THE GENERATION OF PYROPHORIC MATERIAL IN THE CARGO TANKS OF CRUDE OIL CARRIERS

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1. INTRODUCTION

Two minor explosions have occurred in successive years in vessels discharging Qatar crude oil at Sriracha in Thailand. In each case ignition occurred during the early stages of cargo discharge when the ullage was of the order of six feet, and a limited volume of inflammable mixture existed. Consequently the explosions were of small scale, causing only slight damage and no injury to personnel. At the time, there seemed no obvious explanation for the incidents; ignition by mechanical or electrostatic effects seemed unlikely and suspicion centred on the possible presence of a pyrophoric material. That the incidents occurred in the same geographic location and at the same time each year, suggested that climatic factors may also have played some part.

If the source of ignition is attributed to the presence of a pyrophoric deposit then the sequence of stages leading to an explosion would, it is assumed, be:

  i) reaction between ullage gas and metal or deposit-covered metal surface during passage to form a reactive material;
  ii) exposure of reactive material to ingress of air during discharge, giving rise to a rapid exothermic reaction leading to high localized temperatures;
  iii) contact of inflammable gas mixture with hot oxidizing deposit.

It is in fact well recognized that pyrophoric material can form as a deposit in plant distillation systems where steel columns are exposed to vapours containing hydrogen sulphide. The presence of pyrophoric material in gas transport lines has also been encountered. Thus although there is an acceptance of what is often loosely referred to as pyrophoric iron in a number of practical systems, little effort appears to have been devoted to considering the precise nature of the pyrophoric species, its formation and possible control.

From the investigation described in this paper, it is apparent that both the above incidents can be attributed to the presence of pyrophoric material in the ullage space of these vessels. As far as it has been possible to do so, enquiries have been made throughout the tanker industry and these strongly indicate that ignition through this cause is unprecedented. It has not yet been possible to establish the unique factors that combined in these particular instances to activate this potential hazard.

The work described in the present paper and briefly referred to in an earlier publication[1] was devoted to studying the conditions prevailing in the ullage regions of crude oil cargo tanks and the likelihood of their giving rise to the production of pyrophoric material that could present an ignition hazard. Since the incidents referred to earlier involved Qatar crude oil, which is characterized by its high vapour pressure and its high hydrogen sulphide content (ullage gas can contain up to above 5 per cent hydrogen sulphide), attention was in the main focused on deposits and conditions applying to this particular crude oil.

2. NATURE OF DEPOSITS RECOVERED FROM CARGO TANKS

Of particular interest are the deposits that tend to accumulate on tank surfaces in those ullage regions least likely to be wetted by cargo, for example in hatch, sighting port and standpipe areas. Material sampled from such regions on a number of vessels, including those involved in the incidents referred to, was submitted to analysis by x-ray diffraction. Deposits invariably contained hydrated ferric oxide (alpha-FeO (OH)) and elemental sulphur, and in some instances magnetite (Fe_3O_4), ferric oxide (alpha-Fe_2O_3) and hydrated ferrous sulphate ($FeSO_4 . 4H_2O$) were also detected. In no case was a sulphide observed.

Samples obtained from different locations in the same tank were found to vary considerably in composition and in their physical state, consisting in some cases of quite hard laminated scales and in others of quite loose powders. Samples also differed in the amount of occluded oil that they contained. It should also be pointed out that the deposits as sampled had already been exposed to oxygen (air) so that any pyrophoric species would no longer be present.

3. REACTION OF IRON OXIDE (HYDRATED) WITH ULLAGE GAS

The ullage gas, in the case of Qatar crude oil, can, as already mentioned, contain high concentrations of hydrogen sulphide (5 per cent) in addition to hydrocarbon vapour ($\sim$ 85 per cent) and air. Iron oxide (hydrated) is well known to be an effective scavenger of hydrogen sulphide and as such has long been used in the form of "bog ore" as a commercial process for removing hydrogen sulphide from town gas (sweetening). The reaction involved, ignoring hydration effects, is usually represented by:

$$Fe_2O_3 + 3H_2S. \rightarrow 2 Fe S + 3H_2O + S \qquad (1)$$

The oxide scavenger in the process is then regenerated by exposure to air:

$$4 Fe S + 3O_2 \rightarrow 2 Fe_2O_3 + 4 S \qquad (2)$$

The efficiency of the process is such that the hydrogen sulphide content can be reduced to a few parts per million. Values of $\Delta H°$ for reactions (1) and (2) based on Fe_2O_3 are about -168 and -635 kJ (-40 and -151 kcal) respectively. Since both reactions are exothermic, the process represents an overall oxidation of hydrogen sulphide, the hydrated iron oxide fulfilling the role of a catalyst. Providing that conversion, as represented by reaction (2), can proceed rapidly and without undue dissipation of heat, then high local temperatures could result from sudden exposure of a deposit of sulphide to air or even to air/hydrocarbon mixtures.

It is not surprising that much of the information in the literature relates to a consideration of factors that can affect hydrogen sulphide uptake, i.e. reaction (1), and also those that affect the subsequent regeneration of active "iron oxide", i.e. "revivification" as represented in reaction (2), both factors being highly important in the efficiency of the commercial

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process. In a detailed study, Griffiths and Morcomb[2] have for example considered the interconversion of iron oxides and sulphides. Included in their study were the seven known forms of ferric oxide (alpha-Fe_2O_3, alpha-$Fe_2O_3.H_2O$, beta-$Fe_2O_3.H_2O$, gamma-Fe_2O_3, gamma-$Fe_2O_3.H_2O$, delta-$Fe_2O_3.H_2O$ and amorphous Fe_2O_3) and the iron sulphides (Fe_2S_3, $Fe_2S_3.H_2O$, Fe_8S_9 and FeS_2). The work confirmed that not all forms of the oxide were equal in their activity towards hydrogen sulphide, and that the conditions of oxidation of the sulphide in the regeneration process were important if the reactivity of the oxide species was to be preserved. Hydration, porosity and temperature were also influencing factors. Other workers, namely Avery[3] and Moignard[4], have demonstrated the importance of "migration" effects on the reactivity of the oxide. In pursuing an investigation of possible pyrophoric behaviour resulting from reactions (1) and (2) as applied to crude oil cargo tank atmospheres, it would thus seem logical to suppose that these same factors might likewise play an important part.

4. BEHAVIOUR OF RECOVERED TANK SCALES TOWARDS SULPHIDATION/OXIDATION

In an initial series of experiments, deposits recovered from inside tank surfaces, in the regions of hatchways, sighting ports and the underdeck, were exposed to alternate sulphiding and oxidation in order to establish the order of temperature changes that might be expected.

