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14th September 2006

For the attention of Mark Aspinall

RE: Caustic Tank Washings, Abidjan, Ivory Coast

Dear Sir,

In accordance with your instructions of 7th September 2006 in connection with the above matter we advise on the following issues:

- "the chemical consistency of gasoline caustic washings, especially the nature of mercaptans",
- "the toxicity of such washings",
- "the correct method of disposal",
- "the environmental and health impacts of waste".

This report is prepared on the basis of the limited information currently available to us and accordingly our views may change in due course.

1. Introduction

1.1 Three cargoes of approximately 28,000mts of coker naphtha were loaded at Brownsville, Texas by Mt Seapurha (20th March 2006), Mt Moselle (25th April 2006) and Mt Seavinha (1st June 2006). All three vessels subsequently transferred their cargoes to Mt Probo Koala (11th April, 19th May and 18th June respectively).

1.2 In order to reduce the sulphur content of these cargoes, on-board washing took place. To each cargo, 50m^3 of caustic soda ($NaOH$, 33% aqueous) and 8kg ARI-100 EXL catalyst (Cobalt phthalocyanine sulphonate) was added. The mixture was circulated for 24hrs and allowed to settle before the caustic solution was drained to the slops tanks. In order to ensure complete removal, the bottom of the naphtha phase was also removed.

1.3 This process was found to have reduced the mercaptan sulphur content by approximately 47%, and the naphtha was subsequently used as blendstock to make finished gasoline.

1.4 The combined slops from these washing operations were reported as the following:

- 150m^3 $NaOH$
- 370m^3 treated naphtha and free water
- 24kg ARI-100 EXL catalyst.

1.5 It appears that some or all of these slops were disposed of at waste sites in and around Abidjan, Ivory Coast approximately in August 2006. This is alleged to have caused, or in part contributed to, a high incidence of health problems being reported, including nausea, breathing difficulties, vomiting and diarrhea.

2. Technical Discussion

In this section we provide explanations of the various technical aspects arising in consideration of this case.

2.1 Coker Naphtha is a hydrocarbon fraction that has been treated by "coking", a thermal cracking process that produces a straight-run petroleum (C5-C7) fraction from lower value heavy residual oils.

2.2 Mercaptans are organic compounds containing Sulphur, which are also known as thiols. They are analogous to alcohols (e.g. CH_3CH_2OH is ethanol, CH_3CH_2SH is ethanethiol). As a class of compounds they are distinguished by their extremely unpleasant odour. Ethanethiol (ethyl mercaptan) can be detected by humans in concentrations as low as 0.2 parts per billion in air. It is a component of the skunk odour defence described as an intense rotten egg smell and was declared the "World's Smelliest Substance" by the 2000 Guinness Book of Records. It is added in very small quantities to natural gas to allow users to detect leaks.

2.3 The process of the caustic washing of refined hydrocarbons to remove mercaptans and certain other sulphur components, sometimes known as sweetening, is achieved in refineries by the Merox reaction (MERcaptan OXidation).

2.4 **The Merox Reaction**

The first stage of this process is the reaction between Sodium hydroxide and any mercaptans (thiols) present (Equation 1):

$$\mathbf{RSH + NaOH \leftrightarrow RSNa + H_2O} \qquad (1)$$

Where R= hydrocarbon chain.

The product of this reaction is then oxidized in the presence of a catalyst (Equation 2). (In the subject case, the catalyst used was ARI-100 EXL.)

$$\mathbf{4RSNa + O_2 + 2H_2O \rightarrow 2RSSR + 4NaOH} \qquad (2)$$

The products are allowed to separate and the sodium hydroxide fraction is removed. In a refinery it is then regenerated - the waste products are oxidised to relatively harmless sulphates which can be handled by wastewater treatment facilities and the sodium hydroxide returned to the beginning of the process.

2.5 In our view the exercise onboard the Mt Probo Koala was an attempt to replicate this refinery process at sea.

3. Health and Environmental Impacts

In this section, outline information is provided concerning hazard constituents likely to be present in the residues/slops produced by the process conducted on board the vessel. The concentrations at which these compounds are likely to have been present are currently unknown although, as will be seen below, we have made some relevant calculations.

3.1 Sodium hydroxide (NaOH, aqueous solution) is corrosive and can cause severe burns on contact with skin. Any inhalation of mist would lead to burns within the respiratory system.

