SAFETY ASPECTS OF THE STORAGE OF HEATED BITUMEN

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Following investigative studies relating to fires and explosions in heated bitumen storage tanks in the USA, a number of suggestions were made concerning the possible presence of the components of the fire triangle. If such conditions exist then the need for inerting tanks held above certain storage temperatures can be demonstrated. Current practice relating to the handling and storage of bitumens in the UK has been examined. While the presence of flammable atmospheres for certain grades at existing storage temperatures has been confirmed, the role of roof deposits as an ignition source has not been established.
Keywords: bitumen; storage; fires; explosions;

INTRODUCTION

Until recently it was assumed that the storage of heated bitumen was safe as long as guidelines described in the relevant Code of Practice (1) were followed. The Code recommends handling temperatures which were primarily chosen to allow for ease of pumping and application eg mixing and spraying.

Following the investigation of a number of fires and explosions in tanks in the USA, Dimpfl (2) suggested that

(a) smouldering combustion could occur in the coke-like roof deposits, which look like black stalactites on the underside of the roof.

(b) the stalactites could act as sponges by collecting light hydrocarbons evolved from the surface of the heated bitumen.

(c) flammable atmospheres could exist inside the tanks' vapour spaces at existing storage temperatures.

From such an analysis of conditions inside storage tanks, it was apparent that the three components of the "fire triangle" could be present. If experimental evidence confirmed these suggestions then inerting the tanks would be an obvious step towards safe storage, by removal of most of the oxygen component.

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Also if the deposits were confirmed as potential ignition sources and flammable atmospheres were present in road tankers and rail-cars, then the practice of using compressed air to empty these vehicles should be discontinued.

CURRENT PRACTICE

Bitumen is stored at refineries, quarries, roofing-felt manufacturers and a range of smaller facilities relating to surface coatings industry. It is stored in a variety of sizes and types of tanks. Two main methods of heating are used, hot oil and electricity, the latter being used mainly in the smaller tanks at quarries. The storage conditions normally follow the guidance in the Code of Practice. Table I lists the currently recommended handling temperatures for a range of bitumens. These temperatures are based primarily on viscosity measurements and are chosen for ease of handling.

TABLE I

Recommended handling temperatures of selected bitumens

GRADE	Minimum pumping temperature °C	Typical bitumen temperature at time of application Mixing °C	Spraying °C	Maximum temperature °C
35PEN	125	175	-	220
50PEN	115	165	-	200
100PEN	105	155	190	200
200PEN	100	140	175	190
300PEN	95	135	165	190
85/25	165	210	-	230
95/25	175	210	-	230
105/35	195	220	-	230

Bitumen is transported by ship, rail and road. Road tankers are well insulated while rail-cars have auxiliary heating facilities, for use at depots during unloading.

Two main types of bitumen are employed - the Penetration grades used in asphalt manufacture and the Oxidised grades, characterised by their softening point (IP.58) and penetration (IP.49), used in the roofing and weatherproofing industry. The vast majority of static storage tanks in the UK are not inerted. Currently (1985) one company is employing combustion gas inerting for oxidised grades whilst two other companies use low pressure steam, either across the vent or in the vapour space. Inerted tanks are not used for penetration grade storage. The obvious aim of inerting is to minimise the oxygen availability; however 1-2% oxygen is estimated to be required to prevent the formation of pyrophoric iron sulphide inside the tank. It should be stated that the exact requirement is not yet fully determined, since anecdotal evidence suggests 4% oxygen may be required.

The build-up of roof deposits limits the capacity of tanks and regular maintenance is generally provided for both mobile and static tanks.

In an analysis of 14 incidents which occurred at quarries during the period 1972-1982, the causes were as presented in Table II. Heating systems were a significant factor in a number of these incidents.

TABLE II

Causes of fires at penetration grade storage areas in quarries 1972-1982

CAUSE	NUMBER
Overheating of pump bearing	1
Exposure of heating tubes	4
Presence of hot work eg welding on level indicator, use of blow-lamp to remove blockage	3
Ignition of vapour from header tank by hot gases from furnace	1
Presence of water	1
Thermostat failure	1
Lagging fire	2
Auto-ignition of residues near heaters in empty tank	1

THE INVESTIGATION

This was divided into two areas:

(a) on-site measurements of parameters in the vapour space in the tanks, and

(b) laboratory-based experiments on materials taken from the tanks and some simulation studies of both static and mobile tanks.

The on-site studies required the measurement of flammability, presence of oxides of carbon, oxygen depletion, vapour space temperature profile, ullage, bulk-liquid temperature and the collection of samples of the atmosphere, the bitumen and any roof deposits.