Ground deposits were contained in the form of a plug in a glass tube of internal diameter 19 mm. The plug of material, about 40 mm long, was held in position by glass wool inserts, and temperature measurements were recorded by means of suitably positioned thermocouples (Fig. 1). Starting from ambient temperature, the thermal response was recorded
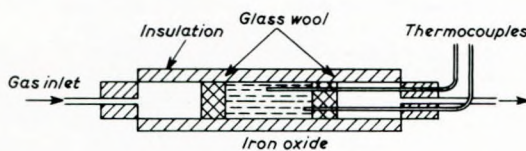

FIG. 1—*Apparatus for plug experiments on sulphidation of oxide and subsequent oxidation of sulphide*

when hydrogen sulphide was passed through the plug at a rate of 100 cm^3/min. After resuming ambient temperature, air at a similar flow rate was introduced and the thermal behaviour was again recorded. Several cycles of sulphidation/oxidation were imposed in this manner. Results for a typical scale are shown in Fig. 2, in which curves 1, 2 and 3 indicate the temperatures realized for successive cycles. As shown, the heat release during sulphidation was sufficient to raise the temperature of the plug, in the zone measured, by some 37°C above ambient. During oxidation the temperature rise for the same zone was greater, some 72°C above ambient. For sulphidation and oxidation, the peak temperatures were reached after periods of about 12 and 25 minutes, respectively. With each successive cycle, the maximum temperature was lowered, both for sulphidation and oxidation, also the times taken to reach temperature maxima were increased. It was thus evident that the scale material was being rendered less reactive towards gas/solid reaction with increased cycling, possibly owing to the effect of the sulphur that is generated in accordance with reactions (1) and (2). Although differing in the maximum temperatures and the times at which these were attained, other scale samples showed a similar pattern of behaviour.

5. BEHAVIOUR OF MODEL OXIDE (alpha-FeO(OH))

On account of their heterogeneous composition, scales recovered from cargo tanks were not suitable for carrying out a systematic study of the factors governing the sulphidation/oxidation reactions involving hydrated iron oxide. In particular, the presence of occluded oil and sulphur was considered likely to obscure the reactions of interest. A pure grade of hydrated alpha-ferric oxide of particle size 37–76 μm (hereafter referred to as model oxide) was therefore selected as a standardized material for use throughout the work described.
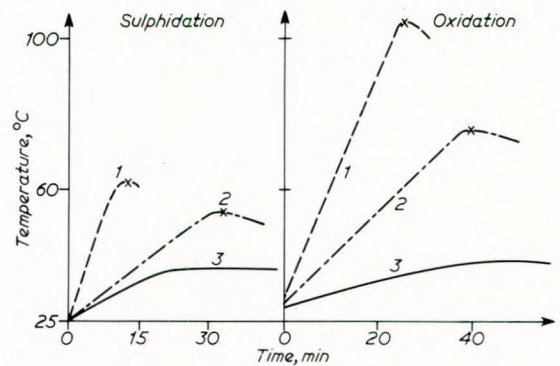

FIG. 2—*Heat release observed for oxide sulphidation and sulphide oxidation in plug experiments*

5.1 *Sulphidation/Oxidation of Model Oxide*

Sulphidation of the model oxide was carried out by exposing a plug of the material to a stream of 100 per cent hydrogen sulphide under the conditions described earlier (see Section 4). The course of the reaction could be followed visually by observing the change of the orange-red oxide to the brownish-black product. On account of the smaller particle size of the oxide coupled with the "caking" effect due to the generated moisture, flow conditions comparable with those employed in the examination of the particle scales could not be maintained, hence no direct comparison could be made of the heat release for the two systems.

5.2 *Pyrophoric Behaviour*

The sulphided product prepared from the model oxide proved to be highly reactive on exposure to air at ambient temperatures. Within minutes, the bulk temperature of the agitated material, as recorded by an embedded thermocouple, rose to about 370°C with evidence of localized glowing and sparking. Quite clearly, the presence of material of this order of reactivity in the ullage regions of cargo tanks could be a potential hazard in circumstances where it could be exposed to a sudden ingress of air in an inflammable atmosphere. An important aspect of the investigation was, therefore, to make a detailed comparison between the behaviour of the model oxide and that of the recovered tank scale material.

6. CRITICAL REACTION TEMPERATURE (CRT)

An important difference in behaviour between the model oxide and the recovered tank scale material was the pyrophoric behaviour of the former when sulphided and exposed to air at ambient temperature. However, it was noted that when sulphided tank scale material was heated in air to a particular temperature the oxidation proceeded spontaneously and pyrophorically. The temperature at which this stage was reached, defined as the critical reaction temperature (CRT), was adopted as a criterion of the reactivity of the sulphided material. For the sulphide derived from the model oxide the critical reaction temperature was thus equal to or less than ambient, i.e. CRT ≤22°C. For cargo tank scales of different origin, sulphided in the laboratory, the CRT values were found to lie between 125°C and 200°C, see Table I. It was also noted that oil and sulphur vapours were being evolved at these temperatures.
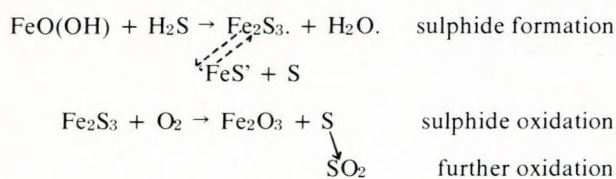
6.1 *Effect of Repeated Sulphidation/Oxidation Cycling on the CRT of Model Oxide*

Model oxide (α-FeO(OH) of particle size 37–76 μm) was subjected to repeated cycles of sulphidation/oxidation. After the second cycle, the product was no longer pyrophoric at ambient temperature, so that for each successive cycle it was necessary to heat the sulphided material to its critical reaction temperature (CRT) in order to regenerate the oxide. The effect of repeated cycling (sulphidation/oxidation) on the critical reaction temperature is shown in Table II.

The progressive rise in the critical reaction temperature is consistent with the idea of a sulphur build-up in the material as a result of cycling. The scheme whereby such accumulation occurs is probably:

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$$FeO(OH) + H_2S \rightarrow Fe_2S_3 + H_2O. \quad \text{sulphide formation}$$
$$\searrow$$
$$\text{'FeS' + S}$$

$$Fe_2S_3 + O_2 \rightarrow Fe_2O_3 + S \quad \text{sulphide oxidation}$$
$$\searrow$$
$$SO_2 \quad \text{further oxidation}$$

A further series of multicycling experiments on model oxide confirmed this general picture. In this latter series of experiments the oxidation stages were allowed to proceed by the controlled (non-pyrophoric) route by keeping the effective $[O_2]/[\text{sulphide}]$ ratio small. Under these conditions it was clear that each oxidation stage led to the formation of substantial quantities of elemental sulphur. In fact, after formation of the third sulphide the sulphur content reached a point where oxidation was not observed over a 24 hour period. This series of experiments thus added further confirmation to the idea that elemental sulphur can inhibit (by virtue of its screening effect) the oxidation of the sulphide, providing a possible explanation for the difference in behaviour between the practical and model oxide/sulphide systems.