3.2 ARI-100 EXL (Cobalt phthalocyanine sulphonate) is listed by the manufacturer as an irritant to eyes, skin and the respiratory system.

3.3 Coker naphtha is volatile and flammable and a possible irritant.

3.4 Alkyl mercaptans (Thiols) are flammable liquids (ethyl-, propyl-) or gas (methyl). They are present in coker naphtha at around 2000ppm. Their toxicity increases with decreasing carbon chain length. Exposure to methyl or ethyl mercaptan can lead to a cough, headaches, nausea and breathing difficulties. All have a strong unpleasant odour. Occupational exposure limits are around 0.5ppm in air. Contact with acid will lead to hydrogen sulphide production.

3.5 Sodium alkyl mercaptides (sodium alkanethiolate, RSNa) are flammable solids that are soluble in water. They are the product of the reaction between mercaptans and sodium hydroxide. As with the mercaptans, toxicity increases with decreasing carbon chain length. Sodium methyl mercaptide (CH_3SNa) is harmful by ingestion and inhalation, corrosive and toxic. Contact with skin can lead to permanent ulceration.

3.6 Sodium hydrosulphide (NaHS) is the product of the reaction between hydrogen sulphide and sodium hydroxide. It is harmful, toxic by inhalation and ingestion and can lead to production of H_2S gas. It will cause skin ulceration and possible corneal damage.

3.7 Sodium sulphide (Na_2S) is a by-product of the reaction. It is soluble in water and is corrosive and harmful. Inhalation of mist may lead to lung damage. Contact with acid will produce H_2S gas.

3.8 Dialkyl disulphides (RSSR) are the product of equation 2. They are not soluble in water. Dimethyl disulphide is flammable and is judged to be very toxic to humans and dangerous to the environment.

3.9 Hydrogen sulphide (H_2S) is a corrosive gas. It is highly toxic. At low concentrations the gas has a strong unpleasant odour. UK Occupational Health guidelines allow exposure to 5ppm for 8 hours or 10ppm for 15 minutes. Between 20 and 100ppm the ability to smell the gas is lost. Negative health effects, such as eye irritation may be observed from as low as 20ppm. Prolonged exposure at these low levels may result in pharyngitis and bronchitis. Between 250 and 500ppm, pulmonary oedema may occur. Above these levels, other effects may occur such as vomiting, breathing difficulties, loss of consciousness and death. A single breath of 1000ppm concentration in air may be sufficient to induce a coma and death.

3.10. There are other components of the naphtha, such as phenols, which may react with the sodium hydroxide to form further harmful chemicals.

3.11 The above comments relate to the likely effect on humans of the compounds mentioned, they would also have a severe and negative effect on soil and aquatic flora and fauna due to their acutely toxic properties and high COD.

4. Discussion

In this section, the specific details relating to the discharge in Abidjan are discussed.

4.1 Although we have little detail of events as they occurred in Abidjan, we understand that the residues and slops produced by the performance of the simulated Merox process on board were discharged from the vessel and found their way onto waste tips in or around Abidjan. By their very nature these residues/slops will have contained all of the potentially harmful substances listed in section 3 above.

4.2 These substances can be subdivided into categories; those that are harmful only on close contact, those that are volatile and may achieve concentrations in the air that are harmful at some distance from the location of the substance or that whilst themselves are only harmful on close contact but may degrade into other substances that are volatile that may cause harm at some distance. In the first category we would put sodium hydroxide (caustic soda), the ARI-100 EXL catalyst and the materials originating from the 'other components' of the naphtha referred to in point 3.10 above. In the second category we would put mercaptans, mercaptides, sodium hydrosulphide, sodium sulphide and dialkyl disulphides. All of these are liable to have noxious smells themselves and, by degradation, are likely to release hydrogen sulphide into the atmosphere.

4.3 Of course the quantity of each contaminant present in the waste and its concentration would be significant in determining the extent of any effects in the locale of the waste. No such information is available. However we have considered the situation concerning the whole cargo and made various calculations as follows.

4.4 Measurements taken before and after the washing process show that the total amount of mercaptan sulphur in the naphtha was reduced by 47%. This is equivalent to 72.765 tonnes of sulphur. This would have been initially converted into mercaptides, as demonstrated in equation 1. Some of these mercaptides would then have been converted into the relevant disulphides and remained in the naphtha, and some would have remained as mercaptides, or been converted to sodium sulphide or sodium hydrosulphide which would subsequently have been discharged with the water. The conversion rate for this reaction is not known in this instance, that is for this shipboard process, although clearly it is relevant because it dictates the quantity of sulphur compounds likely to be present in the waste.