The studies carried out in the laboratory consisted of:

(i) characterisation of the bitumens:-

This consisted of the evaluation of penetration (IP.49), softening point (IP.58) and flash point (IP.34, IP.36) and the application of a series of standard thermal analysis techniques, including Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). Bitumens were also placed in a range of heated tanks and the flammability (% lower explosive limit) measured to allow comparison with on-site data and to carry out preliminary investigations of storage parameters. Auto-ignition temperature, viscosity and thermal conductivity of the bitumens were also measured.

(ii) Characterisation of the roof deposits:

This consisted of elemental analysis, DTA and DSC studies as well as a thorough investigation of auto-ignition and the chemical species evolved on heating of the deposits.

(iii) analysis of the vapour space atmospheres:

The technique of sampling, transportation and analysis developed previously for fire gases was employed (3). Essentially, the sample is collected in an initially evacuated glass vessel and after clamping is stored in solid carbon dioxide. The analysis is carried out using a combined gas chromatograph and mass spectrometer. The results are compared with on-site data obtained, using colourimetric tubes (Draeger), Orsat apparatus and a battery-driven Wilkes-Miran infra-red detector.

Various tanks and operational parameters were investigated, these included ullage, charging/discharging of contents, bulk-liquid temperature, method of heating, tank diameter (ie surface area of bitumen inside tank) and maintenance scheduling (ie presence of roof deposits).

THE INSTRUMENTS

Flammability was measured using a conventional MSA Gascope (Model 53), a Sieger gas analyser (Alarm Model 1602) and a "Snee" explosimeter (4). The latter measures the concentration of gas, mist or vapour in terms of the stoichiometric fuel concentration. The gas/vapour is burnt in a tubular reactor with a known concentration of oxygen, the drop in oxygen concentration gives a direct indication of the flammability of the gas/vapour. This method takes account of both condensible and non-condensible vapours. It therefore gives higher values for the % LEL than the MSA Gascope, which measures the non-condensible vapours and some condensible vapours. Oxygen levels were measured using an Orsat and a Servomex analyser (OA 150).

The thermal analysis equipment used included a Stanton-Redcroft DTA system (10° C min^{-1}) and a Perkin-Elmer DSC 2 (5° C min^{-1} and 10° C min^{-1}). The auto-ignition temperatures were found using a Koehler Instrument Company K270 apparatus, which is the basis of BS 4056. This test procedure is primarily intended for determining the ignition temperature of a vapour or chemically pure gas in air at atmospheric pressure. The procedure was, however, adapted to allow comparison of data obtained by placing bitumen and the coke-like deposits on a hot plate and noting the reading of a central thermocouple when glowing occurred.

The elemental analysis was carried out using a micro-combustion system while a Link Hitachi X-ray analysis system attached to a scanning electron microscope allowed the identification of particular elements present in the deposits. The viscosity and thermal conductivity measurements were carried out using a Brookfield viscometer and a modified Lees' disc assembly respectively.

The analysis of the tank atmosphere samples was carried out using a gas chromatograph coupled to a VG 70/70 magnetic scanning mass spectometer with data processing system based on a PDP-11 computer. The products eluted from the gas chromatograph are detected by flame ionisation and converted to quantitative yields using reference and published calibration data. The mass spectrometer data employs the reference library spectra of the National Bureau of Standards.

RESULTS

It is convenient to divide the experimental results into four sections:

(i) characterisation of the bitumens:

All bitumens decompose according to overall first order kinetics. The decomposition can be initiated at the currently recommended handling temperatures. The rate of decomposition was significantly reduced in a nitrogen atmosphere. DSC indicated measurable exothermic processes at temperatures in excess of 573 K (300° C). At lower temperatures the energy changes were very small. The onset temperatures were virtually independent of the heat-up rates used. The DTA study indicated no significant changes in the range 423-493 K (150-220° C).

Difficulties were encountered in detecting the flash point for some grades in the Pensky-Martens closed-cup apparatus. These may have been due to the rapid build-up of carbon dioxide in the space above the sample. All grades exhibited flash points in excess of 573 K (300° C), except a 105/35 oxidised sample, which flashed at 503 K (230° C). The auto-ignition temperatures for all grades of bitumen were found in the range 723-728 K (450-455° C).

The thermal conductivity of bitumens was 0.07 to 0.20 J m^{-1} $°C^{-1}$ s^{-1} at 295 K (22° C) to 312 K (39° C). The viscosity of bitumens increases exponentially with reduction in temperature. The lower the penetration the higher is the viscosity, and oxidised grades tend to have higher viscosity values than the penetration grades. Typical viscosity versus temperature data is presented in Figure 1.

(ii) characterisation of the roof deposits:

Analysis of the coke-like deposits has shown a typical composition of:-

85% carbon	9% hydrogen
0.7% nitrogen	3% oxygen

The remaining components are sulphur together with traces of metals (Fe, Cr, Cu, K). These metals possibly originate from the refinery processing of the feedstock.

