*	*	‡	†
Chlorinated hydrocarbons	‡	*	*	‡	† c)
Phenols	*	*	*	*	† d)
Aldehydes	*	*	*	*	*
Glycols	†	†	*	†	†
Glycol ethers	*	*	*	*	†
Rubber latex	†	†	†	†	*
Molasses	†	†	*	†	†
Wine	† e)	*	*	† e)	

† Should be suitable if properly formulated and applied.
* Unsuitable.
‡ Varies depending on product position in homologous series or on concentration.
a) Product may be discoloured.
b) Zinc silicate satisfactory if free fatty acid content less than 2 per cent.
c) Zinc silicate satisfactory if acid-free, but free acid may develop in product if moisture present. Therefore limit duration of contact.
d) Product may be discoloured by zinc silicate coatings.
e) Special formulations, including solventless epoxy, to eliminate risk of taint.

Zinc silicate coatings are recommended for most neutral organic liquids. They are not recommended for any product containing acids or alkalis or for products which develop acidity or alkalinity on storage or through contact with moisture.

must be taken to ensure that all the damaged lining is removed (especially around stringers, stiffeners, flanges, etc.) since chemically damaged paint forms a very poor base for re-coating.

Care should be taken to avoid mechanical damage of the coating during inspection, cleaning, etc. Such mechanical damage is, of course, generally very localized and since it represents a small proportion of the whole, it is unlikely to have a serious effect from the contamination point of view. However, such damage should be repaired as soon as convenient since it is a defect from which more general coating deterioration can develop. Regarding the mechanically damaged coatings, repair of the damaged areas only is considered preferable to over coating the whole tank. If the bulk of the coating is still sound, there is little to be gained by overcoating the whole, and apart from the cost, there is a distinct risk of adhesion failure of the new layers. Damaged areas can best be repaired by blast-cleaning using a small Vacublast or similar machine, carrying the pre-treatment for some distance, (say 6 in) beyond the bare area. This can then be coated using the original type of lining. Curing of the repair patches is frequently accelerated by the use of small infra red heaters.

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Discussion

Mr. R. Crawley, M.I.Mar.E., thought that reliability and economics were prime factors in the selection of coating materials. Reduction in the cost of materials, and perhaps a limiting of the use of special materials, had to be considered. Mr. Crawley had seen mention in the past of the possibility of combination systems whereby the special, and the almost inevitably more expensive material was used only for those parts of the tank or system that were in contact with the chemical during storage. There were problems of course, such as the contamination from condensed vapours, but he would be interested to hear if the author had any knowledge of such combination systems or any similar developments in this area.

Mr. Crawley went on to say that throughout the paper Mr. Rogers had, quite rightly in his opinion, placed great emphasis on the need for care in the application of coatings, and reference had been made, both in his paper and in earlier ones, to the use of specialist contractors for this function. There was no doubt that no matter how good a coating, it would not give satisfactory service unless correctly applied.

Although he was perhaps moving away from materials as such, to the area of control and supervision, Mr. Crawley felt that these were aspects that had to be considered in coating development. He suggested that the conditions mentioned by Mr. Rogers in his paper (such as poor lighting, uncontrolled temperature/humidity) as well as inexperienced or careless operators, would inevitably be problems. For this reason he suggested that any developments that would facilitate the more efficient application of a coating and make it less sensitive to environmental conditions during application would lead to appreciable dividends in the future.

A further consideration was the maintenance requirement. The slides had shown a number of test plates which had been exposed to chemicals over various lengths of time. Could the author give an indication of the life expectancy, under operating conditions, of the paint systems he described, assuming of course, that they were correctly selected for their function and initially applied satisfactorily?

The trend these days was to smaller crews onboard ship, and hence the ability of the crew to perform maintenance was more limited than in the past, and there was also a constant attempt to extend the periods between service. Hence the shipowner was always seeking for as long a life for his tank coatings as possible.

Training a ship's crew in the requirements of chemical cargoes and the hazards involved, was mentioned in the paper, but said Mr. Crawley, as well as the careful initial selection of personnel, the shipowner was also faced with the problem of a continually changing crew. The Chamber of Shipping was well aware of this problem, and was producing a code of practice for the safe carriage of liquid chemicals in bulk. This was intended for the master and his officers and included reference to tank coatings. Although there was not much the officers could do about the tank coatings, nevertheless it was essential that they were aware of the limitations of coatings.

Mr. J. A. F. Crook, M.I.Mar.E., although repeating previous comments, felt it necessary to applaud the fact that Mr. Rogers, quite rightly, had emphasized the need for high quality surface preparation. In general, use was made of Swedish standards in coating specifications, but Mr. Crook felt there was some need for a means of simply determining surface finish. It was not enough to have a colour or a visual means of determining coating surface.

There was also a need for some further research into blasting of various types, both with disposable and recycling abrasives in order to obtain an optimum surface. He suspected that a surface was a combination of types of peak and depth of peak, not necessarily one standard peak formation.

Mr. Rogers had also stated that if the profile was incorrect an increase in film thickness might be prudent. Mr. Crook suggested that it was then too late; the specification had been written, the contract signed, and probably even paid for. It was a little late in the day to start getting involved in what, in fact, was an extra to contract, an embarrassment to everybody concerned.

Again, Mr. Rogers had quite rightly mentioned conditions in a shipyard which were not always easy and Mr. Crook accepted his comments in full. There was certainly a need for planning, good liaison between the parties concerned, and full circulation of the standards required to all levels of management and, above all, there had to be a realistic programme.

The last paragraph of the paper contained much of import. Mr. Crook said he had done a fair amount of work over the last year to try and prevent a high incidence of repair work with tank coatings, and he felt that this was what Mr. Rogers was getting at. Mr. Crook added that his company had found that on one ship of 25 000 ton capacity, with 37 tanks, £4000 was saved by removing shipyard-type traditional staging and replacing it, having erected the ship, with sub-contracted tubular staging built off the bottom.

