FIRE SERVICES EXAMINATIONS BOARD

STUDY NOTE

EXAMINATION	STATION OFFICERS' EXAMINATION
PAPER	OPERATIONS
SUBJECT	FIREFIGHTING AND RESCUE INCIDENTS
ITEM	PETROCHEMICAL INCIDENTS
STUDY NOTE No.	3107

INTRODUCTION TO THE STUDY NOTE

This study note has been prepared as the basis of study in connection with the qualifying examinations for promotion.

Candidates will be expected to demonstrate knowledge of the information contained in the study note and understand how it should be applied:

The 'References' made at the end of the Study Note are included for information only and candidates will not be expected to study these as part of the bibliography.

PETROCHEMICAL INCIDENTS

1. Introduction

Oil refining in the United Kingdom is one of the countries largest industries not only providing a source of energy but as the basis of thousands of chemicals, plastics, man-made fibres and detergents.

Although not all fire brigades have oil refineries within their boundaries the majority will come across the products, bi-products or transportation of them.

This study note complements the other study areas for this subject ie

The Fire Service Manual Volume 2, Fire Service Operations, Firefighting Foam:
Chapter 7 - Storage Tank Fires; and
Chapter 8 - Logistics of Dealing with Large Storage Tank Fires.

The Study Note expands on:

(a) General characteristics of mineral oils;

(b) Additional safety information regarding fires in oil refineries; and

(c) Information regarding fires in tanks under repair or demolition.

2. Characteristics of Mineral Oils

Crude oil is a naturally occurring mixture of organic chemicals obtained from beneath the surface of the earth. It consists mainly of hydrocarbon (compound of hydrogen and carbon) together with small proportions of other chemicals, containing sulphur, nitrogen, oxygen and other metal compounds.

The crude oil is generally found as an unstable, highly flammable, corrosive liquid. It has a black colour, an objectionable nauseating odour and it is normally in a flowable form.

It is essential for firefighters to have a good knowledge of the characteristics of mineral oils, and to be able to identify the conditions in which, given a source of ignition, hydrocarbon vapours will fire or explode.

3. Vapour Formation

Petroleum oils at temperatures below their boiling point vaporise only at the surface and in the presence of a vapour space. If the liquid is contained in a closed vessel, vaporisation will occur until the vapour space is saturated at that particular temperature, ie, until the space contains such a concentration of the vapour that condensation occurs at the same rate as vaporisation. *When this condition obtains, the liquid and the vapour are said to be in equilibrium.*

The vapours produced tend to mix more or less readily with air or other gases in the vapour space, and if they are left alone, the space will eventually contain a homogeneous mixture of all the gases contained in it.
This tendency of gases to mix is called diffusion.

The tendency of liquids to vaporise takes place more quickly with some liquids than others. For instance, a small quantity of ether will vaporise almost immediately when exposed to air; petrol requires a longer time, whilst water will take longer still. *This tendency of a liquid to vaporise is called its volatility*.

4. Flammable Limits

It is the vapour which is given off from a flammable liquid that burns when combined with oxygen from the air. Oil, which is not vaporising or has no vapour space above it, cannot burn. Moreover, the air and vapour must be in certain proportions in order to burn. The concentration varies for different vapours.

For information purposes only, the flammability range of petrol vapour in air is between 1.4 - the lower limit, and 5.9 - the upper limit, per cent of petrol vapour by volume; ie. petrol vapour requires a maximum of 98.6 per cent and a minimum of 94.1 per cent of air to support combustion.

A gas (or vapour) with wide limits of flammability is potentially more dangerous than one, which has a narrow flammable range.

5. Flash Point

The flash point of a liquid is the lowest temperature at which sufficient vapour is given off to flash on the application of a flame in the presence of air. The flame can be an arc, spark, naked flame or any other source of direct ignition. The flash point of some hydrocarbons is well below freezing point; petrol for example, has a flash point of about –45 degrees centigrade.

