

Ignition Risk of Hydrocarbon Liquids and Vapors by Hot Surfaces in the Open Air

API RECOMMENDED PRACTICE 2216
THIRD EDITION, DECEMBER 2003

REAFFIRMED, OCTOBER 2010



AMERICAN PETROLEUM INSTITUTE

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Downstream Segment

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FOREWORD

Recommended Practice 2216 *Ignition Risk of Hydrocarbon Liquids and Vapors by Hot Surfaces in the Open Air* was prepared under the auspices of the API Safety and Fire Protection Subcommittee. It is intended to provide information concerning the technical basis for auto-ignition of hydrocarbon vapors by hot surfaces in the open air. This information may be used to determine whether or not hot surfaces are potential sources of ignition should a release of hydrocarbon vapors or liquids occur and to develop safe practices for controlling or preventing such ignition. Other documents referenced in this publication provide supplemental information applicable to this subject.

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Ignition Risk of Hydrocarbon Liquids and Vapors by Hot Surfaces in the Open Air

1 GENERAL

1.1 SCOPE

This recommended practice provides information concerning the potential for ignition of hydrocarbons that are exposed to hot surfaces in the open air. Hydrocarbon liquids, when heated sufficiently, can ignite without the application of a flame or spark. The ignition of hydrocarbons by hot surfaces may occur when oil is released under pressure and sprays on a hot surface or is spilled and lies on a hot surface for a period of time. Understanding the mechanism and dynamics of auto-ignition is an important step in preventing or controlling the ignition of hydrocarbons by hot surfaces in the open air. In addition to the information provided herein, appropriate industry standards and other information may assist users to understand the potential hazards of hydrocarbon auto-ignition (such as spontaneous combustion) not specifically covered by this publication and implement appropriate prevention and control measures.

1.2 APPLICABILITY

Hot surfaces, in areas where hydrocarbon liquids or vapors are present and may be released, are often presumed to be the sources of ignition should fires occur. However, it is generally recognized by the petroleum industry that hot surfaces, even at temperatures considerably above the auto-ignition temperatures (AIT) of the hydrocarbons involved, are not always capable of igniting flammable vapor-in-air mixtures. This publication provides information applicable to the better understanding and controlling of hot surface ignition hazards.

1.3 NON-APPLICABILITY

This recommended practice does not cover every possible hazard or situation that may involve ignition of hydrocarbon liquids and vapors from hot surfaces. This publication does not apply to the ignition of hydrocarbons when certain conditions occur, such as spontaneous combustion (see 2.2). The mechanism for spontaneous combustion is entirely different from that required for ignition of hydrocarbon vapors from contact with hot surfaces in open air. This publication also does not apply to the ignition of hydrocarbon vapors when contacted by heated or glowing metal such as welding slag or by direct impact of super-hot exhaust fumes or gases. In addition, this publication does not cover ignitions arising from hydrocarbon liquids trapped behind rust or oil soaked or saturated insulation or rust covering hot surfaces.

2 DEFINITIONS

2.1 Auto-ignition: The ignition of a material (commonly in air) as the result of heat liberation due to an exothermic

oxidation reaction in the absence of an external ignition source such as a spark or flame.

2.2 Auto-ignition Temperature (AIT): The AIT of a substance is the minimum temperature required to initiate or cause self-sustained combustion (exothermic reaction) independent of an external ignition source. As used in this publication, it is the minimum temperature at which auto-ignition occurs under the specified conditions of the ASTM E 659 test¹ (see Section 6). The terms, “*auto-ignition temperature*,” “*ignition temperature*,” “*self ignition temperature*,” “*autogenous ignition temperature*,” and “*spontaneous ignition temperature*,” are used synonymously in this publication. ASTM E 659.

3 AUTO-IGNITION TEMPERATURE TESTING

3.1 GENERAL

This recommended practice covers the technical basis for the risk of ignition of hydrocarbons by hot surfaces based on AIT and the practical implications thereof. An understanding of AIT is important when hydrocarbon vapors or liquids are exposed to hot surfaces or when handling very hot hydrocarbon liquids. It should be understood that ignition of flammable hydrocarbon vapors by a hot surface at the minimum ignition temperatures (for the specific hydrocarbon) is not likely. Experimental studies, testing and practical experience have shown that hot surfaces must typically be hundreds of degrees above published minimum ignition temperatures to ignite freely moving hydrocarbon vapor in the open air. Even properly operating automotive vehicle catalytic exhaust systems, in most instances, do not create a surface temperature sufficiently high enough to ignite hydrocarbon vapors in the open air². Whether or not flames will develop when a hydrocarbon contacts a hot surface depends not only on the surface temperature, but also on the extent (size) of the hot surface, its geometry and the ambient conditions³.