Mr. E. D. Dolan said that Mr. Rogers had mentioned the need to have a solvent-free coating, which was facilitated by blowing warm air through the paint film; then Mr. Rogers had said it was an advantage to keep the warm air flowing to get the fullest possible cure in the epoxy system. Mr. Dolan said he would be a bit cautious about the length of heating time. He would agree that extended curing at a higher temperature increased the corrosion and the solvent resistence of the coating, but some types did tend to become rather too brittle; in other words, more solvent resistance was attained than was really necessary and tolerance was sacrificed.

Surface preparation in general was fairly well under control in shipyards; if it was put through a breaking machine, then provided the inspection was good enough to ensure SA 2½, and the profile was not too rough there were no really great worries regarding the bulk of the area; but welds were quite a different proposition. Welds were made during erection; and, particularly if they were made with low hydrogen electrodes, their surface was contaminated with weld slag, weld spatter and weld fume, which could be highly alkaline. Also the profile of the welds could sometimes be very rough, and if a breakdown occurred it was most commonly found first on the welds. Mr. Rogers had justifiably said that he was having success with a vacuum-based preparation of welds, but this was a very awkward method for a big tank. Would he comment on other possibilities of preparing welds?

Mr. H. J. Miller, B.Sc., M.I.Mar.E., thought that this was a most excellent paper as it was a subject on which everybody could say something. Everyone had had problems in a shipyard, if not with chemical tankers then certainly with other types of ship, and this paper was of interest because it was full of practical experience.

Mr. Miller was worried to see new things coming in which he did not really know how to control. In the text and illustrated on the screen was a new type of spray gun with which to mix and apply a coating. Perhaps Mr. Rogers could advise on the reliability aspect of this new spray gun.

Mr. Miller was rather surprised when Mr. Rogers was talking about the compatibility of holding primers with the lining as a whole. His paper seemed to suggest that if one was not careful one would get the wrong holding primer to suit the final coat—one would like to feel that this could never happen. Mr. Miller did wonder, however, why this came up at all. Was Mr. Rogers investigating different holding primers to see why they were not compatible with the final coat? This seemed an odd line of approach. Obviously when one considered a final coat one would also consider the compatibility with the holding coat, and the time schedule of the painting sequence, and take advice as necessary.

Mr. Rogers had said: "Some shipowners do in fact lay down specifications for both coating material and its application, and arrange for a full inspection service to control all aspects of the coating system, using either their own inspection personnel or an independent inspection organization." Of course, as a shipowner's technical representative, one would expect him to have considered this fully, but Mr. Miller was surprised that Mr. Rogers did not mention anything about the guarantee, because it was nice to know that one had a coating which was guaranteed for say two years. What usually happened was that the paint manufacturer said: "This product will last for fifteen years." One would answer: "Fine. I do not ask you for a guarantee for fifteen years; just give me a guarantee for ten," to which he would reply: "No, the guarantee is for one year." One could not have much confidence in the product on that basis. If there were a reasonable guarantee then one would not need to throw the onus of inspection on to the shipowner.

Mr. Miller concluded by asking Mr. Rogers to say something about repairs to various coatings. One of the big problems when running a fleet was that one could specify the most expensive coatings and check that these expensive coatings were applied; but even then trouble could occur in service. The real point was, what could be done about it? Perhaps Mr. Rogers could mention some of his experiences with this problem?

Mr. R. K. Roberts, M.I.Mar.E., said that Mr. Rogers seemed to imply that because a primer was not as resistant to the cargo as the final coat one would never achieve as good a finish, or as good protection using a primer as one would, simply using the final coat on the base metal and that therefore there was no such thing as an ideal etch primer. Was this in fact the substance of Mr. Roger's comments?

The diagrams that showed the examples of ineffective coatings and effective coatings illustrated that with sodium hydroxide the epoxy was unaffected after four years. Mr. Roberts presumed that the test plate was on base metal without a primer. Would the author be so optimistic about a four year result with etch primer underneath?

Mr. O. M. Clemmetsen said that although the author stated that chemical tanker cargo tanks were not generally used for salt water ballast, there were many ordinary single skin tankers operating today with coated tanks carrying the less dangerous type of cargoes where it was essential for the cargo tanks to be utilized for ballast. It was only possible to avoid the use of cargo tanks for ballast when a tanker was built with a double bottom and/or side coffer-dams. He assumed he was correct in concluding that the presence of salt water alternating with chemicals always imposed more severe conditions on the coating.

There was also reference to the importance of the type of primer which was to be subsequently overcoated, and Mr. Clemmetsen made the point that this could lead to difficulties – a yard used a certain type of shop primer and the manufacturer of the subsequent coating system was expected to give his usual guarantees, although he might not be completely satisfied with the compatibility of his own coatings with the existing primer. In the author's opinion it would appear that to a certain extent all coatings absorbed the product. To what extent was this absorption of product removed by the cleaning operations, and could it be sufficiently serious to affect the quality of subsequent products loaded into the tank, excluding the matter of wine where taint was also involved?

Regarding the surface preparation, it had been noted in the paper that a maximum profile amplitude of 100 microns was normally satisfactory. He understood that this principally referred to epoxy type coatings – what was the position when one came to zinc silicate coatings which were only applied to a total thickness of 75 microns, and were there any particular types of abrasive more suited to zinc silicate?

It was noted that Swedish standard SA3 was suitable for zinc silicates and SA2·5 for epoxies. Presumably the standard of surface preparation would be related by the author to the thickness and number of coats. In cases of reductions in scantlings due to corrosion control in ordinary tankers, Lloyds Register recommended SA3 for coatings with a total dry film thickness of 125 microns or less and SA2½ for coatings of 150 microns or more, and also strongly recommended that not less than three coats be applied where the thickness was 150 microns or less, and not less than two coats where the thickness was 200 microns or more.

As regards testing of coatings, it was customary in the case of oil tankers to have prolonged tests, but this was clearly impracticable when trying out a coating against a large number of products. Would the author care to suggest a minimum test time in chemical products and state whether such a test should be dealt with by alternately immersing the specimen for, say, two weeks and drying it for one week, or whether there was any other standard practice he would recommend?