6. Self-Ignition Temperature

It should be noted, however, that heat alone could be a source for the ignition of hydrocarbon vapours without the application of a naked flame. For this to take place a source of heat must be provided.

The temperature at which this will occur is called the self-igniting temperature (sometimes it is called the auto ignition temperature) this is the lowest temperature to which a solid, liquid or gas requires to be raised to cause self-sustained combustion without initiation by a spark or flame.

If, for example, some petrol vapour which is leaking and is diluted with air to within its flammable range, comes into contact with a source of heat such as hot brickwork or pipes which are above 246 degrees centigrade then ignition will occur automatically.

This is why if a non-cooling extinguishant such as chemical dry powder is used on a petrol fire, the flame may be quenched; but if there is an incandescent source of ignition or sufficient residual heat build-up, the vapour will almost immediately re-ignite if application of extinguishant is discontinued, before cooling by water spray or blanketing with foam is commenced.

7. Safe Dilution Point

Most petroleum vapours are heavier than air and will travel considerable distances following contours of the ground, depending on wind strength and direction. The further the vapours travel from the point of escape, the more the vapours will be diluted with air until the volume of air will cause the mixture to become outside the flammable limit.

The safe dilution point for petroleum vapour is generally accepted as 15 metres from the source of emission, but in assessing the safety margin, the wind and prevailing conditions *must* be considered. Any heavy emission of vapour could, in favourable downwind circumstances, dilute at greater distances than this, spreading over a wide area to a vapour to air ratio within the flammable range. If such a vapour cloud flashes over, the flame will propagate very rapidly over the whole of the vapour trail back towards the source of leak, and may cause a number of fires in its path.

8. Toxicity

Apart from the flammability of petroleum oils, another important hazard is toxicity. The nature of the toxic hazards arising from hydrocarbons depends on the composition of the fraction, and the important fractions are hydrocarbon gases containing benzene and heavy aromatic oils.

For information purposes only air containing only 0.1 per cent by volume of hydrocarbon vapour can cause irritation to the nose, ears and throat; heavier concentrations can cause dizziness and unconsciousness. A 0.5 per cent concentration could prove fatal.

9. Extinguishing Fires in Refineries

Many fires at large refineries are often successfully dealt with by the refinery firefighting personnel, and the role of the local authority fire brigade is generally one of reinforcing refinery firefighters when larger fires occur.

The technical knowledge of refinery fire officers can be invaluable to a local authority fire officer if that officer has to command a large fire at a refinery. Good liaison is therefore essential.

Firefighting, to be effective, involves both fire control and fire extinguishment.

Prevention of fire spread often determines the success of extinguishing efforts. This involves the protection of tanks, other structures and pipelines that are affected by radiant heat or by direct flame impingement. Cooling streams of water should be directed so as to give adequate water coverage without waste. The maintenance of adequate drainage of a fire area will prevent floating blazing oil igniting unfired areas, and often provides a means of removing fuel with consequent salvage of product and plant. The construction of temporary drains, ditches and dykes is also a phase of fire control, which is especially valuable if a boil-over becomes imminent.

Blanketing un-ignited pools of oil with foam will also guard against fire spread.

Fires in storage tanks can be extremely hazardous, and as a general rule firefighting personnel should ***not*** be allowed to go on to the roof of a tank.

Conditions on the top of a floating roof tank can be dangerous, especially when the pontoon is low, as vapour can collect above the pontoon if there has been a leak at the seal.

Successful fire extinguishment results from the systematic application of planned procedures. Those born of panic often add to the seriousness of the emergency, and at every stage, expert advice should be sought from operatives or refinery fire personnel who have a much greater and more intimate knowledge of the processes and risks involved. Refinery personnel will attend to such control procedures as elimination of fuel supplies by closing pipeline blocks or by re-routing flow elsewhere, depressurising systems, blowing down a complete unit or pumping out tanks.