The following information, covering AIT research, is intended to assist in understanding why the ignition of hydrocarbon vapors by hot surfaces (at published minimum AITs), is highly improbable.

3.2 AUTO-IGNITION TEMPERATURE TESTING CRITERIA

Although the definition for “auto-ignition temperature” is specific, the values observed when testing specific hydrocarbons will be different depending on the conditions at the time of testing and the test method used. AITs observed under one set of conditions may be changed substantially by different conditions⁴. Some of the variables that affect AITs are the molecular structure of the hydrocarbon mixture (i.e., gaso-

Table 1—Auto-ignition Temperatures of Hydrocarbon Liquids at Two Different Pressures⁶

Hydrocarbon Liquid	Auto-ignition Temperature (Approximate)	
	p = 1 atm.	p = 33 atms.
Light Oil	260°C (490°F)	176°C (347°F)
Compressor Oil	308°C (588°F)	188°C (370°F)
Turbine Oil	371°C (700°F)	270°C (521°F)

line), the percentage composition of the vapor-in-air mixture, the shape, size and configuration of the space and the hot surface, the hot surface material, the type and reactivity of other materials present, the rate and duration of heating, and environmental conditions such as the initial temperature and the atmospheric pressure (see Table 1).

Time lags of a minute or more during AIT testing are common⁵. Additionally, the AIT is lower if the test vessel size (or test surface area) is larger, the heat of combustion is greater, the pressure is higher, the hydrocarbon molecular weight is larger or the mixture conductivity is smaller⁶. All of these factors affect the ability to accurately predict conditions under which auto-ignition will occur when hydrocarbons contact heated surfaces.

3.3 STANDARD ASTM AUTO-IGNITION TEST METHODS

The majority of reported AIT data has been previously obtained by one of two standard AIT test methods, ASTM D 286 and D 2155. These two original test methods⁷ (which have now been withdrawn by the American Society for Testing and Materials) involved introducing small measured amounts of flammable or combustible liquids into glass flasks that are uniformly heated with air without an external source of ignition. If ignition occurred, the flask wall temperature and the time for ignition to occur after introduction of the sample (ignition lag) were noted. The tests were repeated using different flask wall temperatures to determine the lowest temperature at which ignition would occur in less than 10 min., which was then reported as the minimum ignition temperature of the liquid tested. Because both of these former test methods relied on visual detection of a flame, the ignition temperatures obtained were the minimum temperatures at which flame ignitions were visually observed.

The current ASTM test standards¹, ASTM D 2883 and ASTM E 659, also use the heated glass flask technique. However, these ASTM tests now use thermoelectric flame detection methodology that will detect non-luminous or barely luminous reactions that are difficult or impossible to detect by sight. This thermoelectric methodology has resulted in a new series of terms used to describe ignition temperature thresholds, as follows:

Hot-flame Ignition: A rapid, self-sustaining, sometimes audible, gas phase reaction of a sample or its decomposition products with an oxidant usually accompanied by a readily visible yellow or blue flame. AIT is defined as the hot-flame reaction threshold temperature.

Cool-flame Ignition: A relatively slow, self-sustaining, barely luminous, gas phase reaction of the sample or its decomposition products with an oxidant. Cool flames are visible only in darkened areas. The Cool-flame Reaction Threshold (CFT) is the lowest temperature at which cool flame ignitions are observed.

Pre-flame Ignition: A slow non-luminous, gas phase reaction of the sample or its decomposition products with an oxidant that it is contacting. The Pre-flame Reaction Threshold (PRT) is the lowest temperature at which an exothermic gas reaction is observed.

The ignition temperatures that are typically reported in flammable and combustible liquid hydrocarbon physical characteristic tables (such as in NFPA 325) are similar to AIT values. However, because the CFT temperature and the PRT temperature are slightly lower than the AIT, both must be considered when assessing the ignition risk of a specific hydrocarbon and a particular system or potential exposure.