In Table 1 giving the chemical resistance of various coatings, Mr. Clemmetsen noticed that phenolic coatings had not been mentioned. There were difficulties with the high temperature curing of such coatings, but in modified form they had been applied in small ships, and he would like to hear if the author had any experience of their use.

Mr. W. D. Harris said that Figs 2 and 3 showed tank linings applied over bare steel and etch primer and immersed in lower homologues of alcohol and toluene. Where applied over bare steel, had a two pack epoxy primer with a relatively high pigment loading been applied beforehand? It would be interesting to know what evidence was available to show if an epoxy resin-based, highly pigmented holding primer could be made which had the same level of solvent resistance as the epoxy top coats, i.e. could one be made which was any better in resistance to low molecular weight alcohols and aromatic hydrocarbons than a reinforced etch primer?

Reference was made towards the end of the paper to the limited resistance of epoxy resin tank coatings to lower molecular weight ketones and esters. What was the resistance of these coatings to lower molecular weight aromatic hydrocarbons and alcohols?

Because of the reservations on the suitability of epoxy resin amine-cured coatings to certain cargoes and the fact that to some of these, particularly the solvents, zinc silicate coatings were resistant, would it not be more sensible to use zinc silicate coatings than epoxy coatings for these cargoes?

Correspondence

MR. S. H. FREDERICK wrote that the author referred to the difficulties encountered by operators during both blast cleaning and spraying, due to the geometrical configuration of the tanks and scaffolding. He rightly emphasized the dependence of coating performance on the quality of surface preparation and the need to remove all dust and spent abrasive before spraying was carried out.

The need for careful attention to these factors could not be too often repeated as many coating failures could be attributed to one or other of them.

Where the ship's side formed one wall of the tank, the problem of obtaining SA $2\frac{1}{2}$ standard of blast cleaning in the way of all the frames was a very real one. More thought should be given at the design stage to making the surfaces more suitable for coating.

Would the author detail any experience he has had with regard to tank heating prior to coating. BSRA carried out limited trials with mass air flow heaters supplying warm air through trunking into tanks. These trials showed that it was possible to achieve a significant rise in air temperature with a reduction in humidity and such heaters would appear to be of considerable value when tanks were being coated under adverse ambient conditions.

Author's Reply

Mr. Rogers first answered a point made by Mr. Crawley. This concerned the use of combination coating systems whereby, in order to keep costs to a minimum, the special lining was applied only to those parts of the tank which would be in contact with the cargo, and a different, less expensive coating was applied to the remaining parts. The author was not aware of this being done in chemical carriers. Theoretically, the deck head could be regarded as being under somewhat different conditions than the rest of the cargo tank, but in practice this also, on occasions, came into contact with the cargo itself. In any event, the vapour space above a liquid cargo was frequently as aggressive as the liquid phase. Although Mr. Rogers had not heard of the use of such combination systems in chemical carriers, in oil tankers a lining was often applied to the deck head of otherwise unlined cargo tanks, but this was to reduce corrosion by condensation.

The author agreed with Mr. Crawley that the development of coatings more tolerant to application under poor conditions would be of great value, though he did not feel optimistic of any great progress in this direction with thin film coatings.

As regards life expectancy of coatings, it was difficult to generalize. Mr. Rogers said he had examined many lined tanks, both ship and shore based, and in quite a proportion, examination was called for because of lining failure. He had perhaps seen an unduly high proportion of failures but practically all could be attributed to improper surface preparation or paint application. In general, it could be taken that if the surface preparation was correct, the coating application correct and the use of the lined tank correct (in other words a zinc silicate tank was not filled with caustic soda) then the lining should last many years—something in the order of 10 to 15. So much, however, depended on operating and cleaning conditions. For instance, cold or warm fresh water was generally sufficient to clean coated tanks, and steaming was not necessary. If live steam was played onto the coatings, at least some of them would be damaged.

Mr. Crook had mentioned the use of Swedish standards of coating specifications and argued that a visual standard was not sufficient. Mr. Rogers agreed with him in this, since the photographic standards mentioned did not specify size or type of abrasive to be used, nor did they specify maximum amplitude of profile. On the other hand these photographs were most useful in showing the operator the standard of blast cleaning required but, in addition, it was also necessary to ensure that he was using a suitable abrasive under correct conditions of air pressure, etc. Considerable research had in fact been carried out on types of abrasives and methods of assessing the surface profile, and the paper by Wilson and Singleton[6] provided much useful data on assessing important factors such as freedom from rust and mill scale and maximum amplitude. The simplest, though not infallible, method of controlling profile was to specify the particle size of the abrasive. One of the practical problems in lining was that some contractors used a much coarser grade than they should. Perhaps they felt the job would be done more quickly, whereas in fact, the reverse was true. Furthermore, the coarse grit would not reach and clean the bottom of pits in pitted or rough steel. Ideally, the best results were obtained using relatively fine abrasives containing a range of particle sizes.

Mr. Crook had suggested that it was too late to apply an extra coat to cover the peaks of an excessively rough profile since the contract would have been signed and perhaps the bill already paid. This eventuality would, of course, not arise if the blast cleaning was properly specified and controlled.

Mr. Dolan had expressed concern regarding the prolonged use of warm air to remove solvents and assist curing of a tank lining. It was true that in general, two-pack coatings became less flexible as they lost their solvents and the two components reacted together to give the chemically resistant film; and this hardening continued for a considerable time. However, even when the coating had reached its ultimate hardness or brittleness, its flexibility was still better than some other, still satisfactory, types of coatings, e.g. linings based on heat-cured phenolic resins. Mr. Rogers felt there could be some confusion between brittleness and adhesion. If the adhesion was good, the impact resistance of the coating remained excellent, withstanding considerable deformation of the coated metal. If the adhesion was poor (resulting perhaps from poor surface preparation) then the coating would tend to show loss of adhesion and poor impact resistance as it hardened. Certainly the temperatures likely to be encountered in a tank by blowing warm air through it would not cause undue brittleness, even if prolonged indefinitely.