TABLE I

Origin of oxide	Critical reaction temperature (CRT) of sulphided oxide °C	Vapours observed during oxidation
Model oxide	<25	SO₂,
Vessel 'A'	200	SO₂, S, oil
Vessel 'B'	180	SO₂, S, oil
Vessel 'C'	160	SO₂, S, oil
Vessel 'D'	125	SO₂, S, oil
Vessel 'E'	125	SO₂, S, oil

TABLE II—EFFECT OF MULTIPLE SULPHIDATION/PYROPHORIC OXIDATION CYCLES ON THE ACTIVITY (CRT) OF SULPHIDE FORMED FROM MODEL OXIDE

After cycle No.	Critical reaction temperature (CRT) of sulphide, °C
1	25
2	65
3	130
4	140

6.2 Effect of Removal of "Screening Materials" on the Critical Reaction Temperature of Sulphided Practical Scales

If screening effects arising from the presence of sulphur or occluded oil were the explanation for the differences in behaviour between the sulphided model oxide and the practical tank scale material, then removal of this screening material should result in the production of sulphides of equal activity. Accordingly, a sulphided bulked sample of oxide scale obtained from the cargo tanks of several vessels was "descreened", by roasting in air, at a temperature of 700°C for one hour to remove sulphur and occluded hydrocarbon. The roasted scale material was sulphided in the manner described earlier and the reactivity of the product was examined by measuring its critical reaction temperature. The results were compared with those obtained for the model oxide after similar and varied treatments. As seen from Table III, the derived oxide in each case, following sulphidation, showed similar activity towards aerial oxidation; the CRT values all fall in the range 25–30°C. It was thus concluded that "screening" is a major factor inhibiting the pyrophoric oxidation of iron sulphide produced in the manner considered. These experiments also demonstrated that the removal of "screening" materials can restore the activity of a sulphided corrosion product to what must be considered dangerous from a practical standpoint.

In other experiments, where descreening of scales was achieved by extraction with carbon disulphide, a similar increase in sulphide reactivity resulted.

TABLE III—THE REACTIVITY OF VARIOUS IRON SULPHIDES TOWARDS OXIDATION IN AIR

Origin of oxide	Particle size, μm	Treatment of oxide prior to final rigorous* sulphiding	CRT, °C
Model oxide α-FeO(OH)	37–76	Successively sulphided and oxidized (pyrophoric route) 4 cycles. Roasted at 700°C for one hour.	25–30
Bulked sample of oxide scale from cargo tanks of several vessels	37–76	Sulphided, followed by roasting at 700°C for one hour.	25–30
Model oxide α-FeO(OH)	37–76	Sulphided followed by roasting at 700°C for one hour	25–30
Model oxide α-FeO(OH)	37–76	Roasted at 700°C for one hour.	25–30

* Continuous agitation of solid during sulphidation.

7. ELECTRON MICROSCOPY OF IRON OXIDES

Whilst the "descreening" of oxides by the roasting procedure described in Section 6.2, produced sulphides of similar reactivity, it was noted that this degree of reactivity was somewhat less than that observed for sulphides prepared from hydrated model oxides (unheated). For example, in the case of the roasted oxides (model oxide and tank scale oxides) it was necessary to impose rigorous sulphiding conditions (see note Table III) in order to produce materials with CRT values of 25–30°C. In the case of the unheated model oxide, normal sulphiding, as described in Section 4, sufficed to produce a material of CRT ≤22°C.

This somewhat lower reactivity, it was thought, might be attributed to modifications in the "oxide" surface area arising from differences in article geometry even though the aggregate sizes were similar, 37–76 μm. With this possibility in mind, the following samples were examined by transmission electron microscopy.

A. Model oxide, α-FeO(OH).
B. Model oxide, α-FeO(OH), after heating at 700°C for two hours.
C. Model oxide, α-FeO(OH), after four sulphidation/pyrophoric oxidation cycles, subsequently heated at 700°C for two hours.
D. Model oxide, α-FeO(OH), after heating at 350°C for two hours.
E. Model oxide, α-FeO(OH), after three sulphidation/pyrophoric oxidation cycles.

Examination of the above samples at low to medium magnifications showed that sample A differed considerably in its fine structure from samples B and C. Sample A was highly crystalline, showing well-defined dendritic clusters, whilst B and C were seen to consist of aggregates of small rounded particles (see Figs. 3 and 4). Samples D and E had fine structures intermediate between those of A and B.

Examination at higher magnifications up to 120 000 provided additional information. It revealed in particular the needle-like crystals, normally less than 0·25 μm long protruding from the aggregate edges. Samples B and C were seen to be similar in structure, both comprising rounded granules apparently sintered together in aggregates of varying size. The granules of B were, in general, slightly smaller than those of C, the latter having diameters up to 1 micron. Other features noted were that sample D still retained noticeable needle-like form in its fine structure, whilst sample E consisted of angular granules of about 0·1 micron maximum diameter. In general the aggregates of B and C were larger than those of A, D and E.

The results indicated an order of decreasing surface area A > D > E > B ⇌ C, which paralleled the intensity of thermal treatment for the various samples. The findings were consistent with the fact that those samples shown to be of

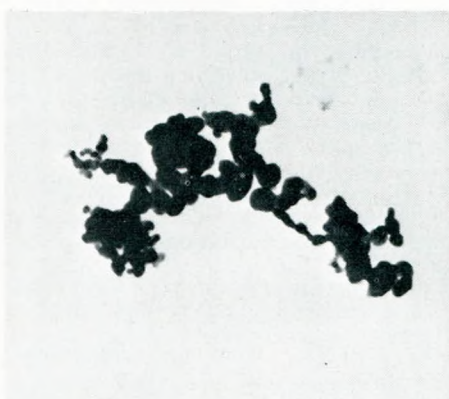FIG. 3—*Electron micrograph of model oxide (A) x 25 000*

FIG. 4—*Electron micrograph of roasted oxide (B) x 25 000*

diminished surface area were the same materials that required rigorous sulphidation to ensure complete conversion into the reaction product.

