POLAR EFFECTS IN HOT SURFACE IGNITIONS
SURFACE MEDIATED SUPERBASE REACTIVITY

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BACKGROUND

There are two generally accepted indices regarding fuel flammability. The more commonly used flash point of the fuel is the minimum temperature for a liquid fuel to sustain sufficient levels of vapor concentration in the air immediately over the surface to produce ignition, when an open flame is passed directly over the surface. There is, therefore, the requirement for a preexisting flame. Autoignition temperature (or hot surface ignition temperature [HSIT]) is the minimum temperature of a fuel "required to cause self-sustained combustion, independently of the heating or heated element." In this determination, there is no open flame involved in the ignition. Ignition temperatures are typically determined by applying minute portions of the fuel onto a hot surface and waiting for up to 10 min until ignition is observed. If there is no ignition, the process is repeated with increasing temperatures, until ignition is finally achieved, There are a number of flame processes, including hot-flame ignition (as indexed by autoignition temperatures [AIT], accompanied by a "rapid, self-sustaining ... readily visible yellow or blue flame"); cool-flame ignition ("relatively slow, self-sustaining barely luminous ... cool flames ... visible only in a darkened area"), indexed by cool-flame reaction threshold (CFT, "the lowest temperature at which cool-flame ignitions are observed"); and pre-flame reactions, indexed by preflame reaction threshold (RTT, "the lowest temperature at which exothermic gas-phase reactions are observed" [1].

The presently accepted ASTM method [2] (Figure 1) for hot surface ignition temperature determinations is highly subject to the method of determination. Recently, for example, an attempt was made at Tyndall **AFB** to repeat the previously cited [1] ignition temperature (240 "C) for JP4 jet fuel using this type of approach, and to determine this value for the much less volatile JP8. Surprisingly, the same ignition temperature was observed for both fuels, but at a much higher reading (ca. 540 ± 20 °C).

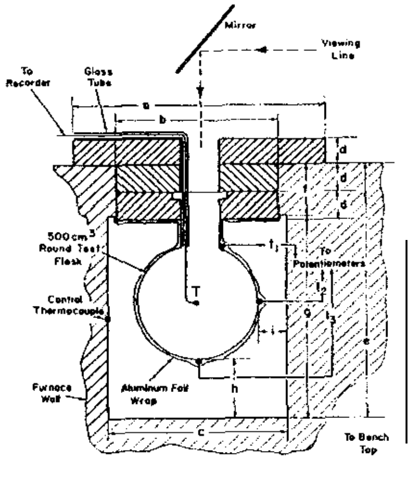


Figure 1. ASTM E569, Standard test apparatus for autoignition temperatures for autoignition temperatures of liquid chemicals [2].

On close examination of the videotaped experiments, we noted several interesting previously unidentified features. After application of liquid fuel dropped onto a hot stainless steel surface, a dark envelope expanded outward from the application point, with wisps of smoke. Red-hot incandescent spots were seen fleeting over the surface outward from this dark patch, at heating temperatures as low as 380 "C, although red incandescence of iron typically occurs above 525 °C [3]. (Other workers [4, 5] have also noticed 'red spot' anomalies in hot surface ignitions.) Blue "cool" flames were seen flickering at the outer periphery of these red spots, with sudden transformation from these flickering blue flames to a sheet of white-hot flame over the entire test area. Other workers have shown that combustion occurs prior to flaming combustion, with carbon monoxide (CO) production being a prominent product **[6]** (Table **1**).

TABLE 1. OXIDATION OF 9% CH_4/AIR AT 1050 °C (ABOUT 500 °C BELOW MAXIMUM HSIT).

Gas Present	With Pt° bar, %	With Ni° bar, %
Natural gas, at start	***9.1***	8.99
CO„ after 8 min	1.01	0.05
CO, after 8 min	0.72	0.50
Natural gas, at start	8.75	8.77
CO„ after 20 min	1.96	0.07
CO, after 8 min	0.22	**0.36**

In this situation, the liquid fuel drop vaporizes and temporarily cools the hot surface. The fuel rich cloud spreads over the hot surface, thermally decomposing without oxidation (as evidenced by frequent smoke emissions). At the periphery of the fuel cloud, the fuel/air mixture is lean enough to afford pre-flame combustion to produce CO. CO has a greater bonding potential than inert alkane fuel components and adsorbs preferentially to the metal surface. Thus, the observed ignition temperature of 540 °C as seen for both JP4 and **JP8** could correspond to CO formation. (The literature HSIT value for CO is somewhat higher, 609 °C [7]; however, the transient incandescent red spots, which do not persist long enough for true temperature registration, would be hot enough for CO ignition.) Thus, more often than not, hot surface ignition temperature determinations may pertain not to the substrate being measured, but rather to decomposition products.