With regard to surface preparation of welds, blast cleaning after construction followed by the priming and building up of the coating system was by far the best method. The vacuum blasting machines, into which the spent abrasive was sucked back for re-use, although somewhat slow, were very suitable for cleaning narrow strips such as welds. In practice, coatings did tend to break down on welds before they did on other surfaces due to inadequate cleaning of the welds or to the use of films of paint which were too thin.

With zinc epoxy primed steelwork, wire brushing of the weld followed by a further coat of zinc epoxy had been widely used in oil tankers built on the continent. Mr. Rogers was not aware of any failures arising from this practice, but personally he felt that it would be better to lightly blast clean rather than wire brush these surfaces. The argument for wire brushing was that the plates had been grit blasted before welding and apart from some slag formation they were still free from mill scale so that wire brushing cleaned them satisfactorily. But Mr. Rogers thought that blast cleaning would be preferable, at least for chemical cargo tanks.

Mr. Miller expressed concern about the reliability of applying solventless epoxy coatings by means of spraying equipment in which the components were mixed in the spray gun itself. This was a fairly new development and the author had had only limited experience with it, but it was mentioned in the paper because it appeared to be ideally suitable for rapidly lining the relatively large surfaces of ships' tanks, giving a single heavy coating of good chemical resistance. One failure had occurred where spraying continued for a short time after the hardening component tank became empty, resulting in uncatalyzed resin being sprayed onto the tank wall. The author did not, in his limited experience, know of any failure of the equipment as such, but obviously it was fairly sophisticated and needed to be operated and maintained by reasonably skilled and trained personnel.

Mr. Miller also asked how one could be sure of getting the right holding primer. Mr. Rogers felt that most paint manufacturers were familiar with the point made in the paper about the etch type primer's lack of resistance when used under epoxy linings in contact with chemical solvents, and any of them, provided they were aware of what was required, would be able to supply a suitable material. Mr. Harris had mentioned that the highly pigmented epoxy primer might be the answer, and Mr. Rogers thought he was probably right. The main advantage of the etch type primer was that it was quick drying, thus giving a minimum of delay in blast cleaning adjacent surfaces. In general, epoxy primers were slightly slower drying. The zinc rich epoxy primer was widely used, but because of its zinc content it could be suspect in contact with acids or alkalis. Mr. Rogers favoured the highly pigmented red oxide epoxy primers mentioned by Mr. Harris as primers for epoxy coatings in chemical service. In answering Mr. Miller's question regarding the reasons for investigating holding primers, it had to be realized that the lining of chemical cargo tanks was a small and relatively new part of shipyard painting. For many years, steelwork had been blast cleaned and coated with temporary or holding primers which were normally over-coated by conventional paints, subsequently exposed to normal marine conditions. Relatively few types of primers, including the etch primers, had been used for this work and obviously it became necessary to examine their performance as priming coats under the more specialized materials being introduced for lining tanks in chemicals service.

Coming to Mr. Miller's point about guarantees Mr. Rogers said the difficulty was that paint manufacturers felt, quite understandably, that they had insufficient control over the application or subsequent service to give a guarantee. They undoubtedly knew from their own laboratory tests and from practical experience, that their coating or coating system would withstand certain conditions, but if the coatings were not properly applied or were misused after being applied then they would fail. Equally coating contractors had insufficient control over quality or formulation of coating materials to justify giving a guarantee except in conjunction with a paint manufacturer. If a guarantee was given, both paint manufacturer and contractor would perhaps feel that in the event of failure the owner would claim, regardless of whether the coatings had been misused or not, and the loss to the company arising from a successful claim could easily outweigh the profit involved in supplying and applying the coating in the first place.

Lining repairs should not be necessary with normal cargo tank usage, but linings did occasionally suffer mechanical damage and tanks could even be filled accidentally with a product which would partially or completely strip the lining. If a coating was stripped in this way there was no alternative but to grit blast completely and start again, taking particular care to get rid of all the coating residues, since a chemically damaged paint film formed a very poor foundation for subsequent recoating. If small areas were damaged mechanically this was a different matter and patching the damaged parts with a coating of the same type was generally adequate. It would be necessary to grit blast or abraid these patches to white metal before recoating, in order to get the necessary adhesion. There was little point in recoating the whole of the tank because of the presence of small areas of mechanical damage. Apart from the possibility of intercoat adhesion problems, complete over-painting was unnecessary since that part of the coating which had not been damaged would be as good as new.

Mr. Roberts had felt it was implied in the paper that a lining system which included a holding primer could never be as good as when the main coating was applied directly to the bare metal. The point the author wished to make was that the chemical resistance of any system could be reduced by using incompatible or unsuitable primers. If an epoxy coating was applied over a suitable epoxy holding primer, the chemical resistance would be no less than if the coating were applied to bare steel.

Mr. Harris had raised similar queries regarding the preparation of the test panels illustrated, and Mr. Rogers confirmed that no primer had been used under the coatings described as "applied to bare steel". To the author's knowledge there was no evidence to suggest that the use of a properly formulated highly pigmented epoxy primer would result in any lowering of the chemical resistance of the coating system. The epoxy primer would, on the contrary, undoubtedly be superior to the etch primer in resistance to low molecular weight alcohols and aromatic hydrocarbons. As regards the resistance of epoxy coatings to low molecular weight alcohols and aromatic hydrocarbons on the one hand and esters and ketones on the other, the latter groups were considerably more aggressive towards these coatings, and epoxy and polyurethane tank linings could not be recommended for these products. Both types of coating should, however, be suitable for alcohols and aromatics, with the possible exception of methyl alcohol.

Mr. Harris had finally asked if it would not be better to use zinc silicates for these cargoes. If the tank was to carry only solvents of the type mentioned, then undoubtedly zinc silicates would be the obvious choice. If epoxy or polyurethane coatings were applied (and other cargoes to be carried might necessitate this) then it would be a pity to use a holding primer under them which would reduce their solvent resistance and therefore unnecessarily preclude their use in solvents service.

Mr. Clemmetsen had raised the question of absorption of chemical products by coatings and asked if this could give rise to contamination of subsequent cargoes. While such absorption of some solvents undoubtedly did take place as indicated by the effect on etch primers, Mr. Rogers had been unable to obtain any quantitative figures for the extent to which it occurred. It did, however, appear to be very small relative to the tank volume, and normal tank cleaning, carried out between cargoes, removed it. Mr. Rogers had not heard of any contamination arising from this cause.