Dimpfl suggested that the cokes exhibit a sponge-effect by taking up light hydrocarbons evolved from the surface of the heated bitumen. The cokes collected from storage tanks were heated to typical storage temperatures and the gases/vapours collected and analysed. Table III lists the organic products from a coke-like roof deposit from a storage tank containing 95/25 oxidised bitumen at 358, 408 and 493 K (85, 135 and 220° C).

Similar results were obtained from deposits from rail-cars, using an analysis range of C_1 to C_{10} (see Table IV).

The ignition source proposed by Dimpfl was the smouldering combustion of the stalactite deposits. The deposits taken from a range of tanks had auto-ignition temperatures of 658 to 773 K (385-500° C). However, a deposit from the underside of the roof in a refinery tank containing 35PEN bitumen had an auto-ignition temperature of 523 K (250° C) ie the sample glowed.

DSC also indicated that significant exotherms could occur at onset temperatures as low as 523 K (250° C) in the deposits from all grades of bitumens. DSC curves indicated the evolution of volatiles at temperatures as low as 348 K.

The X-ray elemental analysis attachment linked to the electron microscope detected substantial quantities of sulphur in comparison to trace amounts of iron in samples from the large stalactites. In a small number of smaller-sized deposits the iron and sulphur content could suggest that pyrophorics are present.

(iii) analysis of the vapour space inside storage tanks:

A typical on-site vapour space investigation consisted of:

(a) measurement of the tank dimensions, ullage and bulk liquid temperature.

(b) determination of the temperature profile in the vapour space of the tank between the inspection hatch and the bitumen surface. A typical profile is shown in Figure 2.

(c) measurement of the amounts of oxygen, carbon dioxide, carbon monoxide and hydrogen sulphide at various levels. The results (based on weighted average readings) for carbon dioxide and carbon monoxide for various grades and bulk liquid temperatures are presented in Figure 3.

TABLE III

Organic products from a roof deposit (95/25)

Compound	Type	358 K		408 K		493 K	
		Micro gm	Mass % Conv.	Micro gm	Mass % Conv.	Micro gm	Mass % Conv.
Methane	H			0.02	0.000	1.84	0.006
Acetylene	H	0.35	0.025	0.65	0.010	7.64	0.023
Ethylene	H	0.05	0.004	0.03	0.000	232.73	0.705
Ethane	H	0.02	0.001	0.11	0.002		
Propene	H	0.03	0.002	0.05	0.001	10.99	0.033
Propyne	H	0.02	0.001	0.38	0.006	9.04	0.027
Propadiene	H	0.04	0.003			1.16	0.004
Unknown	H	0.10	0.007				
Propane	H	0.17	0.012	0.40	0.006	29.04	0.088
Methanol	O	1.56	0.111				
Acetaldehyde	O	0.38	0.027	1.09	0.018	9.87	0.030
Butene	H	0.08	0.006	0.27	0.004	9.39	0.028
Butadiene	H	0.03	0.002			3.98	0.012
Butane	H	0.29	0.021	0.19	0.003	32.48	0.098
Acetone	O			0.12	0.002	7.10	0.022
Propan-2-ol	O					2.90	0.009
Acetic Acid	O					30.15	0.091
Pentene	H	0.07	0.005	0.33	0.005	4.02	0.012
Pentadiene	H	0.09	0.006				
Pentane	H	0.04	0.003	0.10	0.002	21.90	0.066
Crotonaldehyde	O			0.16	0.003		
Methylethylketone	O			0.03	0.000		
Cyclohexane	H					3.25	0.010
Hexene	H	0.22	0.016	0.25	0.004	2.58	0.008
Benzene	A			0.17	0.003	10.99	0.033
Hexane	H	1.58	0.113	0.79	0.013	16.96	0.051
Cyclohexadiene	H	0.13	0.009				
Heptene	H	0.24	0.017	0.39	0.006	7.83	0.024
Toluene	A	0.56	0.040	0.06	0.001	7.71	0.023
Heptane	H	5.79	0.414	0.44	0.007	9.22	0.028
Octene	H	0.48	0.34	0.25	0.004	6.76	0.020
Octane	H	1.53	0.109	0.93	0.015	12.46	0.038
Xylene	A	1.11	0.079	0.84	0.014	51.11	0.155
Styrene	A	0.58	0.041			51.48	0.156
Nonene	H	3.90	0.279	2.37	0.038	49.86	0.151
Nonane	H	5.69	0.406	2.08	0.033	86.87	0.263
Trimethyl benzene	A			1.47	0.024		
Decene	H	3.61	0.258	5.40	0.087	96.36	0.292
Decane	H	5.76	0.411	4.44	0.071	105.40	0.319
Undecene	H	3.48	0.249				
Unknown	H	3.38	0.241			0.14	0.000
Methyle decene	H			2.69	0.043		
Dodecene	H	11.79	0.842	6.42	0.103		