A water displacement procedure may be suggested whereby water could be introduced into equipment from which flammable liquid is leaking, although this can only be done if the temperature of the hydrocarbon is below the boiling point of water, such action will be closely monitored by plant operations supervision.

10. Process Unit Fires

These are extinguished principally by fuel removal. This depends upon operatives being able to reduce pressure, introduce steam or nitrogen to the systems and to depressurise part or the entire unit involved. The area and intensity of the fire will indicate the proper method of extinguishment.

Small fires can be combated with dry powder or steam, and foam should be used where it can blanket the burning fuel.

Water in the form of fine spray is most effective on large areas or intense fires that threaten damage to supporting structures and adjacent equipment. Care should be taken in the use of water, as contraction may cause flanges and joints to leak, thereby adding more fuel to the fire. The water stream should be adjusted where necessary to very fine spray to lessen this danger.

Tower structures, such as fractionating towers, which form part of process units are often difficult to deal with on account of their height. The first step is always to get the feedstock shut off and the system taken out of service and depressurised. Water from spray branches may not have sufficient trajectory to reach fire at the top, and it may be necessary to use large solid jets which can be trained either to impinge on each other so that the spray is carried on to the structure, or so that they break up near the top of the structure and the wind or convection currents carry the spray to the tower.

The jets must not be played directly on to the structure. If quantities of oil are flashed to lower levels and continue to burn in pools, foam or dry powder should be applied. Large fire areas should be covered with water spray so as to protect supporting structures, especially while operatives attempt to control the supply of fuel.

Fixed deluge systems will be an added advantage.

It should be remembered, however, that water streams used on surrounding risks will soon flood the area and may float the contents of oily water drainage systems to the surface in a short time. To prevent flash over and immediate danger to personnel, a foam blanket should be laid down quickly and maintained even after extinguishment until all possible sources of re-ignition have been checked.

It should be remembered that where large quantities of water are being used, much of it will run to waste. It may be possible to recycle the water, ie, to use pumps at suitable places where their suctions can be set in to the wastewater, which can be directed back on to the fire.

11. Storage Tank Vent Fires

If a fire at a tank vent is burning with a yellow-orange flame emitting black smoke this indicates a vapour-rich condition within the tank that is above the flammable or explosive limits. This type of fire is usually dealt with by refinery personnel by smothering with steam, dry powder, carbon dioxide or wet blankets. Danger of an explosion is not indicated under these conditions.

If a fire at a tank vent burns with a snapping blue-red nearly smokeless flame this indicates a vapour-air mixture within the tank that is within the flammable range.

There is danger of an explosion should the flame reach the inside of the tank and no one should go on to the roof while this condition exists.

The vapour space of the tank might be converted into a vapour-rich condition by refinery operatives pumping liquid into the tank, thereby maintaining a positive pressure, or by the introduction of fuel gas or other light flammable products. When a vapour-rich condition is indicated by a change in the flame character to a smoky or yellow-orange flame, danger of an explosion has subsided. Extinguishment can then be attempted by smothering with steam, water spray, dry powder or wet blankets.

Any action to convert the vapour space within the tank into a vapour-rich condition should not be attempted by firefighters without prior consultation and agreement with responsible officials at the refinery, and then every precaution must be taken to prevent exposure of personnel to the danger of explosion.

NOTE:

Any attempt to extinguish a tank vent fire using only dry chemical must take into consideration that the pressure vacuum valve may have been damaged by heat from the fire and may not close after the flames have been extinguished. Under these conditions a P/V valve failed in the open position could enable *flash-back* into the tank if the fire is initially extinguished with dry chemical and re-ignition occurs. Flashback into a tank containing a flammable vapour/air mixture could produce an internal explosion resulting in the roof being blown off or severely damaged, with possible fragmentation.