Mr. Clemmetsen had also raised the question of the relationship between standard of surface preparation and paint film thickness, and mentioned that Lloyds Register recommended SA 3 for coatings of less than 150 microns thickness and SA 2½ for coatings of 200 microns or more. This suggested that the standard of surface preparation required, depended on film thickness of the applied coating. This generalization was somewhat misleading. The difference between SA 2½ or SA 3 ratings was more a question of surface cleanliness and freedom from rust and scale rather than a measure of profile, and the degree of blast cleaning specified should be related to the type of coating to be applied to ensure adequate adhesion of that particular coating rather than to considerations of film thickness per se. Most zinc silicates, for instance, required an SA 3 finish and it was unlikely that in this case the application of an additional film thickness would compensate for poor adhesion arising from the use of a lower standard of surface preparation.

Mr. Clemmetsen had also commented on the relationship between recommended amplitude of surface profile (100 microns) and film thickness (75 microns) of zinc silicate. The explanation was probably that zinc silicate coatings flowed less in the wet state and therefore the metal peaks remained reasonably well covered—in other words the zinc silicate layer tended "to follow the profile" rather than flow from the peaks into the valleys.

As Mr. Clemmetsen had mentioned, it was usual to have prolonged testing of coatings for oil tankers, but the purpose of these coatings was to provide long-term protection against corrosion. In the case of chemical tankers the purpose of the coating was generally to give protection to the product carried for relatively short voyages. In this respect ships' tanks also differed from shore based chemical storage tanks where the product remained in contact with the coatings for very long periods. As regards laboratory testing of coatings for chemical carriers, both continuous and intermittent partial immersion of test panels was normally carried out for a few months at ambient or transportation temperatures. The test procedure was, however, frequently modified to investigate specific operational conditions. In practice, if failure occurred, this usually took place in the first few days of exposure, and therefore testing over a period of a few months was considered adequate. Although accelerated tests were not always reliable, these were sometimes necessary and normally took the form of immersion of test panels in the product, maintained at a higher temperature—usually 45°C. Possible adverse effects of the coating on the product, as well as the effect of product on coating, was, of course, checked in these immersion tests.

Mr. Clemmetsen mentioned the possible use of heat cured phenolic coatings. High temperature stoving phenolics and epoxy modified phenolics, curing at about 200°C were mainly used in small containers such as drums and small tanks which could be transferred bodily to an oven for curing at this temperature. Mr. Rogers did not think these coatings were used to any extent in ships' tanks, since it was virtually impossible to reach the required curing temperature. An example had, however, been reported in the United States for the transport of ethoxylated alcohols. There were phenolic modifications of the two-pack epoxy coatings and although these normally cured at ambient temperatures, some improvement in chemical resistance was achieved by moderate heating. Again, their use so far appeared to be rather limited.

Mr. Rogers fully supported Mr. Frederick in his plea for more thought to be given at the design stage to making ships' tank surfaces more suitable for coating. Not only in this field but in all branches of engineering insufficient thought was given to the ultimate problems of painting and coating when designing steel structures.

Mr. Rogers' own practical experience with heating systems for ships' tanks, he said, was rather limited. Obviously good circulation of warm, dry air was required, and technically a system consisting of electrically heated elements and a fan blowing warm air into the tank would be most suitable. Although the large type being used on a limited scale in the U.K. was, he understood, rather costly to operate, he felt that the improved results could well justify the higher cost. Alternatively, banks of infra-red heaters inside the tank, in conjunction with an electric blower, had been used with success. A low cost system used on shore-based storage tanks at a U.K. refinery consisted of a large electric fan blowing air through the tank manhole over portable, steam heated steel coils—the low cost in this case depending on the readily available, ample supply of low pressure steam. This might not apply in shipyards.

Heaters based on the direct combustion of oil, propane or other gases, had not been very successful in tanks, since the moisture produced by combustion caused condensation which was only partly overcome by the increased circulation of unheated air.

Related Abstracts

Design and Construction of Liquefied Gas Carriers

Liquefied gas carriers can be divided into four basic types. Fully pressurised ships are generally designed to carry LPG and anhydrous ammonia but may also carry other hydrocarbons. The ships are simple in design with a maximum capacity of about 2000 m^3 and the cargo is usually carried in six uninsulated cylindrical pressure vessels. The working pressure is equivalent to the vapour pressure of the cargo at the maximum anticipated ambient temperature (Lloyds Register of Shipping consider this to be 45°C (113°F), at which temperature anhydrous ammonia has a vapour pressure of about 17 kg/cm^2 (240lb/in^{2}g).

The general arrangement of Semi-Pressurised ships and the cargoes they carry are similar to the above but their cargo capacities may range up to a normal maximum of about 5000 m^3. The pressure vessels are designed for a maximum pressure of about 8 kg/cm^2 (113 lb/in^{2}g) and are constructed of carbon steel suitable for a service temperature of about -5°C (23°F). The reduction in cost due to reduced wall thickness of the pressure vessels is partly offset by a requirement to fit a refrigerating plant which utilizes the cargo as the refrigerating medium to maintain the vapour pressure of the cargo. The tanks are insulated to reduce the required size of refrigerating plant, but cargoes may also be loaded from fully pressurised shore storage tanks and at higher pressures than the working pressure of the ship's tanks; it is then necessary to refrigerate the cargo during loading by drawing off the vapours from the top of the tank. This process usually determines the size of the refrigerating plant if a reasonable loading rate is to be maintained. Few of these ships are on order by comparison with those of Type 3. Ratio of cargo weight (propane) to tank weight is about 4 : 1.