3.4 OPEN AIR AUTO-IGNITION TESTS

The occurrence of hydrocarbon vapor releases in open air constitutes conditions that are very different from those experienced in the standard ASTM laboratory ignition temperature tests described above. Because actual field conditions differ greatly from laboratory conditions, ignition of vapors in open air often requires surface temperatures considerably different from published ignition temperatures of specific hydrocarbons.

3.4.1 Open Air tests

Small scale laboratory tests that were made on relatively unconfined butane/air (AIT 550°F [287°C]) and gasoline/air (AIT 536°F [280°C]) mixtures determined that metal surfaces had to reach temperatures of approximately 1400°F (760°C) before ignition occurred. A number of other, more realistic tests were made in open air where normal wind and convection currents were present. The results of these tests (see Table 2) were essentially the same for both hydrocarbon droplets sprayed on hot surfaces and for hydrocarbon vapor-air mixtures released at the hot surfaces⁸ and verified the results of the laboratory tests.

Another test method developed at the National Institute of Standards and Technology has been used to conduct short duration AIT measurements of hydrocarbon fuels under atmospheric pressure conditions. AITs were determined under steady flow conditions where the contact time between the controlled hydrocarbon/air mixture and the heated metal

Table 2—Open Air Auto-ignition Tests under Normal Wind and Convection Current Conditions

Hydrocarbon	Published Ignition Temperatures (Approximate at Time of Test)		Hot Surface Temperature Without Ignition Occurring	
	°C	°F	°C	°F
Gasoline	280 – 425	540 – 800	540 – 725	1000 – 1335
Turbine Oil	370	700	650	1200
Light Naphtha	330	625	650	1200
Ethyl Ether	160	320	565	1050

Table 3—Effect of Ignition Lag Time on Auto-ignition Temperature

Ignition Lag (sec.)	100		10		1	
	°C	°F	°C	°F	°C	°F
Hydrocarbon						
Pentane	215	419	297	567	413	775
Hexane	216	421	288	550	384	723
Heptane	202	396	259	498	332	630

Table 4—Effect of Wind Velocity in Auto-ignition Tests Using Kerosene

Wind Velocity Over the Hot Surface		Surface Temperature Required for Ignition	
meters/sec.	ft/sec.	°C	°F
0.3	1.0	405	760
1.5	5.0	660	1220
3.0	10.0	775	1425

Table 5—Auto-ignition Temperatures of Motor Fuels (NFPA 325)

Product	Ignition Temperatures	
	°C	°F
Gasoline (60 – 140 Octane)	280 – 455	540 – 850
Pure Ethanol	363	685
Pure Methanol	464	867
Diesel Fuel	257	494
MTBE	374	705

surface were well controlled. AITs measured under short contact time conditions were higher than previously found (with longer exposure times and less controlled test conditions). These tests resulted in slightly narrower ranges of AITs than the same hydrocarbons tested using the ASTM (longer time) contact criteria, and therefore indicate a reduced hazard⁹.

3.4.2 Effect of Lag Time

The effect of ignition lag time on hydrocarbon liquids in the open air indicates that flammable mixtures heated for

short periods of time, require exposure to higher surface temperatures in order for ignition to occur¹⁰ (see Table 3).

3.4.3 Effect of Wind Velocity

In open air near a hot surface, the time of contact is only seconds or a fraction of a second because convection currents and normal wind disturbances move a flammable vapor-in-air mixture past the hot surface rapidly. Because the contact time under open-air conditions is so short, the surface temperature required for ignition must be substantially higher than reported minimum AITs. The effect of wind velocity on the surface temperature required for ignition of kerosene (AIT of 410°F [210°C]) was determined in wind tunnel tests¹¹ (see Table 4).

3.5 GASOLINE AND OXYGENATE BLENDS

The addition of ethanol, methanol and other oxygenates will slightly alter the ignition temperature of motor gasoline. The ignition temperatures of MTBE, alcohol and methanol fall within the range of ignition temperatures for gasoline (see Table 5). Test data indicated that the AIT of motor gasoline containing up to 10% ethanol is similar to that of straight gasoline. Gasoline blended with ethanol, in contact with a hot metal surface at a temperature of 475°F (265°C) above the published AIT of gasoline, would not ignite. However, gasoline blended with 10% methanol/isobutanol had a tendency to ignite at about 360°F (200°C) above the published AIT of gasoline (because it wetted the hot surface more effectively than the gasoline/alcohol mixture)¹².