12. Dike Area

Typical tank storage bunds in the UK are 3m high sloping sided earth banks topped with a 3-4m wide roadway. The height of the dike (bund) wall as measured from outside ground level should be sufficient to afford protection for personnel when engaged in firefighting and the wall should be located so that a reasonably close approach can be made to a tank fire to allow the use of mobile firefighting equipment.

In many cases, concrete stepped walkways are provided to give access to personnel.

As a general safe operating practice, diked areas should be treated as confined spaces during firefighting operations. Personnel required for *operational necessity* to enter a diked area, must follow standard procedures for safe entry and accountability.

A dike area fire can present the firefighter with many problems, not least radiated heat and in the UK British Standards recognise bunds/dikes as dangerous areas. It makes specific recommendations to protect bunds with foam.

13. Spill Fires

This type of fire can be most difficult to deal with especially if it is flowing and being fed by a storage tank or pressurised pipeline. The source of the leak should be identified and isolated as soon as possible.

Should the leak be continuous (eg tank bottom failure) refinery personnel will endeavour to take the equipment out of service, however emergency personnel must be aware that this action may be prolonged over a course of many hours.

Small fires can be blanketed with steam or dry powder, but care must be exercised to avoid surface disturbance and spreading the burning product.

Larger fires areas should be attacked using diffused water spray in order to protect supporting structures, this attack should be maintained until refinery personnel can control the flow of fuel, the inherent danger of flash-back should be remembered.

Large pools covering greater areas should be blanketed with foam using low expansion and medium expansion foam branches, firefighters making every effort to apply foam gently where possible using spray techniques to avoid surface disturbance.

With a flowing spill fire it is generally best to commence at the furthest point of the fire and work towards the source of spillage, it is good practice to form a deep blanket of foam beyond the farthest point at the lowest level so that flowing burning product will flow beneath it and be extinguished. Under certain circumstances it may be necessary to dig a trench or provide earthen dikes to retain burning product, sandbags may also prove adequate.

A further complication can be created when spillage enters the refinery sewer system, situations will arise where flammable liquid causes explosions within the sewer network flowing into interceptor bays (oil/water separators); under these conditions large foaming operations may well be required.

14. Loading Rack Fires

Fires involving road tankers or rail cars at a petrochemical plant usually occur whilst filling operations are in progress. Loading operations should be stopped immediately, loading pumps shut down, emergency isolation valves in product lines supplying the loading rack should be closed (depending on design this may be an automatic operation linked into automatic leak fire detection).

In the event of a fire situation, cooling water sprays from a deluge system, fixed monitors or portable trailer monitors should be used to provide protection, covering road tankers or rail cars.

In many gasoline road/rail facilities automatic foam deluge systems will be provided, supplemented by portable equipment.

Water from spray-branches should be maintained to cool the tankers and all metal parts and should be maintained after the flames have been extinguished until all danger of re-ignition has been eliminated, where foam has been used, ensure foam blanket is maintained (consider medium expansion foam for product coverage).

If possible close valves on a tank truck providing they are operable and accessible, to shut off supply of fuel to the fire.

Adjacent refinery equipment and other tankers should be protected by cooling. Where possible unaffected rail-cars should be removed from the vicinity.

15. Fire Management

Fires in refineries represent a major risk within the petrochemical industry, such incidents can pose a major threat to life and property not only to those persons on site but also to the surrounding community. When presented with a serious incident firefighters can exert some control over the sequence of events, to keep loss of life and damage to property to a minimum. This will be achieved through confinement control, established operating procedures, realistic meaningful training with a common understanding of tank design, fixed fire protection systems, tank firefighting techniques and fully understanding the value of firefighting foam concentrates. Close liaison between industry and local authority fire and rescue service is of paramount importance, and every opportunity should be taken to train together.

FIRES IN TANKS UNDER REPAIR OR DEMOLITION

16. Introduction

It should be borne in mind that there are many wharves or industrial concerns where flammable liquids are stored in tanks, and it is generally in these smaller establishments where the greatest risk arises as they do not always maintain the high standards of safety and efficiency which are to be found at the major refineries. The firefighting techniques which are suggested for dealing with fires in tanks under repair or demolition should be taken as applying to all establishments where such work is carried out.