Semi-Pressurised/Fully Refrigerated tankers are designed to carry the full range of LPG and similar chemical cargoes in cylindrical or spherical tanks which are constructed of low temperature carbon or low nickel alloy steel, and designed for minimum service temperature of about -45°C (-50°F) and pressures in the order of 5 to 8 kg/cm^2 (70 to 113lb/in^{2}g). The ships are usually designed to carry a number of cargoes simultaneously, and occasionally, to load and discharge simultaneously more than one product. Whilst the building cost of these ships is appreciably higher than conventional semi-pressurised types their flexibility in service makes them popular with charterers, and there is a growing demand for this type of ship.

Fully Refrigerated at Atmospheric Pressure tankers can be sub-divided into three types:

Fully Refrigerated LPG Tankers: Cargoes carried are generally similar to those in previous types and in addition these ships may also be designed for the carriage of such chemicals as vinyl chloride and ethylene oxide. This type has grown in cargo capacity from 10 000 m^3 to 75 000 m^3, and ships up to 100 000 m^3 are under construction.

Fully Refrigerated Ethylene Tankers: This cargo is an important base chemical but as it is transported by sea in relatively small quantities there are, at the present time, less than ten small ships in service specially designed for the carriage of this cargo. The tanks are insulated and may be of the self-supporting type, either cylindrical, spherical or prismatic in shape or of the membrane type, and are designed for a minimum service temperature of -104°C (-156°F) at atmospheric pressure. Suitable tank materials would be aluminium or nickel steels (5 per cent or 9 per cent) for the self-supporting tanks with stainless steel or Invar for the membrane tanks.

LNG Tankers: These ships have usually been designed to carry LNG exclusively for a 'liner' trade, but a number have the equipment installed and their tanks designed to enable other liquefied gases including ammonia to be carried. At the present time 75 000 m^3 capacity vessels are in service with 120 000 m^3 vessels on order and larger vessels contemplated. The tanks may be of the self-supporting type either prismatic or spherical, constructed of aluminium or 9 per cent nickel steel materials or of the membrane type constructed of aluminium, stainless steel or Invar (36 per cent nickel iron), and designed for a minimum service temperature of −164°C (−263°F) at atmospheric pressure.—*Paper presented by Gray, R. C. and Johnson, L. at a meeting of the North-East Coast Institution of Engineers and Shipbuilders, 7 December 1970.*

Advanced Cargo Control for Turnbull Scott Products Carrier

More than 100 types of chemical products, including acids, alkalis, and solvents, as well as vegetable oils, wine, and other liquid cargoes with specific gravities of up to 2·0, can be carried in the 14 all-stainless steel cargo tanks of the newly completed 2650 dwt *Stainless Warrior*.

Built for the Whitehall Shipping Co. Ltd., an associate of Turnbull Scott Management Ltd., who will be operating the vessel, the design of *Stainless Warrior* is modelled on a similar vessel, *Stainless Transporter* (2800 dwt), built by Ernst Menzer Werft in Germany for the Copenhagen-based owner A. H. Basse Rederi.

Principal particulars are:

Length, o.a.	284 ft 6 in
Length, b.p.	268 ft 0 in
Breadth, moulded	40 ft 0 in
Depth, moulded	20 ft 3 in
Draught (maximum)	17 ft 9 in
Gross register	1599 tons
Deadweight (total)	2650 tons
Deadweight (cargo)	2375 tons
Service speed	13 knots

The most interesting aspect of the new tanker is its cargo tanks and associated equipment, the installation of which is to U.K. Board of Trade (now renamed the Department of Trade and Industry) highest requirements for dangerous cargoes. Hence, the complete complex of 14 tanks is surrounded by a double skin, including double plating at the main deck, with cofferdams fore and aft. Other special precautions have been taken to ensure that vessel contamination by the cargo is eliminated so far as possible.

A feature of the cargo tanks is the extensive use of stainless steel: the perimeter bulkheads of the whole tank section are entirely manufactured from Colclad stainless steel veneer on mild steel—a product of the British Steel Corporation's Ravenscraig works (formerly Colville's), while all tank transverse and longitudinal corrugated bulkheads are fabricated from solid 10-mm thick Firth-Vickers Staybrite F.M.B.(L)—corresponding to American I.S.I. 316 (L) type—low-carbon (0·03 per cent) stainless steel.

All the cargo tank piping is of 2 mm thick stainless steel, and each of the 14 tanks has its own filling line and deep-well cargo pump. The latter are of the NH 80-4-K impeller type, manufactured—in 316 stainless steel—by Svanehøj Pumpefabrik, of Svenstrup, Denmark, and each rated at 40 m^3/h at 1450 rev/min. Each pump is driven by a Brown Boveri vertical electrical motor, mounted on deck. This type of pump—fitted on *Stainless Warrior* with 11 m shafts—is designed for hazardous cargo duties and is so constructed that the bearings and pump casing can be inspected, removed or replaced without taking the pump from the bottom of the tank. Specially constructed PTFE bearings are fitted, which are lubricated by the cargo being pumped. Two seals are fitted: a lower one to ensure that if a leak occurs, the liquid will run back into the tank, while an upper one in the deck stool prevents gas leaking to the electric motor.

Elaborate precautions have been taken to prevent cargo spillage and to contain the flow of vapour given off by chemical cargoes.

The engine room of *Stainless Warrior* is designed to Lloyd's UMS classification, the heart of the unmanned operation being a unique 50-way alarm panel, engineered by Clifford and Snell Ltd. and which is situated alongside the Electrical Controls Humberside switchboard on an upper forward flat in the engine room.