DETAILS OF ANALYSIS

	358 K	408 K	493 K
Total micro gm	53.15	32.92	933.21
Total mass of conversion	3.794	0.528	2.825
% Hydrocarbons	92.145	87.689	81.628
% Oxygenated hydrocarbons	3.637	4.356	5.381
% Aromatic compounds	4.217	7.955	12.991
Type of Analysis	Furnace: Air $1.67 \times 10^{-6} m^3 s^{-1}$	Furnace: Air $1.67 \times 10^{-6} m^3 s^{-1}$	Furnace: Air $1.67 \times 10^{-6} m^3 s^{-1}$
Sample Size	5.8344×10^{-4} kg	3.2353×10^{-4} kg	7.4399×10^{-4} kg
Residue	5.8063×10^{-4} kg	3.1311×10^{-4} kg	6.7795×10^{-4} kg
Amount used	2.81×10^{-6} kg	1.242×10^{-5} kg	6.604×10^{-5} kg
Chromatographic conditions	Poropak Q 303-523 K @ 0.13 K s^{-1}	Poropak Q 303-523 K @ 0.13 K s^{-1}	Poropak Q 303-523 K @ 0.13 K s^{-1}
Hexane count Kg^{-1}	64.8224713	64.8224713	59.0744834
Analysis range	$C_1 - C_{12}$	$C_1 - C_{12}$	$C_1 - C_{10}$
Additional measurements	CS_2	CS_2	CS_2, SO_2, COS

TABLE IV

Organic products from roof-deposit of rail-car using furnace decomposition technique

	358 K	408 K	453 K
Total micro-gm	17.83	110.26	627.54
Total mass % converted	1.916	6.408	19.674
% hydrocarbons	97.651	98.221	89.885
% oxygenated hydrocarbons	2.085	1.404	8.31
% aromatic compounds	0.313	0.375	1.804
Amount used	1.87×10^{-6} kg	3.44×10^{-6} kg	6.38×10^{-6} kg

(d) collection of a sample from various depths in the vapour space from the inspection hatch. A typical analysis is presented in Table V.

TABLE Va

Typical results of permanent gas analysis of vapour space of 35PEN air rectified bitumen at 473 K (200° C) and 2 m depth

GAS	CONCENTRATION %
CO	0.06
CO_2	2.48
O_2	18.93
N_2	78.54

TABLE Vb

Typical results of organic products in vapour space of 35 PEN air rectified bitumen at 473 K (200° C) and 2 m depth

COMPOUND	TYPE	MICRO GM	PPM
Methane	H	10.91	173.735
Acetylene	H	28.74	281.640
Ethylene	H	10.91	99.277
Ethane	H	40.24	341.758
Formaldehyde	0	98.68	838.088
Methanol	0	88.21	702.343
Propane	H	116.51	674.671
Ethanol	0	146.45	811.172
Acetaldehyde	0	64.52	373.614
Butene	H	17.68	80.441
Butane	H	118.98	522.670
Propanol	0	29.67	130.338
Acetone	0	50.90	223.600
Pentene	H	23.09	84.044
Pentane	H	26.03	92.113
Butanone	0	32.97	116.672
Crotonaldehyde	0	50.46	183.667
Hexene	H	16.27	49.350
Hexane	H	23.64	70.037
Benzene	A	28.79	94.043
Toluene	A	5.60	15.509
Octene	H	25.11	57.123
Octane	H	20.34	45.460
Nonene	H	7.47	15.105
Nonane	H	64.79	128.967
Xylene	A	133.06	319.833
Trimethyl Benzene	A	58.91	125.080

Total micro gm = 1381.41
Total ppm = 0758.585
%hydrocarbons = 41.793
%oxygenated hydrocarbons = 50.003
% aromatic compounds = 8.204

The infra-red gas detector gave good agreement on each occasion with respect to the permanent gas analysis (CO_2, CO) and xylene, benzene and toluene content. Also the values for the amount of hydrogen sulphide (H_2S) present from the colourimetric tubes were confirmed using infra-red. H_2S readings varied between 13 and 140 ppm.