4.5 To investigate this question we have considered the refinery process. The manufacturer of the ARI-100 EXL catalyst have produced approximate figures for the percentage of the waste products above that may be found in typical refinery caustic waste. These figures are shown below. Where a range is given, the highest number is used to indicate the maximum potential presence of each species.

Waste product	% of Waste by Weight	Mass in 285 mt slops on Mt Probo Koala (Tonnes)
NaOH (Sodium hydroxide)	10	28.5
Na_2S (Sodium sulphide)	2	5.7
NaHS (Sodium Hydrosulphide)	2	5.7
NaSR (Mercaptides)	4	11.4

(Suarez, 1996)

4.6 However, the reaction may not have occurred efficiently because of the high concentration of sodium hydroxide used. Research into the Merox reaction by Liu et al (2005) found that the optimum concentration for use in the sweetening of LPG was 2.75 moles/litre. Above this concentration, the reaction efficiency declined steeply and at 8.25 moles/litre , the conversion rate from mercaptides to disulphides was just 20%. The 33% aqueous solution used on the Mt Probo Koala was approximately 11 moles/litre. This was clearly well above the most efficient concentration and so limited conversion might be expected.

4.7 While it is not appropriate to apply these figures directly to the operations on the Mt Probo Koala, it is not unreasonable to surmise that there was a considerable quantity of mercaptide, sodium sulphide and sodium hydrosulphide dissolved in the aqueous phase of the slops, possibly far greater then found in refinery produced caustic waste.

4.8 The organic naphtha fraction that was also drained into the slops tanks (46.5% of the total volume according to the AVR analysis) would have contained some of the original mercaptans, at approximately 950ppm, along with some of the alkyl disulphides that are the product of equation 2.

4.9 The effect of the preceding is that the slop/residue waste discharged from the vessel is likely to have contained very high concentrations of noxious sulphur compounds dissolved in the water phase and high concentrations in the naphtha (hydrocarbon) phase.

5. The likely effects of improper disposal of such residues.

5. In this section we discuss the potential effects of such waste on people exposed to it as a result of improper disposal.

5.1 The most severe symptoms are likely to be experienced by those living and working at or near the dump sites who may come into direct contact with the liquid slops residues and high concentrations of gas. For these people, the possible consequences are burns to the skin, eyes and lungs, vomiting, diarrhea, loss of consciousness and death.

5.2 Of significant concern is that the sulphur compounds can break down in the environment and release hydrogen sulphide gas.

5.3 The high number of reported casualties suggests that, unless the waste tips are frequented by large numbers of people, the extensive presence of gaseous pollutants as the cause. This is clearly consistent with there having been a significant release of hydrogen sulphide gas. This would cause effects ranging from serious respiratory and eye problems at high concentrations near to the source through to discomfort and nausea brought about by the unpleasant smell in areas further from the source where the gas plume is more diffuse. These are the precise effects reported in this incident and we conclude hydrogen sulphide release to have been the likely cause.

6. Further Considerations

In this section we raise any matters that are pertinent to the issue and may require further investigation.

6.1 The company employed by the operators of the Probo Koala to dispose of this waste may have attempted to treat or partially treat the material before dumping. These attempts included the addition of acids, which may have seemed logical in order to neutralise the sodium hydroxide. Such actions would in fact have been inappropriate unless conducted under tightly controlled conditions as it would have exacerbated the production of hydrogen sulphide gas. Knowledge of any treatment attempts would be invaluable in determining the final constituency of the waste.

6.2 The waste site is likely to contain a variety of other compounds, some of which may have been toxic and reactive. This is especially likely if the sites have previously been used by the waste disposal companies for other, perhaps improper, chemical disposal operations. Information concerning the dump sites may help to identify the presence of other harmful compounds and which might have been partly responsible for this incident by reacting with the Probo Koala slops, or (and unlikely) even solely responsible.

6.3. Press reports of such incidents are notoriously unreliable and often overstate the problem. Further it is well known that 'mass hysteria' can cause a general over-statement of effect. It may well be that local enquiries may establish that the effects of the incident were less than have been reported.

7. Questions

In this section we raise questions that may be useful to investigate.