Control of the main propulsion unit, a six-cylinder MaK K551AK tubrocharged and intercooled engine developing 2400 bhp at 300 rev/min, and of the Stone Manganese Marine Novoston four-bladed c.p. propeller (which is directly driven from the engine), is principally from the wheelhouse.—*The Motor Ship, December 1970, Vol. 51. pp. 398–400.*

Infra-Red Microscope for Detection of Internal Flaws

A microscope was designed and constructed to detect surface and internal discontinuities in materials which are opaque to visible radiation but transparent at infra-red frequencies. Flaws were made by ruling a number of lines on the surface of sample materials, which were then examined under the microscope. Internal flaws were simulated by clamping two samples together and observing the defects in the boundary layer. It was found that the microscope could easily detect surface and internal flaws at about 10 μ in size. The microscope is used with a mechanical scanning table and a storage oscilloscope to provide a visual display of the detected signal.—*Simpson, W. A., Deeds, W. E., Cheng, C. C. and Dodd, C. V. Materials Evaluation, September 1970, Vol. 28, pp. 205–211.*

Properties of Stainless Steel Fasteners

Various types of stainless steel (ferritic chromium steels, martensitic chromium steels, austenitic chromium steels), their compositions, characteristics and applications such as bolts, screws, nuts, etc., are discussed. Protection against corrosion (atmospheric, galvanic stress, intercrystalline, crack corrosion) of stainless steel fasteners is also referred to.—*Cornelissen, B. L. Polytechnisch tijdschrift 25 (1970), No. 24, pp. 1066/1076.*

Acousto-Optical Imaging for Nondestructive Testing

Visual images of flaws inside optically opaque objects are being produced by a technique called acousto-optical imaging.

Tests to date have demonstrated the ability of the technique to detect voids in structures and to identify areas lacking bond integrity in composite structures.

The basic principle is relatively simple: ultrasonic waves are made to enter the object to be inspected and, upon emergence from the body, interact with light from a laser resulting in a real-time optical image of what the sound waves have "seen".

The technique makes it possible not only to locate the defect but also to quantitatively assess the extent or size of a flaw. One of the principal features of the acousto-optical imaging technique is that it has successfully eliminated the need for a receiving transducer and is insensitive to ambient mechanical vibration.—*Materials Evaluation, September 1970, Vol. 28, p. 57A.*

Fatigue Crack Initiation and Propagation in High-Yield-Strength Steel Weld Metal

Full penetration, double-vee butt welds with reinforcement removed have been fabricated using a high-yield-strength steel, HY-1e0. Various filler metals and welding techniques were used. Most welds contained intentionally incorporated weld discontinuities such as slag, lack of fusion and/or porosity. Fatigue specimens were cut from these welds and tested in zero-to-tension, axial fatigue.

The point at which a fatigue crack began to propagate within the specimen was determined by radiographic measurements. The fatigue life of a specimen could therefore be separated into two parts—that portion spent in initiating a fatigue crack and that spent in fatigue crack propagation. The influence of flaw size and geometry upon the crack propagation portions of the fatigue life was found to be large and to depend upon the thickness of the member.

The results of these studies were found to be in good agreement with the fatigue lives predicted on the basis of a fracture mechanics analysis.—*Laurence, Jr., F. V. and Radziminski, J. B., Welding Journal, October 1970, Vol. 49, pp. 445s–452s.*

Effect of Flame and Mechanical Straightening on Material Properties of Weldments

Distortion is a perennial problem in the shipbuilding industry, and extensive research has been undertaken to determine the causes of distortion and to minimize its occurrence. While distortion can be produced by any of the fabrication methods used in shipbuilding, its principal cause today is welding. Welding is used extensively in modern shipyards because of its advantages over other assembly methods. However, as with any complex structure, distortion is encountered when ship hulls and other structural sections are assembled by welding. The amount of distortion can be controlled and minimized by proper design and careful attention to the details of welding, but some distortion inevitably occurs. When the degree of distortion exceeds recognized acceptance standards, it must be removed.

Distortion can be removed by producing adequate plastic deformation in the distorted member or section. The required amount of plastic deformation can be obtained by the thermal or mechanical methods discussed in the following paragraphs:

1) Thermal or flame straightening has been used most successfully in the shipbuilding industry to remove distortion. The area to be straightened is heated to about 1100–1200°F and then quenched with a water spray; repeated applications of heat in specific areas in a selected sequence or pattern are normally needed to straighten a distorted member or structure. The patterns are usually variations of the spot or linear heating techniques;
2) Distorted members can be straightened in a press if the members can be moved and if the press is large enough to handle them; heat may or may not be required for straightening;
3) Jacking is closely related to pressing in that distortion is removed by the application of pressure with or without added heat. Although its use is frowned upon, hammering of locally-heated areas is sometimes used for straightening also. Cutting of plates and rewelding is used on occasion to remove distortion. This technique is perhaps the most expensive of all because of the time required.

Flame straightening is well-established in the shipbuilding industry (and in other industries as well) as the most suitable method of removing distortion in welded assemblies of low-carbon steel. It is a relatively simple method and requires a minimum in equipment. However, flame straightening is not without its disadvantages. Despite its wide acceptance, flame straightening is an empirical process at best, and conscientious and well-trained workers and supervisory personnel are required for its effective application.

An experimental study was conducted to determine the effects of mechanical straightening and flame straightening on the properties of steels used in shipbuilding. The steels investigated during this programme included an ordinary carbon steel (ABS-B), two low-alloy, high-strength steels (A441 and A537), and a quenched and tempered steel (A517, Grade A). The removal of distortion in unwelded and welded test plates was accomplished by mechanical straightening at room temperature, 1000°F, 1300°F, and flame straightening in the temperature ranges of 1100–1200°F and 1300–1400°F. Controlled amounts of distortion were provided in unwelded plate by mechanical bending; distortion in welded plates was provided by jigging the restraint control. Drop-weight tear tests were conducted to assess the effect of the straightening parameters on the notch-toughness behaviour of the respective steels.