8. SULPHIDATION OF HYDRATED IRON OXIDE IN ATMOSPHERES OF VARIED HYDROGEN SULPHIDE CONTENT

In the work so far referred to, sulphidation of iron oxide samples had been carried out in an atmosphere of 100 per cent hydrogen sulphide. In cargo tanks the concentrations of hydrogen sulphide in the ullage gas are, of course, considerably lower. With Qatar crude, hydrogen sulphide concentrations up to 3·5 per cent by volume have been measured and could be as high as about 5 per cent by volume depending on seasonal variation of hydrogen sulphide in the crude oil. Accordingly it was necessary to establish whether pyrophoric material could form at hydrogen sulphide partial pressures corresponding to practical levels, also to examine the influence of oxygen on the course of the sulphidation reaction. If for example the oxygen partial pressure (P_{O2}) were to be such that sulphidation and oxidation could proceed concurrently, then it would seem reasonable to expect that pyrophoric activity could be suppressed by the screening effect of the generated sulphur.

8.1 *Effect of Hydrogen Sulphide Concentration on the Reactivity of the Sulphided Oxide*

Samples of model oxide (of particle size range 37–76 μm) in the form of plugs were exposed at ambient temperatures to nitrogen streams containing hydrogen sulphide at concentrations of 1, 3 and 5 per cent by volume at gas flow rates of 6 litres/h. Under these conditions sulphidation of the iron oxide occurred within minutes in all cases, the resulting materials being pyrophoric on exposure to air at ambient

temperature. It was thus established that for the range of hydrogen sulphide concentrations examined there was no evidence that any threshold level existed below which a pyrophoric species of iron sulphide would not form. It was also established that changing the diluent gas from nitrogen to propane affected neither stage of the sulphidation/oxidation cycle.

8.2 *Effect of Oxygen Concentration on Reactivity of Sulphided "Oxide"*

Model oxide (α-FeO(OH) of particle size 37–76μm) was exposed to nitrogen streams containing hydrogen sulphide and oxygen. Experiments were carried out wherein the concentration of hydrogen was maintained constant whilst varying the concentration of oxygen. In this manner it was possible, for each [H_2S] concentration, to impose conditions that favoured either sulphidation or oxidation. After treatment times sufficient to ensure complete reaction, the product was examined for its reactivity towards aerial oxidation by determining its critical reaction temperature.

The results obtained for a fixed hydrogen sulphide concentration of 3 per cent by volume are shown in Fig. 5. As
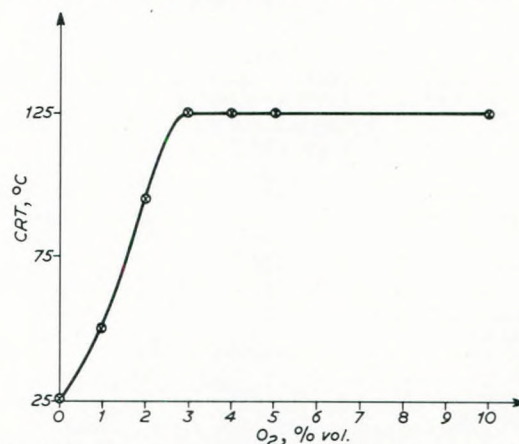

FIG. 5—*Effect of oxygen on reactivity of model oxide sulphided in nitrogen containing 3% vH_2S*

is seen, concentration ratios [H_2S]/[O_2] less than unity favour the formation of an inactive product and a point is reached where the reactivity of the product is insensitive to any further increase in oxygen concentration. This levelling-off effect is probably associated with the accumulation of elemental sulphur in the system whereby rapid oxidation of the product can no longer occur.

In further experiments where hydrogen sulphide concentrations [H_2S] were maintained at 1 per cent and 2 per cent by volume it was likewise found that concentration ratios [H_2S]/[O_2] less than unity favoured the formation of a product that was non-pyrophoric at ambient temperature.

8.3 *Production of Reactive Iron Sulphide via the Aqueous Route*

For iron sulphide formed by the gas/solid reaction, adjustment of the oxygen concentration to an appropriate value would appear to provide a means of preventing the formation of a pyrophoric species in the practical situation, i.e. in the ullage regions of cargo tanks. However, the presence of water in the system, produced either as condensate or as a product of the sulphidation reaction, provides an alternative route for the formation of iron sulphide. Experiments designed to examine the role of water have established several important points. Firstly, model oxide (α-FeO(OH)) exposed to water saturated with hydrogen sulphide is rapidly converted into iron sulphide at ambient temperatures; furthermore the product so formed, after drying in an inert atmosphere, was confirmed to be pyrophoric on exposure to air at ambient temperature. Secondly, on account of the fact that hydrogen sulphide is preferentially soluble in water to the extent that the equilibrated [H_2S]/[O_2] ratio in water is 400:1, the aqueous route provides for the ready formation of pyrophoric iron sulphide in systems where the partial pressure of oxygen may be substantially greater than that of hydrogen sulphide.

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9. OXIDATION OF REACTIVE IRON SULPHIDE IN ATMOSPHERES OF CONTROLLED OXYGEN CONTENT

In practical circumstances the obvious hazard arises when reactive sulphide is exposed to aerial oxidation (i.e. 21 per cent volume oxygen), under which conditions the reaction can proceed pyrophorically. It seemed reasonable to suppose that in atmospheres of sufficiently low oxygen concentration, oxidation of the sulphide could be encouraged to proceed in a controlled manner, thus avoiding the high temperatures associated with the pyrophoric route. To ascertain whether in principle this is the case, laboratory experiments were carried out at various oxygen concentrations. Employing sulphided model oxide of $C\bar{R}T \leqslant 22°C$ and carrying out the oxidation in duplicate in a standard manner, with no agitation, the maximum temperature attained by the oxidizing sulphide was recorded by a thermocouple embedded in the bulk of the material. The type of oxidation occurring was also noted. The results, summarized in Fig. 6, show that two types of
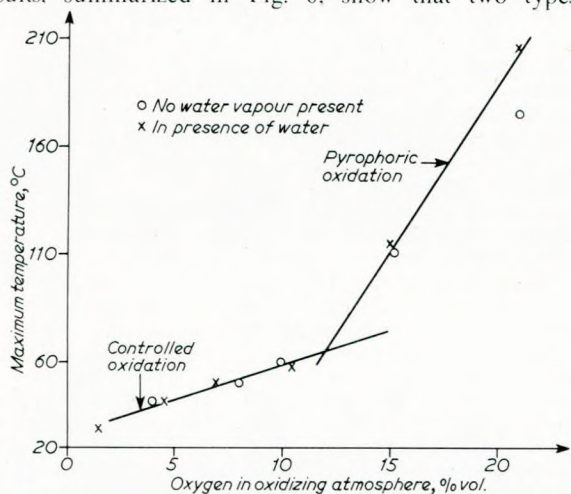

FIG. 6—*Oxidation of model sulphide by atmospheres containing various percentages of oxygen in nitrogen*

oxidative behaviour were observed. For oxygen concentrations of less than 11 per cent, oxidation was not accompanied by pyrophoric activity but proceeded in a controlled manner. Only at oxygen concentrations of 14 per cent and greater were high temperatures realized and pyrophoric behaviour observed.