(e) measurements of flammability (%LEL) of the various grades at existing storage temperatures, using the explosimeters described above. An investigation was also carried out on the variation of %LEL with distance from the heated bitumen surface. Figure 4 shows a typical variation of %LEL with distance and illustrates that the %LEL is relatively uniform in the vapour space except near the bitumen surface. Figure 5 illustrates a typical %LEL versus storage temperature plot (105/35 oxidised bitumen is illustrated). The %LEL data assumes the "equilibrium" value and the curves resemble saturated vapour pressure data. Figure 6 shows that similar %LEL versus storage temperature curves can be obtained for each grade. It should be noted that Figures 4, 5 and 6 employ data obtained using the "Snee" explosimeter.

(iv) simulation of storage tank conditions in the laboratory:

Since it was impracticable to carry out some studies on production facilities, a number of investigations were carried out on the laboratory scale. These methods tended to overestimate some parameters, such as the %LEL, but they have provided guidance in the following areas:-

(a) charging and discharging of tanks

These processes tended to significantly alter the %LEL of the vapour space. In discharging, the %LEL decreased due to dilution effects whereas in charging the %LEL increases. Full scale investigations have recently started.

(b) variation of %LEL with different static heights for each grade of bitumen

This was studied to support the data found in the full-sized storage tanks. A typical graph is shown in Figure 7.

(c) inerting of tanks

Three methods of inerting, namely the use of nitrogen, combustion gas and low pressure steam were studied and the reduction in flammability assessed. This work will be the subject of a future paper.

(d) emptying of rail-cars

Compressed air at 3.4 to 6.8 x 10^4 N m^{-2} was forced into simulated rail-cars causing the tank contents to be discharged at the rate of 1.5 x 10^{-2} m^3 s^{-1}. From the results, it is expected that the air rapidly dilutes the flammable vapour concentration below the lower explosive limit. However, it was found that exposure of the heating elements was a strong possibility as the bitumen level drops.

DISCUSSION

This investigation was initiated by the findings of Dimpfl in the USA and was primarily aimed at examining UK practice with regard to bitumen storage. Such information may aid any direct comparison of USA and UK practice with regard to manufacture, storage, handling and the requirements of end-users.

A total of 108 different static storage tanks and a small number of rail-cars were used in the study. A number of visits were made to investigate the effects of storage parameters. Little time was spent on examining road-tankers because most incidents are not specifically bitumen dependent eg failure of flexible hoses.

The discussion can be conveniently divided into sections relating to Dimpfl's findings, this investigation and the possible consequences regarding changes in practice.

(a) evidence for smouldering combustion of the roof deposits:

> Dimpfl presented information that the coke-like deposits could be a source of ignition, assuming the presence of oxygen in non-inerted tanks and a flammable atmosphere. A large number of deposits were collected from UK tanks *and subjected to a range of tests carried out at typical* UK storage temperatures.

In only one example was the auto-ignition temperature found to approach the recommended maximum temperature and any energy changes detected by standard methods also generally occurred above the existing recommended temperatures. Also in only one tank (containing 105/35 oxidised bitumen) was evidence found of very high concentrations of carbon dioxide and carbon monoxide (7 and 6% respectively) in the vicinity of the stalactites, suggesting possible combustion reactions. The oxygen content in the tank's vapour space was 17.5%. The particular tank had been maintained at 503 K (230° C). When some of the deposits from this tank were examined, a slightly higher than normal oxygen content, (1.5% above normal) was found in the elemental analysis.

In general, a higher oxygenated-hydrocarbon content was found near the surface of the heated bitumen than near the roof of the tanks.

The current work in this area at the Polytechnic of the South Bank is examining the possibility of two types of roof deposit. The first is a product of the condensation of bitumen vapours and the physical movement of bitumen in charging and discharging. The second type is much smaller in size and pyrophoric in nature.

If more substantial evidence becomes available to support the smouldering combustion proposal, then regular removal of the deposits will reduce the probability of ignition.

(b) evidence for the sponge-like effect in roof deposits:

The deposits were investigated by thermal methods and by chemical analysis of evolved products from the deposits placed in a furnace and held at the existing storage temperatures. It is apparent that the stalactites decomposed in a similar manner to the bitumen and the species identified by the combined gas chromatograph and mass spectometer were similar in both cases. No substantial evidence was found for the additional release of light hydrocarbons in typical storage temperatures. Longer term studies on stalactite formation are required.

(c) evidence for flammable atmospheres:-

Oxygen is present in non-inerted tanks and if an ignition source is available then the only requirement for a fire is a sufficient flammable vapour. Earlier, it has been shown that the viscosity of all grades of bitumens are markedly affected by temperature and hence the storage temperature is critical with regard to transport and end-use application. However, an examination of the flammability data indicates that for each grade a relatively high %LEL is found at current handling temperatures.

The American Petroleum Institute (API) is currently suggesting a guidance temperature of 450 K (177° C), above which tanks containing all grades of bitumen should be inerted. As a guide for safety in the UK, tanks should register less than 25% LEL using the conventional gascope. Table VI provides details of %LEL (using both MSA gascope and "Snee" explosimeter) at the Institute of Petroleum's recommended maximum temperature for the grades thoroughly investigated.