The notch-toughness properties of A517, Grade A decreased markedly when flame straightening was done at 1300–1400°F; somewhat less effect was observed when A517, Grade A test plates were straightened at 1100–1200°F. The notch-toughness of A517, Grade A was affected significantly by the time required for straightening. The impact properties of A537, A441, and ABS-B steels were not affected seriously by flame straightening. Mechanical straightening had little effect on the notch-toughness properties of any of the steels, because the time required for heating and straightening was minimized.—*Pattee, H. E., Evans, R. M. and Monroe, R. E., Ship Structure Committee, Report SSC-207, 1970.*

New Nickel Superalloys for Marine Gas Turbines

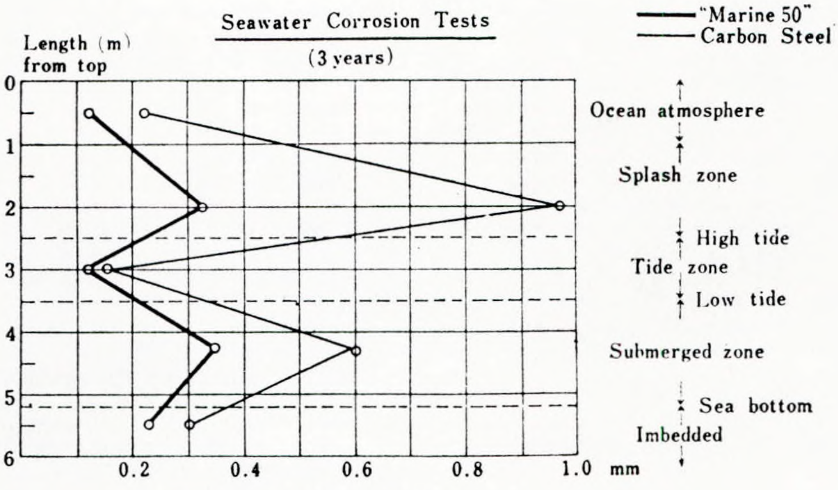
The growing use of gas turbines for industrial applications and in land and marine transport has led to a demand for longer operating life and the use of cheaper and lower grade fuels, both of which impose further demands on materials. In particular there is need to improve resistance to hot corrosion by combustion products of the fuel and contaminants from the operating environment. To combat these more severe oxidation and corrosion problems at high temperatures, International Nickel research workers increased the chromium content of existing high-temperature alloys. Normally, such an increase has the undesirable effect of reducing the strength of these alloys but this problem has been overcome by modifying other major alloy constituents. A variety of new nickel-based wrought high-chromium (between 25 and 30 per cent Cr) creep-resistant alloy has been developed giving considerably better resistance to hot corrosion than alloys presently used, while their strengths and other characteristics range nearly up to those of the strongest wrought Nimonic alloy.

Three new alloys, designated IN 586, IN 587 and IN 597 have been selected for further development and assessment in various industrial applications. Alloy IN 586 is a solid-solution alloy similar to Nimonic alloy 75, but with improved oxidation resistance and creep strength at temperatures above 1000°C. This alloy has attractive properties for static engine components subjected to the highest temperatures.

Alloys IN 587 and 597 are precipitation hardened and have high-creep strengths corresponding to those of Nimonic alloys 90 and 105 respectively, but they have advantages over the Nimonic alloys in terms of corrosion resistance for blades in industrial and marine gas turbines.—*Marine Engineer and Naval Architect, November 1970, Vol. 93, p. 515.*

Relaxation of Compression Springs at High Temperatures

An analysis is developed to determine the relaxation of cylindrical compression springs at temperatures where creep is predominantly steady state and the effect of transient creep and an elastic strain is small. Springs which operate under these conditions must be designed for limited life. Equations are derived which predict the relaxation of springs directly from tensile creep data for various materials. Using creep data for 18-8 stainless steel and Inconel-X, families of design curves are presented which give the time-temperature initial-stress relationships for various stress-relaxation ratios.—*Siegel, M. J. and Athans, D. P., Transactions of the ASME, Journal of Basic Engineering, September 1970, Vol. 92, pp. 627–632.*



Nippon Kokan 'Marine 50' corrosion-resistant steel

Japanese Corrosion-Resistant Steel Developed

Nippon Kokan—NKK—has recently announced details of a seawater corrosion-resistant steel which it has developed and which is now ready to be produced on a commercial scale.

Known as Marine 50, the new steel can be regarded as a significant development, especially in view of the rapidly expanding ocean-development field which is likely to demand considerable quantities of such steels for structures such as drilling rigs.

The new steel has a high level of strength with physical properties which meet the requirements of JIS G 3106 SM 50 which is similar to ASTM A 440. The JIS specification stipulates that high strength structural steels have a minimum tensile strength of about 70 000 lb/in^2.

Compared with carbon steel, in the area affected by seawater splashing, the resistance is two to three times higher and in the submerged area it is 1·7 to two times higher.

The new steel has, like some other low-alloy seawater resistant steels, low alloy additives whose effectiveness is multiplied geometrically to form a fine-grained oxydized surface layer having a uniform thickness that inhibits corrosion. The corrosion-resistant effects of the layer is expected to increase with the passage of time.—*Shipbuilding and Shipping Record, 18 September 1970, Vol. 116, p. 31.*

Stress Corrosion in Aluminium Alloys

The phenomenon of stress corrosion is described and examples of service failures are given. These concern a casting, an extrusion and a forging. The influence of the alloy type, heat treatment and grain orientation on the susceptibility to corrosion are discussed. Theories regarding stress corrosion are surveyed. Ways to combat stress corrosion are indicated. Assembly stresses, residual stresses, design, surface, protection, alloy selection and heat treatment are considered.—*van Leeuwen, H. P., Polytechnisch tijdschrift, 1970, No. 20, Vol. 25, pp. 872–880.*

Corrosion and Corrosion Protection

By chemical treatment with certain media, depending on the type of metal, it is possible to produce on metals so-called conversion layers which are able to protect the metal against corrosion. Conversion layers are both cover layers and protection layers which are generated by conversion of the material surface under formation of a metal compound. The protection layers are produced by the action of gases, aqueous solutions or salt melts (without or with electrical current).—*Wiederholt, W., VDI-Z, 1970, Vol. 112, No. 18, pp. 1253–1257.*

Fibre Reinforced Materials—Theory, State of Development and Tendencies in Fibre Production

Fibres of glass, ceramics, boron, carbon, tungsten and beryllium and steel are being used at present for the production of fibre-reinforced composite materials. Which combination of fibre and matrix material is selected, depends on the intended use of the composite. Most of the emphasis, however, is placed on reinforcing metallic and non-metallic matrices with non-metallic fibres. In the near future, glass fibre reinforced plastics will be used to increasing extent, and will not be supplanted by composites reinforced with carbon, boron or silicon carbide fibres.—*Clasing, M., VDI-Z, 1970, No. 19, Vol. 112, pp. 1333–1335.*