A further important finding in this laboratory work was that pre-exposure of sulphide to relatively low concentrations of oxygen could suffice to prevent pyrophoric activity when the oxygen concentration was subsequently raised to atmospheric values.

Mechanistic studies, which will be described more fully in a future paper, suggest that the intermediate product undergoing pyrophoric oxidation may be ferrous oxide (FeO).

It appears that as well as being formed by the thermal reaction of FeO(OH) with sulphur, there may be another route for FeO formation arising from the direct oxidation of a sulphide, possibly Fe_3S_4 (greigite).

10. ON-BOARD TESTS

Tests carried out on board tankers carrying Qatar crude have provided information that is consistent with our laboratory findings and the predictions made therefrom. In addition, the tests have provided information concerning the nature of the ullage gas composition and the changes that it can undergo during passage under non-inerted conditions. The climatic pattern has been shown to play an important part. Not only can it promote conditions conducive to the production of reactive material, but it can also be responsible for inducing a screening mechanism via condensate effects whereby the likelihood of pyrophoric activity is much reduced.

In the course of such tests, ullage gases extracted at different stages of a voyage were used to treat samples of model oxide α-FeO(OH). In this manner it has been possible to confirm at what stage, during passage, the composition of the ullage gas can favour the formation of reactive deposit

and to relate this information to the above mentioned factors. A full description of this aspect of our study is, however, beyond the scope of the present paper and will be covered in a future publication

11. CONCLUSIONS

1) Rust of a type found in the ullage regions of cargo tanks can react with hydrogen sulphide at ambient temperatures to form a material that, on exposure to air, undergoes spontaneous pyrophoric oxidation and can accordingly act as a source of ignition in circumstances where the incandescent material comes into contact with combustible vapours.

2) The reactive material can form in atmospheres of nitrogen or hydrocarbon (propane) containing hydrogen sulphide at concentrations comparable with those that can occur in the ullage regions of cargo tanks of vessels transporting Qatar crude, for which the hydrogen sulphide content of the ullage gas can be as high as 5 per cent by volume.

3) The reactivity of the sulphided model oxide (initially α-FeO(OH)) towards aerial oxidation declines according to the number of cycles of sulphidation/oxidation that it has undergone. The decline in reactivity can be attributed partly to a progressive build-up of elemental sulphur in the system and partly to changes in the geometry of the particles constituting the oxide aggregates, such changes leading to a reduction in surface area of the oxide.

4) Apart from the above mentioned factors, the presence of occluded oil and water can also serve to reduce, by their direct screening effect, the reactivity of sulphided material towards aerial oxidation and in this manner prevent pyrophoric activity.

5) For the gas/solid reaction, the formation of reactive sulphide from rust can be avoided by ensuring a concentration for hydrogen sulphide/oxygen, $[H_2S]/[O_2]$, less than unity. Under these conditions, controlled oxidation can proceed concurrently with sulphidation, thus leading to the simultaneous generation of sulphur and the screening effect derived therefrom. The validity of this ratio requirement has been established for hydrogen sulphide concentrations ranging from 1 to 3 per cent by volume.

6) In the presence of condensate water, maintaining a concentration ratio $[H_2S]/[O_2]$ in the gas phase less than unity no longer suffices to prevent the formation of a reactive sulphide. Preferential solubility of hydrogen sulphide in water dictates a concentration ratio $[H_2S]/[O_2]$ of the two gases in the aqueous phase of about 400 : 1.

Material formed by the aqueous route, after drying in an inert atmosphere, oxidizes pyrophorically on exposure to air at ambient temperatures.

7) Laboratory tests have shown that control of the oxygen concentration in the gas phase during the oxidation of sulphided material can serve as a means of avoiding pyrophoric activity. The threshold oxygen concentration in atmospheres of nitrogen was found to be 11 per cent, at and below which value oxidation of sulphided material proceeded slowly in a controlled manner, thus preventing the high temperatures associated with oxidation by the pyrophoric route.

8) Onboard tanker tests have provided detailed information on the nature of the ullage gas, the compositional changes that can result from oxygen depletion/replenishment processes and the effect of condensation associated with climatic conditions. This information, taken in conjunction with the principles established in laboratory studies, provided a guide to the selection of conditions least likely in practice to lead to the production of pyrophorically reactive material in the cargo tanks of vessels transporting Qatar crude oil.

12. DISCUSSION

The work described serves to emphasize the relative ease with which pyrophoric material can form as a result of the interaction of hydrogen sulphide with rust in suitable form.

The optimum conditions for the formation of pyrophoric material have been identified in laboratory studies and it has been further demonstrated in on-board tests that these conditions can be realized in practice.

In the absence of screening effects pyrophoric oxidation of the reactive material occurs on exposure to air at ambient temperature. The hazard thus arises in those circumstances where inflammable gas mixtures can encounter deposits that

are in a state of incandescence. The early stages of cargo discharge under non-inerted conditions can provide just such circumstances.

The incidents recorded represent an extremely small proportion of the total number of cargo tanks containing Qatar crude oil that have been discharged at Sriracha over the years (a rough estimate provides a figure of about 12 000). That incidents arising from the presence of pyrophoric material are not more frequent can be attributed to the interplay of factors that can either reduce the likelihood of formation of reactive material or else suppress its oxidation by the pyrophoric route. Low concentrations of hydrogen sulphide, high concentrations of oxygen and a low vapour pressure of the crude oil are all desirable characteristics likely to disfavour the production of pyrophoric material in cargo tanks. Qatar crude unfortunately is characterized by a high hydrogen sulphide content (ullage gas can contain as much as 5 per cent by volume) and by a high vapour pressure; TVP values of 0·86 bar (12·5 lbf/in^2) at 32°C (90°F) have been recorded for this crude indicating a cargo derived gas content in the ullage of about 85 per cent by volume. If at atmospheric pressure the remaining 15 per cent is assumed to be air, then this would correspond to a maximum value of 3 per cent by volume for the oxygen content. Oxygen depletion processes can reduce this value; hence for a Qatar crude the requisite hydrogen sulphide/oxygen volume ratio well above unity for the gas/solid reaction leading to the production of pyrophoric material can readily be realized.

Sulphur build-up arising from repeated sulphidation/oxidation cycling, together with the presence of occluded oil or water constitute the agencies that can in practice suppress oxidation by the pyrophoric route.

The role of water is of particular interest; it is at least threefold. It takes part in the formation of the hydrated oxide, its presence provides an easy route for the formation of reactive material and by its "screening" role it can prevent pyrophoric oxidation.