TABLE VI

%LEL information at the recommended maximum temperatures

GRADE	IP Maximum Temperature K	IP Maximum Temperature °C	%LEL Snee	%LEL MSA
35 PEN	493	220	108	28
50 PEN	473	200	30	14
100 PEN	473	200	43	18
200 PEN	463	190	90	26
300 PEN	463	190	90	40
85/25 OXIDISED	503	230	163	> 100
95/25 OXIDISED	503	230	189	> 100

Note; The %LEL at these temperatures are direct measurements or extrapolations of direct measurements at industrial storage tanks.

TABLE VII

Temperatures at which 25 and 100% LEL occur

GRADE	Temperature for 25% LEL K	Temperature for 25% LEL °C	Temperature for 100% LEL K	Temperature for 100% LEL °C
35 PEN	463	190	490	217
50 PEN	459	186	519	246
100 PEN	448	175	510	237
200 PEN	422	149	487	214
300 PEN	420	147	477	204
85/25 OXIDISED	431	158	462	189
95/25 OXIDISED	469	196	495	222
105/35 OXIDISED	466	193	496	223

The above %LEL data is supported to a degree by the investigation using thermal methods and by the chemical analysis of the vapour spaces. It is clear that flammable atmospheres can exist at the currently recommended maximum temperatures for the oxidised grades of bitumen, and for certain penetration grades the %LEL is higher than the suggested maximum of 25% LEL. The API suggestion of a maximum 450 K (177° C) ensures that bulk vapour space %LEL will always be lower than 100% in non-inerted tanks.

(d) inerting

From a practical viewpoint, the handling temperature of bitumen is the key to its applications. This temperature controls the viscosity and the discussion now needs to examine whether a reduction in temperature to reduce the %LEL will alter the viscosity to such an extent that handling and use become difficult. The reduction in temperature required to reduce the %LEL for the penetration grades does not significantly alter the viscosity. However, the reduction in temperature for the oxidised grades can be significant and inerting may be required to maintain temperatures for specific handling and end-use applications. A reduction in storage temperature from 503 K (230° C) to 483 K (210° C) will increase the viscosity of 105/35 oxidised bitumen from 40 cp (0.04 N s m $^{-2}$) to 74 cp (0.074 N s m $^{-2}$). However, it should be remembered that although oxygen and flammable atmospheres are present, the third component of the "fire triangle" has not been substantiated in the UK tanks. Tanks can be inerted using nitrogen, combustion gases and low pressure steam but it is essential to consider the oxygen requirement to eliminate pyrophoric formation.

(e) emptying of rail-cars

From the laboratory simulation of emptying rail-cars using compressed air, it is apparent that the emptying process at currently recommended rates reduces the hazard of the flammable atmosphere. However it is recommended that heating elements should always be in the "off" position when discharging, and sufficient time should be allowed for them to cool before discharge starts.

CONCLUSIONS

Although some studies are continuing, the following conclusions can be drawn.

(i) No substantial evidence was found for smouldering combustion in the coke-like deposits at the existing tank storage temperatures in the UK. This finding does not support the findings of Dimpfl in the USA. In an analysis of a very limited number of incidents relating to the storage of penetration grades of bitumen, smouldering combustion was not found to have been the initiating factor for fires. There have, however, been several incidents where a fire or explosion has occurred with no obvious source of ignition.

(ii) The coke-like deposits decompose in a similar manner to bitumen and they did not produce a significantly larger amount of light hydrocarbons per unit mass than bitumen. Further work on deposit formation is required for support of "sponge-effects".

(iii) The current UK practice with regard to bitumen storage may in some cases permit two components of the "fire-triangle". The presence of the third component, an ignition source, must be eliminated by regular maintenance and good working practices. Flammable atmospheres do exist in UK tanks at temperatures selected on the basis of viscosity of the bitumen. Oxidised grades of bitumen have particularly high values for the %LEL at these temperatures.

(iv) Compromises between %LEL and viscosity may need to be established. The reduction in temperature required to reduce the %LEL in penetration grades does not significantly alter their viscosities. In general, a reduction in the current bitumen handling temperatures is recommended, whenever end-user applications permit.

(v) The %LEL can be reduced by a number of methods including a reduction in temperature or inerting the vapour space with say nitrogen, combustion gases or low pressure steam. A certain amount of oxygen is required to eliminate the formation of pyrophorics. For Oxidised grades in particular the possibility of inerting tanks should be considered where the handling and end-use applications require high storage temperatures.