4 IGNITION BY HOT SURFACES

4.1 EQUIPMENT SURFACES

Many small leaks and discharges of flammable and combustible liquids and vapors have occurred in process units without ignition by nearby hot equipment or uninsulated hot surfaces with temperatures several hundred degrees above minimum ignition temperatures of the hydrocarbon involved. However, ignition of hydrocarbons by heated surfaces has occurred when the liquid contacted a fired furnace or other similar direct source of ignition. For example, one statistical

review of offshore fires reported that during the ten year period from 1980 – 1990, 190 of 539 fires (35%) occurred from gas or liquid releases contacting extremely hot surfaces of equipment, usually the exhaust system piping of an engine or turbine driver¹³. Another more recent paper, indicated that the U.S. Air Force experiences over 100 engine fires a year involving leaking fluids¹⁴.

4.2 SIDES OF STORAGE TANKS

Hot surfaces may also cause ignitions in high flash point hydrocarbon storage tanks. Fixed (cone) roof tanks storing small amounts of fuel oil, diesel fuel and lubricants are more likely to explode when involved in surrounding fires than are tanks containing low flash products. This is because vapors are not usually present in these tanks (above the liquid level) when fires occur. A considerable amount of time is required for the radiant heat of a fire impacting on the side of one of a high flash point hydrocarbon storage tank, to produce enough vapors to fill the empty space above the liquid level with a concentration that is too rich to burn (above the upper explosive limit). If the side of the tank is heated sufficiently enough during the time the vapors are forming, and if the vapor concentration reaches the explosive range at the same time that the side of the tank reaches ignition temperatures, an internal explosion is likely to occur¹⁵.

4.3 IGNITION OF HEAVY OILS BY HOT SURFACES

Hot surface fires have occurred involving heavy oils such as hydraulic oil, motor oil, lubricating oil and gear oil. One example of such an ignition would be the release of a fine spray or oil mist from a broken or leaking hydraulic line, against an overheated surface, such as that caused by a bearing failure. Allowing a spill or stream of heavy oil to contact a hot surface for a period of time (depending on the surface temperature) that is long enough for decomposition (cracking) to occur, will result in ignition. An example of this would be a motor oil spill on the hot manifold of an automobile engine.

5 SUMMARY

5.1 GENERAL

All of the testing (to date) indicates that surface temperatures must be several hundred degrees (Fahrenheit) above the laboratory measured minimum AITs to ignite flammable vapors in the open air. However, it should be recognized that both pre-flame ignition and cool-flame ignition may occur at temperatures lower than the AIT (see 3.3). In addition, both wind velocity and ignition lag time will impact the AIT (see 3.4).

The size of the heated surface also affects the ability to cause ignition. Heated surfaces may be too small (in size) to

cause ignition whereas a flame or large, ignitable spark (such as an electrical spark) could be the source of ignition in an identical situation (same hydrocarbon, same temperature, etc.). In fact, a heated surface may be so small that no increase in temperature will compensate for volume (such as the size of a small piece of hot sparking metal that results from the use of hand tools on steel surfaces).

It appears that a number of other factors also influence the AIT of a hydrocarbon when contacting hot surfaces. These include the rate of liquid spread on the hot surface, the rate of heat transfer between the heated surface and the hydrocarbon, the temperature and molecular changes within the liquid and the ambient temperature, rate of vaporization and diffusion of the liquid. These factors affect the ability to accurately predict conditions under which auto-ignition will occur when hydrocarbons contact heated surfaces.

5.2 CONCLUSION

The identification of a heated surface as the cause of ignition can often lead to an incorrect analysis of the real source of ignition. In general, ignition of hydrocarbons by a hot surface should not be assumed unless the surface temperature is approximately 360°F (182°C) above the accepted minimum ignition temperature of the hydrocarbon involved. Test data and field experience both indicate that the ignition of flammable hydrocarbon vapors by hot surfaces in the open air requires temperatures considerably above the reported minimum AITs of the hydrocarbons involved.

Typically, there is little risk of ignition of hydrocarbon vapors or liquids by hot surfaces under normal operating conditions. Years of industry experience support this conclusion. It is therefore important to recognize and understand the characteristics and nature of ignition of hydrocarbons by hot surfaces in open air, including the impact of ambient temperature, hydrocarbon molecular structure; pressure; the size, composition, temperature and configuration of the hot surface and many other factors, so that investigation of an incident does not result in identification of an incorrect or improper source of ignition.

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