From a practical standpoint, a complete solution to the problem depends on the extent to which the above-mentioned factors can be controlled. if, for instance, the presence of rust (α-FeO(OH)) could be completely eliminated in all the upper tank regions by say the application of a highly effective durable paint system then this measure alone would decrease the likelihood of pyrophoric material forming. Such an effective treatment is however not readily available, hence the presence of accumulations of rust must be accepted as possible if not inevitable. The amount of hydrogen sulphide and the hydrocarbon vapour pressure are characteristics of the particular crude oil and these likewise are beyond any imposed control.

If practical, continuous maintenance of a sufficiently high O_2 concentration in the ullage gas would appear to offer a possible solution for non-inerted vessels. In an empty tank or a cargo tank that has been ballasted before loading, a high oxygen content will normally obtain. The oxygen in the tank becomes the sole agent available for promoting deactivation of the sulphide as it is formed during and after loading. The oxygen content is, of course, reduced as a consequence of the gas-liquid equilibrium of the hydrocarbon — the extent and rate of equilibration are clearly important factors in determining the oxygen content of the ullage gas at these early stages.

Two other factors are important in determining oxygen content, firstly, the extent to which oxygen depletion involving the cargo occur and secondly, the incidence of tank breathing during loaded passage — in this latter case, climatic factors can play an important part.

If, during passage, extremes of temperatures experienced are such that the pressure limits for operation of the PV valves are not exceeded, and assuming no leakage, then at no stage will air/oxygen be admitted to the tank and according to the oxygen-absorbing propensity of the cargo, a zero or near zero concentration of oxygen may obtain for the greater part of the voyage. Such conditions, which also entail a low humidity, may well give rise to the production of unscreened reactive deposits.

If, on the other hand, conditions are such that the frequency of tank breathing is sufficient both to outstrip the rate at which oxygen can be removed by cargo absorption, and to maintain its concentration near to its maximum

theoretical value of about 3 per cent by volume, (corresponding to 85 per cent hydrocarbon in vapour — see earlier discussion) then the product so formed by the sulphidation of the rust in ullage atmospheres where the H_2S concentration is less than 3 per cent by volume, would not, on the basis of laboratory experiments, be expected to show pyrophoric behaviour at ambient temperature, provided reaction occurs by the gas/solid route.

Where inert gas is used to control the ullage gas atmosphere, several important points arise in the light of our studies. If, for instance, the oxygen content of the inert gas in the tank prior to loading cargo is about 4 per cent (a typical value when scrubbed boiler flue gas is used) and the tank is kept pressurized with inert gas during the subsequent loaded passage, then the oxygen concentration of the equilibrated ullage gas, assuming a hydrocarbon content of about 85 per cent by volume, is unlikely to exceed about 0·6 per cent by volume.

In the presence of α-FeO(OH) and H_2S this low concentration of oxygen, which may be reduced further by cargo absorption, could provide, from the outset, conditions conducive to the formation of reactive deposits. Also, the fact that the inert gas may be water saturated and give rise to greater amounts of condensate could provide for the formation of reactive material via the "easy" aqueous route irrespective of oxygen content. In these circumstances it would appear vitally important to prevent any sudden ingress of air during cargo discharge by ensuring an adequate supply of inert gas to the tank throughout this operation.

Screening of tank deposits provides the only other route to the prevention of pyrophoric activity. The inherent screening arising from the presence of free sulphur in a deposit will depend entirely on its history, i.e. the number of sulphidation/oxidation cycles to which the deposit has been exposed. Whilst this will dictate the amount of sulphur build-up, i.e. screening, there is also evidence to suggest that processes may occur in the ullage regions whereby sulphur may be segregated from sulphided deposit as a result of either mechanical separation or solvent elution effected by tank condensates. Sulphur screening cannot for such reasons be considered as providing a completely governable method of controlling the oxidation of reactive material.

Aqueous condensate is another agent that can provide a screening effect. Whether condensate is present will depend on the temperature profile of the particular loaded voyage under consideration, and for this reason is an uncontrollable device for disfavouring pyrophoric oxidation.

Although oil wetting has been demonstrated in the laboratory to be an effective method of preventing the pyrophoric oxidation of a reactive sulphided deposit, as a practical procedure it would be difficult to apply. By cargo "rolling" or even spraying, it could not be guaranteed that inaccessible regions where deposits might accumulate could be thoroughly wetted, and whilst any untreated reactive material remained, however small in amount, the risk of ignition by pyrophoric activity would exist. A further point worthy of mention in considering oil screening is the fact that if by chance, immediately prior to oil spraying, the reactive material were to be water saturated through condensation effects in the tank, promoted by a particular climatic pattern, then it is unlikely, on account of the hydrophilic nature of the deposit, that oil would displace the already adsorbed and absorbed water, in which case its application would be ineffective.

The extent of screening that normally prevails in practice is thus fortuitous, arising from a combination of uncontrolled conditions, e.g. deposit history, cargo properties, climatic factors etc.

It is appreciated that certain fundamental chemical aspects of the problem have not been discussed in the present paper. The identity of the reactive sulphide is, for example, one topic on which contradictory views have been expressed in the literature.

It is the authors' intention to deal with such aspects in a future publication devoted to the chemistry of the sulphidation/oxidation cycle. In the meantime, the use of the term FeS and Fe_2S_3 should be viewed as a convenient simplification.

The Generation of Pyrophoric Material in the Cargo Tanks of Crude Oil Carriers

Messrs. A. D. Steele and B. W. Forster who have carried out much of the laboratory work described in this paper.

They thank various members of the Analytical Division of Thornton Research Centre for providing technical assistance and also acknowledge the co-operation of colleagues in Shell International Marine Ltd. with whom many helpful discussions have been held.

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Discussion

MR. C. A. SINCLAIR, F.I.Mar.E., said that after reading the paper one was left with certain questions unanswered, such matters as at what stage during the passage could the composition of the ullage gas favour formation of reactive deposits (after all, one might be talking about quite a limited time). It was noted that a full description of this aspect would be gone into in a future publication which would probably be, in scope, somewhat beyond the understanding of the average marine engineer but was, nevertheless, awaited with interest.

It was noted that pyrophoric material could form as a deposit in distillation systems and that this was no new problem to the oil industry. Perhaps also it was an older problem in the marine industry than had been generally realized, in areas other than tanks. Years ago, many fires taking place in boiler air heaters were generally attributed to the negligence of the engineers or faulty operation, although it was admitted that deposits showed proportions of ferrous sulphate as high as 74 per cent. Most of these fires occurred shortly after shutting down the plant, at reduced steaming, or upon reactivating, and it might well be that availability of oxygen and the prime cause was rather similar to that described in the paper in relation to the tanker explosions. Bell stated, in his paper*, that it was conceivable that, with the limited supply of oxygen available in the flue gases, and even lower supply available under the deposits, ferrous oxide might be formed. Ferrous compounds oxidized readily and, indeed, impure ferrous oxide ignited spontaneously at room temperature. Did the authors feel free to comment on this matter?