- Was the waste properly characterised before hand over to the waste disposal company?
- Were samples taken before or during the pumping to shore?
- Did the waste disposal company treat the waste in any way prior to disposal?
- Was the waste pumped onto the disposal site or dumped in containers?
- Have any samples (soil/water/air) been taken at the site since the dumping?
- Has any analysis of air samples in the affected area taken place to establish exactly what chemical species are present and causing the problems?

8. Further Action

8.1 Samples from the dumping locations and air and water samples from the surrounding area would aid the investigation and help to show whether the incident in question is partly or wholly responsible for the health effects reported, as would any analysis of the slops/residue waste before or during discharge. Sampling should be conducted carefully and to a proper program which would be entirely dependent on local circumstances. It should be born in mind that the sampling and any subsequent analysis should be capable of identifying other and unexpected contaminants to establish whether dumping of toxic wastes on the sites was a regular occurrence.

7.2 Information on the waste sites, including a summary of the types of waste disposed there, especially any toxic or reactive chemicals, would be helpful if available (which we doubt) to thoroughly establish the type and/or source of the pollution

8. Proper disposal regulations, as defined within the EU.

8.1 These compounds are hazardous, are so identified on the relevant manufacturer's safety data sheets and as such their disposal is governed in Europe by Council Directive 91/689/EEC on the Disposal of Hazardous Waste. This legislation describes the need to separate hazardous and non-hazardous waste and to report any waste disposal occurrences with full details of the type of waste and the method of disposal used.

8.2 The spent caustic waste produced on-board the Mt Probo Koala appears to have been dumped on terrestrial waste sites. This means that the incident would be covered in Europe by Council Directive 1999/31/EC, commonly called the landfill directive. Inspection of this legislation reveals that this dumping was in contravention of these regulations on several counts. The Landfill Directive prohibits the disposal of waste that is:

- liquid;
- corrosive or
- flammable.

One may therefore conclude that the landfill disposal of this waste, which is liquid, corrosive and flammable, would be forbidden in a European Union member state.

8.3 While it is possible to dispose of these compounds by incineration, the odour and potential harmfulness of the resultant fumes mean that this is not practical in populated areas. Ideally, the solution would be treated by "Wet Air Oxidation" during which the Chemical Oxygen Demand (COD) is significantly reduced and these compounds are oxidised to relatively harmless sulphates and carboxylic acids which can then be handled by standard wastewater treatment facilities.

8.4 So far as we are aware there are no local regulations special to Ivory Coast. However an ex member of our staff with whom we still work has recently toured African countries on behalf of the UN to discuss the establishment of such regulations. He advises that the intent of most Countries that he visited is to implement regulations similar to those applicable in Europe.

8.5. Consideration should also be given to the effects of the Basel Convention on the Transboundary Movement of Hazardous Wastes and their Disposal.

9. Conclusions

9.1 The slops produced during the caustic washing of three cargoes of Coker Naphtha, totalling $500m^3$, were identified as a mixture of "spent" NaOH, naphtha, free water and an organo-metallic catalyst used in the Merox reaction. This mixture was also likely to contain several reaction intermediates and by-products, including but not limited to Na_2S, NaHS, NaSR, RSSR and H_2S.

9.2 Appropriate disposal methods for such a material include separation and treatment using wet air oxidation followed by wastewater treatment.

9.3 The compounds listed above are capable of causing severe human health effects through inhalation and ingestion. These include headaches, breathing difficulties, nausea, eye irritation, skin ulceration, unconsciousness and death. There would also be a strong and unpleasant odour over a large area. All of these effects were as reported in this incident.

9.4 Some of these symptoms may only be experienced by those in direct contact with the waste whilst others are a consequence of gas inhalation. Some symptoms such as nausea may be a result of exposure to low levels of foul smelling fumes.

9.5 Other factors such as any treatment method adopted by the disposal contractor or the presence of other chemical waste on the site may have exacerbated the problem.

9.5 Under Council Directive 1999/31/EC, disposal of this waste onto landfill sites would be forbidden in a European member state.

This report was prepared prior to the arrival of documents providing details of events at the discharge port and will be updated in due course.

We trust that the above is of assistance and will be pleased to assist further as required.

Yours faithfully,
Minton, Treharne & Davies Ltd.

John Minton.

References

Suarez, F. J. (1996) Proper use and spent solution management ensure the safest and most cost-effective operations. Hydrocarbon Processing

Liu, R., Xia, D., Xiang, Y. and Tian, Y. (2005) Effects of Caustic Concentration on LPG Sweetening. Petroleum Science and Technology, **23**: 711-721