17. Hazards

It is a requirement of Health and Safety Legislation that any tank or vessel which contains or has contained any explosive or flammable substance must be rendered inert before any welding, brazing or soldering or any cutting operation which involves the application of heat is started. The reason for this requirement is, of course, the very high risk of fire or explosion occurring where partially closed vessels which might contain flammable materials are subject to such operations.

Solid deposits tend to accumulate on the inside surfaces of tanks, or sludge forms in the base of a tank, and this can be as hazardous as the original contents. Furthermore, this may not necessarily be removed by normal processes of cleaning. In consequence, the demolition or repair of tanks is always a hazardous operation.

It must be borne in mind that substances not normally regarded as presenting an explosion hazard can give off flammable vapours when heated or as a result of reaction with other substances, and these flammable vapours can form an explosive or combustible mixture when mixed with air.

It is not practicable to give an extensive list, but examples are oils, paints, and the less volatile solvents etc. In some cases old deposits adhering to the internal surfaces or sludge at the base of a tank may in this way be more hazardous than the original contents.

For small vessels, such as motor car fuel tanks, and tanks up to about 27,000 litres), both vapours and residues can usually be readily removed by steaming out.

With larger tanks, the problem is somewhat different. Owing to the high heat capacity of the tank, steaming out cannot be relied upon to volatilise all residues unless very large quantities of steam are readily available. However, explosive concentrations of vapour in the tank can usually be eliminated either by forced ventilation using a blower or eductor system or, for vertical tanks, by natural ventilation by removing top and bottom manholes.

Ventilation by itself, however, will ultimately only remove the volatile materials present in the tank and will never remove the heavy ends or solid residues and tars. These types of residue themselves can contain considerable quantities of volatiles and unless they are removed, can and do give rise to a very high fire risk.

18. General Precautions

If the fire brigade is called to a fire which has broken out when a tank is being demolished or repaired it will be likely that the proper safety procedure has not been observed. (Although it is less likely, fire may occur in any empty storage tank not under demolition or repair; but the advice in the following paragraphs is equally relevant.)

The situation should be treated as potentially extremely hazardous.

Normally for a fire to be sustained in a tank there must be openings in the tank to admit air. If these openings are limited the fire may have extinguished itself before the brigade arrives. But even if the fire has apparently gone out, the vapour mixture in the tank may still be highly dangerous because the fire may have caused decomposition or vaporisation of residues which may produce a flammable or explosive mixture, probably with toxic hazards as well.

It should always be assumed that there is a risk of a violent explosion except when the top or end of the tank has been previously removed.

In no circumstances should personnel go on top of or inside a tank in which there is a fire or in which one has recently occurred unless it is essential for rescue purposes.

If it is essential to enter a tank, the probability of toxic hazards should be borne in mind and breathing apparatus should be worn.

If anyone is on top of a tank, they should be told to come down. Nor should anyone go on top of an adjacent tank unless it is essential for operational reasons.

No attempt should be made to open or close manholes or other fitments, because this may adversely affect the atmosphere in a tank. If forced ventilation is being used, for example by means of a blower or eductor, it should be switched off if this can be done remotely.

19. Firefighting Techniques

Neither water jets nor high or low pressure sprays must be directed into a tank in which there is fire (or a fire is suspected) because entrainment of flammable materials - ie gases or vapours - by the water can cause rapid mixing to give a *potentially explosive mixture*.

Similarly, the *cooling of* the outside of a tank in which vapour has been ignited should be avoided, because of the danger of an intake of air following condensation of the vapours inside the tank.

The action to be taken must in the final analysis depend upon the circumstances of each case, and be subject to a risk assessment.