Similar phenomena to those now reported had also been previously noted in sulphur storage tanks, and could possibly have been the reason for fires with the subsequent loss of some sulphur carrying vessels.

Speaking in particular with regard to the carriage of the Qatar crude oil with its high hydrogen sulphide content, it was noted that the problems had been few and only two reported cases were reviewed, it having been necessary for several factors to play a part. With the advent of new oil fields scattered throughout the world was it not possible that further problems would occur as similar oils were found in other areas?

Throughout the paper, in discussing this problem, it was noted that the authors made no particular reference to the thickness of scale or depths at which reactive deposits might occur. He wondered whether this might be relevant and whether, in fact, periodic descaling to avoid excessive thicknesses of deposit might be adequate to avoid incurring this particular hazard, or whether the screening provided by the scale minimized the risk.

Turning to the authors' conclusions, it was noted that a relatively low concentration of oxygen could suffice to prevent pyrophoric activity when the oxygen concentration was subsequently raised to atmospheric values. This would seem to suggest that in non-inerted ships it might well pay to maintain a certain controlled air supply over the top of the cargo during the passage.

It was understood that another owner reported a case where, when carrying high hydrogen sulphide crude and gas, a tropical storm cooled the deck. The P.V. valve probably admitted air into the ullage space and, later, a plume of sparks was seen coming from an improperly dogged down inspection cover. However, by the time fire fighting equipment was assembled, the event was over. Could this be from similar cause and was it possible that many unreported events

*Bell, A. 1960. "Corrosion and Fires in Marine Boiler Air Preheats". *Trans.I.Mar.E.,* Vol. 72, p. 309.

had occurred?

It was noted that the type of rust found in the ullage regions could react with hydrogen sulphide at ambient temperatures to form a material that on exposure to air could cause a source of ignition in circumstances where incandescent material came into contact with combustible vapours. It would seem, therefore, highly desirable that rust was, in fact, avoided.

The authors appeared to have little confidence in the prevention of this formation by the use of a painting system. However, with modern exotic coatings one would have thought this was an entirely practical proposition and with Shell's very considerable experience of these coatings it came as a surprise to find that the authors were sceptical of their ability to provide a solution.

The authors' reference to the ship's movement and operation of P.V. valves was interesting and, of course, did assume that this equipment was in proper working order. In view of the very many cases which come to the Salvage Association's attention, where this was not so, it was felt that a positive solution, as mentioned earlier, might be the answer to providing a sufficient quantity of oxygen in the tank at all times. The problem then arose, of course, as to whether in providing oxygen in order to avoid a condition of pyrogenic overheating, one might not provide an explosive atmosphere which would be ignited by some other source. Thus it would seem that gas monitoring would be necessary throughout the voyage in order to remain between the limits of what was necessary to avoid pyrophoric activity and yet remain below (or above) the explosive limit.

In Section 2 of the conclusions, the authors stated that the reactive material could form in atmospheres of nitrogen or hydrocarbon. This one would take to mean that even if the tanks were inerted, the reactive material could still form. Of course, no explosion risk would exist provided the inert gas was maintained during discharge and subsequently. This raised, of course, the whole question of the reliability of inert gas equipment, and some recent explosions on very modern ships had left considerable room for doubt as to whether the degree of reliability necessary had yet been attained. Before the authors' company had accepted the use of inert gas systems, they expressed considerable reserve as to the possibility of crews building up to a dependence upon such systems, with the result that insufficient care was taken in other respects and casualties followed. It would be interesting to know now that Shell were, in fact, using such systems and whether they felt their original attitude was justified.

DR. R. A. COLLACOTT, B.Sc. (Eng.), F.I.Mar.E., in a contribution read by Mr. R. G. Boddie, F.I.Mar.E., said that the hazards resulting from the generation of pyrophoric materials suggested that means should be possible for monitoring the extent and danger-potential of this material, such that a surveillance system could be included in the control of tank operation under such circumstances. During discussions among members of the UK Mechanical Health Monitoring Group, it had become apparent that there was a direct need for such monitoring facilities. Would the authors please state whether any efforts had been made to establish such facilities and the techniques used: alternatively could they state the operational, technical or commercial problems which had impeded the development of such monitoring techniques?

MR. G. VICTORY, President I.Mar.E., said that the best defence against danger was knowledge, and the history of tanker operations was a story of the identification of various forms of ignition of the flammable vapours in the cargo tanks

and those released from the tanks as a result of tanker operations. Too often such identification had been the result of a serious tanker casualty or casualties, and in each case research and investigation had had the aim of preventing similar occurrences in the future.

The Court of Informal Investigation which investigated the serious explosion which occurred in the British steam tanker *Mactra*, one of the three VLCC which suffered catastrophic in-tank explosions in December 1969, considered the possibility of fourteen sources of ignition and at least another three known possibilities which were ruled out as not appropriate to the case. One of the possibilities considered was the pyrophoric reaction of cargo tank deposits and although at that time little was known of this mechanism and no positive case had been identified, the conditions were such as to render this one of the less possible causes of the explosion. However, it was thought that some of the flash fires known to have occurred whilst chipping of tanks was in progress in repair yards might have been caused by breaking the crust on a pyrophoric scab of iron sulphide.

Now at least two minor explosions had occurred wherein it seemed that ignition from a pyrophoric reaction was the major probability, and the authors and their company were to be congratulated on the effort and energy put into determining the mechanism of the formation and self-heating of the products of reaction between iron, oxygen and sulphur, and of the limiting conditions on the formation and reaction of the products of the reaction. The improved knowledge gained could lead to the improved safety of tankers in general — a cause we should all support vigorously.

Finally, one had to consider how the possibility of a catastrophic explosion from this cause could be eliminated. This cause should not be taken in isolation. It was only one of the many possible causes — and a method or methods must be sought which would be effective in all known causes — and for all one knew, there were probably some not known yet. The paper had stressed quite correctly that no in-tank explosion could take place from any cause if the tank was effectively inerted and maintained in an inert state. The possibility of air entering the tank during changes in temperature or at the beginning of discharge should never happen with a well designed and effectively operated inert gas system, whilst if the type of crude oil and other conditions were conducive to the formation of sulphides, any gas freeing of the tanks should be preceded by purging with inert gas to reduce hydrocarbon vapours to a safe proportion, e.g. below the critical O_2/hydrocarbon ignition line, so that a flammable vapour could not be encountered during the dilution of the tank atmosphere by air.