(vi) The current practice of discharging rail-cars using compressed air is not hazardous as long as other safety procedures are carried out prior to emptying.

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British Petroleum
Philmac Oils Ltd
Amey Roadstone
Mid-Essex Gravel
Mobil Oil Company
Tarmac Ltd
English China Clay
Permanite Ltd

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IP = Institute of Petroleum (1978) "Methods of Analysis and Testing".

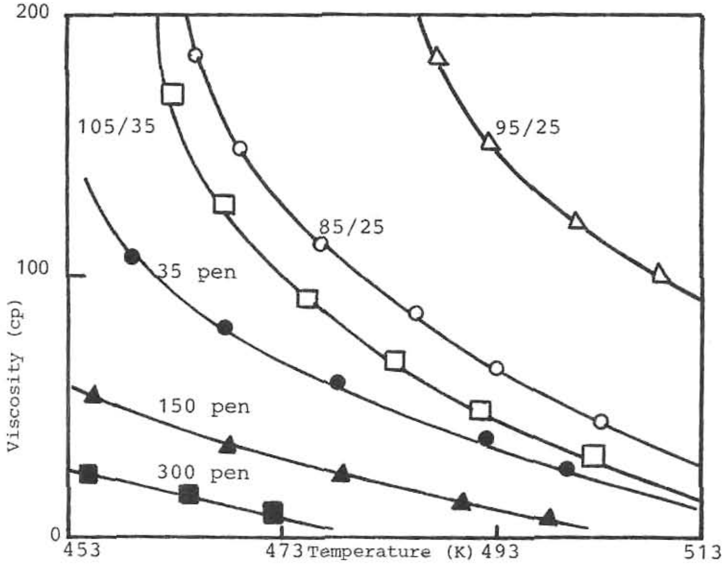

Figure 1: VARIATION OF VISCOSITY WITH TEMPERATURE

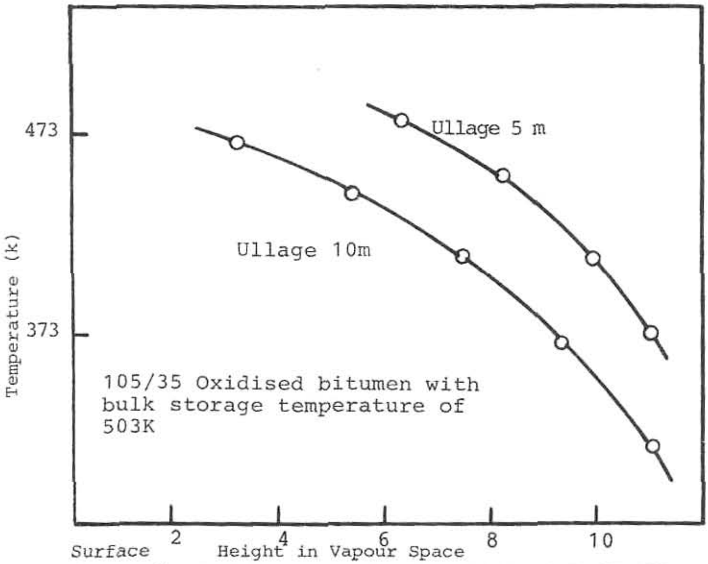