In addition to deciding whether the situation is one in which one of the recommended firefighting procedures is appropriate, fire brigade officers should bear in mind that any attempt to tackle a fire will possibly involve some degree of risk to their personnel, and they must judge whether the need to save lives and/or to prevent further damage to the tank itself or the spread of fire to surrounding property justifies taking that risk.

In any event whether the fire is fought or allowed to burn out, action should be taken to protect persons in the area from the effects of a possible explosion and to minimise the effect of radiant heat on adjacent property and installations.

20. Fire in a Tank Being Steamed

If a fire occurs in a tank which is being steamed, the supply of steam should be maintained and, if possible, increased as a means of both inerting the tank and purging it of hazardous vapours. If this is unsuccessful, the fire should be allowed to burn out, notwithstanding the possibility of explosion. Water should under no circumstances be used in or on the tank, for the reasons given above in paragraph 19.

21. Fire in a Tank Not Being Steamed

If a fire occurs in a tank not being steamed, then, unless it is clear when the brigade arrives that the fire has gone out, one of the following procedures may be appropriate:

If there is a gas or vapour flame burning outside an opening on the top of the tank, an attempt should be made to achieve quick extinction by means of a high pressure jet from a distance in order to remove the risk of a flash-back. The jet should be swept quickly across the aperture, care being taken to avoid as far as possible large quantities of water either entering the tank or cooling the outside surfaces, for the reasons given above in paragraph 19. If the attempt shows no sign of immediate success, or after initial success the flame reappears, the attempt should be discontinued since the implication is that the primary source of the fire is inside the tank. In these circumstances the fire should be allowed to burn out notwithstanding the possibility of an explosion.

If there are signs of fire but no external flames are visible, the fire may have to be allowed to burn out notwithstanding the possibility of explosion.

If, however, a *bottom manhole is open*, and it is felt that, for example because of surrounding risks, the fire must be tackled, this may be practicable in the following circumstances. Assessment of the location of the fire within the tank will be difficult because only a very restricted view of the inside of the tank can be obtained from a distance, and even this is likely to be obscured by smoke. It is still possible that the source of the fire inside the tank may either be visible or can be confidently estimated from a safe distance. If so, and if the fire is at the base of the tank, low expansion foam may be introduced. If, however, the fire is higher up and high expansion foam is available, it can be used provided its application does not entail undue risk to personnel and is operationally feasible.

If available, the use of carbon dioxide may be considered as an alternative to foam, *but only if the tank is known to be on fire*, because of possible static hazards during discharge operation which may themselves give rise to fire or explosion. Even if the foam or carbon dioxide does not succeed in extinguishing the fire it should have the effect of restricting it. Whatever extinguishing agent is used, it must be introduced only at entry points that are already open at the base of the tank.

22. Fire in a Small Tank

If a fire occurs in a small tank (which as a general rule should be regarded as one having a maximum capacity of approximately 57,000 litres) which has only one manhole open, the fire can only be attacked by playing a low expansion foam jet through the manhole from a distance. It should be appreciated that this is a difficult operation to carry out.

23. Fire in a Tank with the Top or End Off

If the top or end of the tank has been completely removed, normal firefighting procedure with low expansion foam or water spray should be effective and there should be no risk of disruptive explosion. Water should not be used if light residues are present and likely to float.

24. Subsequent Action

In all cases the situation should be treated as hazardous. The period of danger must be regarded as lasting until the whole of the tank and its contents are cold - 24 hours should be sufficient for this. It will not always be easy to tell whether the fire has in fact been extinguished.

It must also be remembered that the atmosphere in a tank in which a fire has occurred may still be both explosive and toxic and strict precautions must be observed before such tanks are entered. The operator should be warned that it is essential that all materials involved in a fire should be removed from the tank or other positions before demolition or repair work is resumed. The operator should be advised to consult the Health and Safety Executive. The operator should be particularly warned against further use of any heating device until expert advice has been obtained.

References

Fire Service Manual Volume 2 – Petrochemical Incidents