Authors' Reply

In reply, the authors said that, as referred to in their paper, the on-board tanker tests, which would be described more fully in a future publication, included tests wherein, at intervals throughout the loaded voyage, samples of ullage gas were extracted and used to treat standard amounts of model oxide. Instances where the treated oxide produced a pyrophoric material thus identified the stages, during the voyage, when the composition of the ullage gas, which was also being monitored, was conducive to the formation of pyrophoric material.

The occurrence of pyrophoric material in locations such as boiler air heaters could not be completely discounted, since reactive material could originate via routes other than sulphidation. It was, for example, well known that ferrous oxide in a particular state of subdivision readily underwent pyrophoric reaction on exposure to air. It was thus conceivable that ferrous oxide, in the appropriate physical state, might form under certain conditions, particularly where there was a limited supply of oxygen. From the authors' laboratory studies it was also foreseen that certain conditions in sulphur storage tanks could give rise to pyrophoric activity.

The events referred to in the paper involved the transportation of Qatar crude, hence, in much of the experimental work, conditions appropriate to the properties of this material were always uppermost in mind. This crude was characterized by its high hydrogen sulphide content, and its high vapour pressure. These properties would simultaneously encourage a high value for the partial pressure of hydrogen sulphide (P_{H_2S}) and a low value for the partial pressure of oxygen (P_{O_2}) in the ullage gas. Both factors served to favour the formation of reactive material. It would thus seem logical to suppose that other crudes, displaying these similar characteristics, would be equally prone to give rise to the same hazards regarding pyrophoric activity.

No mention was made in the paper of the thickness of scale or depths at which reactive deposits occurred, since experience had shown that, when considering the ullage region, one was not usually confronted with a uniform deposit, but rather with zones where deposit loosened from adjacent regions could collect to produce pockets of variable thickness, as, for example, in the bends of stand pipes. The authors had mentioned the heterogeneous nature of the deposits, both physical and chemical and their view was that the most obviously dangerous were those which consisted of accumulated hydrated iron oxide of fine particle size. Regarding the depth at which deposits occurred, their evidence suggested that any deposit which occurred below the cargo level would be screened, even if in reactive form, by occluded oil so that, on subsequent exposure to air, the oil saturated material would be unlikely to undergo pyrophoric oxidation.

Periodic descaling might lessen the hazard. It would result, for example, in fewer sites in the cleavage fissures of laminated scales in which fine oxide could accumulate. It would, however, be no guarantee that the hazard was completely removed, since the existence of only the smallest amount of unscreened reactive material could constitute a potential source of ignition.

The observation that maintaining a relatively low concentration of oxygen could suffice to prevent pyrophoric activity, when the oxygen concentration was subsequently raised to atmospheric levels, emerged from the laboratory work and applied to small scale, well-controlled experiments. There were a number of difficulties to be borne in mind when extrapolating such results to the full practical case. Firstly, controlled oxidation of deposits could be interfered with if screening by condensed phases occurred. Secondly, inadequate distribution of oxygen throughout the ullage zone could well result in the production of localized pockets of inflammable gas; if reactive deposits were to be present in the cargo tank, then the poor oxygen distribution could allow oxygen-rich pockets to contact the potentially pyrophoric material and pyrophoric oxidation could result, possibly leading to an explosion.

For these reasons, the addition of air to maintain the oxygen concentration of the ullage gas at the requisite level to promote controlled oxidation, could itself introduce as great a hazard as it was meant to remove.

The reported case where a carrier, transporting high hydrogen sulphide crude, was subjected to deck cooling by a tropical storm, the effect resulting in a plume of sparks from an inspection cover, was of particular interest. In the light of the authors' findings, such an incident would be quite consistent with the following sequence of events. If, during the days preceding the storm, the oxygen content of the ullage gas had been severely depleted by cargo absorption, with little replenishment by "breathing" induced by climatic temperature and pressure variations, then in the presence of rust scale and hydrogen sulphide, one could expect the formation of pyrophorically reactive material. In the event of the tank humidity being low, the material would be unscreened (assuming also that there had been little sulphur build-up) and would thus be in its most potentially dangerous state. Reheating of the deck after the storm would raise the tank pressure, causing an escape of gas which swept out with it pyrophoric material which reacted with and ignited gas diluted by the atmosphere into inflammable mixture.

Mr. Sinclair rightly had taken the view that, since rust

was the necessary precursor for pyrophoric material, steps should be taken to prevent its formation and was surprised that this could not be achieved by an effective painting system. Whilst any means of reducing the amount of rust present was obviously a step in the right direction, the authors did not believe that painting would provide the complete answer, for the following reasons. Firstly, it would be difficult to ensure, during application of the paint, that complete coverage had been achieved in less accessible regions; secondly, abrasion damage could rupture the paint film. In both instances, sites would thus be available for the development of rust and reactive deposit. Thirdly, even if a perfect coating was achieved and which would remain perfect throughout the life of the ship, there was still a possibility of rust from other sources, such as ballast water being deposited on the coating surface.

Periodic descaling of surfaces might lessen the hazard. For instance, removal of laminated scale would leave fewer sites in which fine oxide could accumulate. However, descaling would not remove all rust and, in any case, its effect would be temporary and unpredictable.

It would not escape notice that the ullage areas they were concerned with were the least accessible as regards coating, maintenance of coatings and descaling.

Regarding Mr, Sinclair's reference to the preparation of reactive material in atmospheres of nitrogen and hydrocarbon, the purpose of this work was to examine to what extent the nature of the diluent gas could affect the reactivity of the pyrophoric species, formed in atmospheres where the partial pressure of hydrogen sulphide was similar. Inerting a tank,

the authors would emphasize, did not prevent the formation of reactive material; it could, in fact, in certain circumstances produce conditions more conducive to its formation by maintaining the oxygen concentration at a low level of about 0.4 per cent whereas, if the system were equilibrated with air, the concentration could be as high as about 2-3 per cent. Inerting could produce a further encouragement for the formation of reactive material by its tendency to maintain a higher humidity in the ullage atmosphere, so providing a greater likelihood for reactive material to be formed, via the aqueous condensate route. Thus, while inerting could under certain circumstances encourage the formation of reactive material that could act as a source of ignition, it did at the same time minimize the hazard by ensuring a non-inflammable atmosphere. However, in the event of inerting being improperly maintained, or its actually failing during the discharging operation, the risk of an explosion, in the light of the authors' findings, might well be increased in circumstances where cargo discharge and air induction continued.

Monitoring directly for the presence of reactive material in a tank would, in the authors' opinion, present an almost impossible problem on account of inaccessibility and the extreme heterogeneity in composition of deposits in different regions of the ullage space. For these reasons the approach adopted in their investigations was to assume the presence of the most effective precursor and then ascertain, from compositional monitoring of the ullage gas, at what stages the latter favoured or disfavoured the formation of pyrophoric material.