Figure 2: TEMPERATURE PROFILE IN VAPOUR SPACE

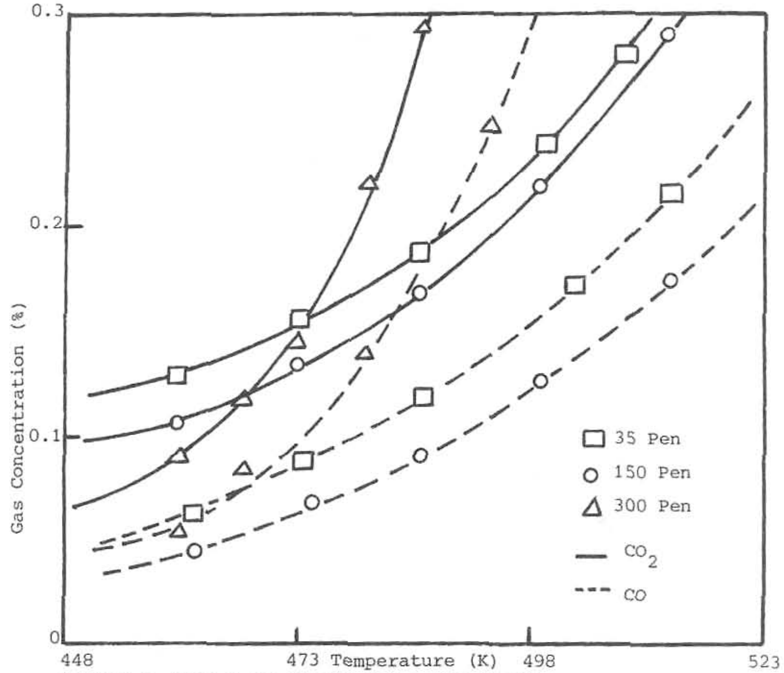

FIGURE 3: OXIDES OF CARBON IN VAPOUR SPACE

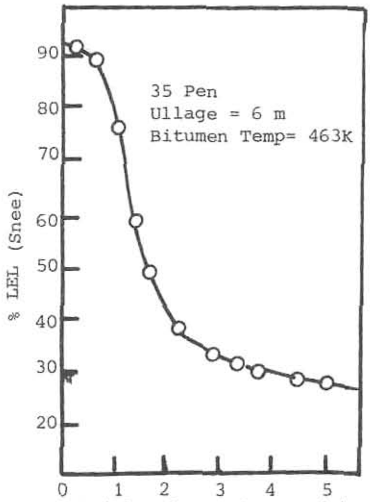

FIG. 4: VARIATION OF % LEL WITH HEIGHT IN VAPOUR SPACE

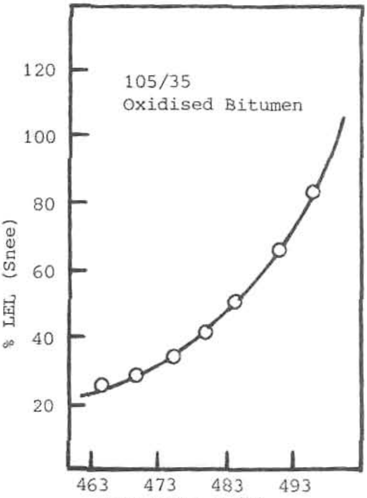

FIG. 5: VARIATION OF % LEL WITH BITUMEN STORAGE TEMPERATURE

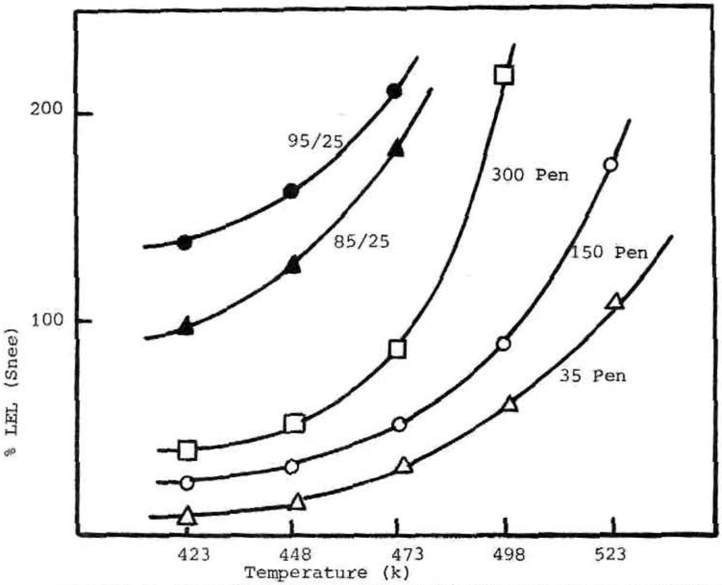

FIGURE 6: FLAMMABILITY OF VAPOUR SPACES FOR RANGE OF BITUMENS AT TYPICAL STORAGE TEMPERATURES

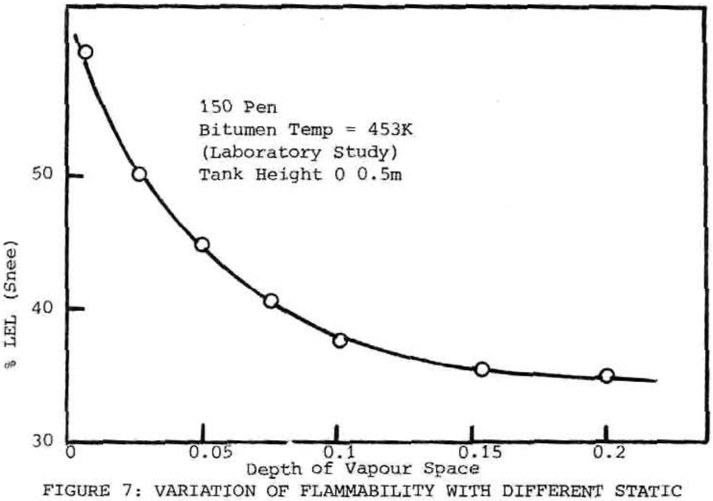

FIGURE 7: VARIATION OF FLAMMABILITY WITH DIFFERENT STATIC HEADS OF BITUMEN