In 1991, workers at NIST devised a "Short Duration Autoignition Temperature" apparatus (Figure **2)** in which "a flowing gas phase fuel stream impinges on a hot surface. **...** The conventional ASTM procedure does not control the fuel/air stoichiometry. **...** [In the new] apparatus **...** the fuel/air stoichiometry, the nature of the hot metal surface, and the contact time are well controlled" [7]. Rapid results (Figure **3)** with this apparatus are obtained with minimized contact times in which spurious decompositions can take place, with excellent reproducibility and with greatly increased accuracy in the resulting HSIT data. Ignition temperatures are routinely higher than is the case for data derived by the ASTM system; these higher figures probably reflect actual ignition temperature profiles for all fuels, which thus are higher than has been suspected previously (Figures 3 and 4).

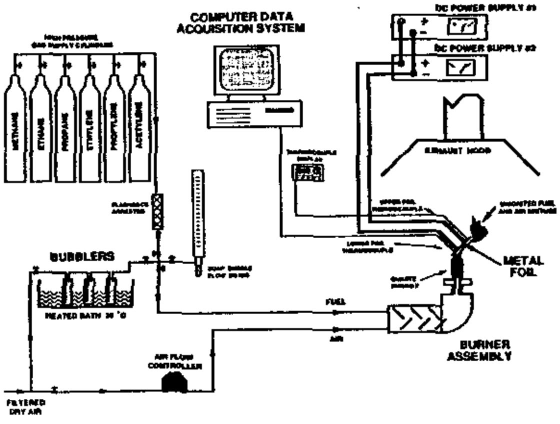


Figure 2. NIST Short Duration Autoignition Temperature Apparatus.

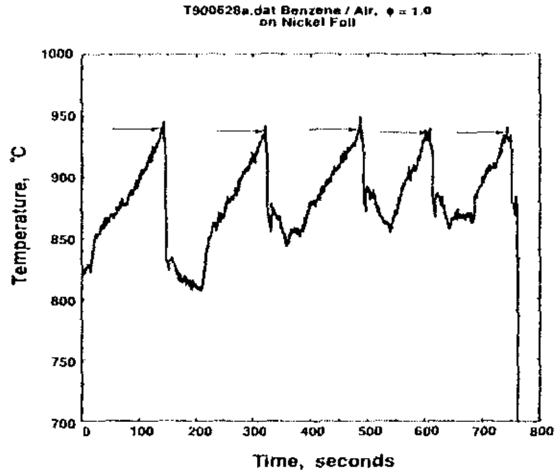


Figure 3. Temperature as a function of time for a benzene/air mixture for five repeat determinations of HSIT [8].

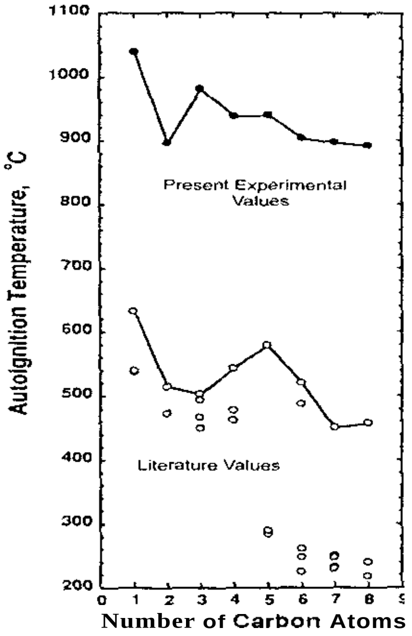


Figure 4. Comparison of measured HSIT as a function of carbon number for linear alkanes [8].

Propane and pentane have anomalously high ignition temperatures. As shown in Figures 5 and 6, this may be due to recently studied "packing effects" for lower (C3, C5, and C7) odd-numbered alkanes, which have lower melting points than even-numbered analogs, which pack better due to reduced end methyl group repulsions [9, 10]. Thus, packing effects may be important in assembling fuel molecules on a hot surface—better packing for even numbered molecules would be consistent with the lower ignition temperatures that are indeed encountered, at least for the lower molecular weight alkanes. The general downward trend in ignition temperatures accompanying higher molecular weights may thus be attributable to better packing for longer chain molecules, and for greater statistical opportunities for interactions of adsorbed oxygen and fuel carbon-hydrogen bond moieties.

Although the NIST Short Duration Autoiguition Temperature apparatus is valuable for accurate and precise measurement of ignition temperatures, there are disadvantages in terms of cost, bulk, ease of operation, and general use. Recently, NIST has innovated new microthermal analysis equipment, and in particular a "MicroHotPlate" (Figure 7), capable of determining heat flow at very small dimensions (60 μm), which is well suited for measurement of extraordinarily small thermal effects for very sensitive operations [11, 12].

Our group is proposing to miniaturize the existing NIST autoignition apparatus by incorporation of the newer NIST MicroHotPlate features, with a view to obtaining a more user-friendly approach to ignition temperature determinations.

THEORY POLARIZING EFFECTS

Although flame reaction mechanisms are emphatically of a propagating high-energy free radical nature, anomalies exist which indicate that earliest initiation stages may be of an ionic rather than free radical nature. As shown in Figures 8a and 8b, arenes and olefins which are most susceptible to free radical attack [13] are most resistant to hot surface ignition. Also, contrary to the order of ignitions in Figure 8a, free radical attack for branched chain alkanes and cycloalkanes is easier than for n-alkanes [13]; and

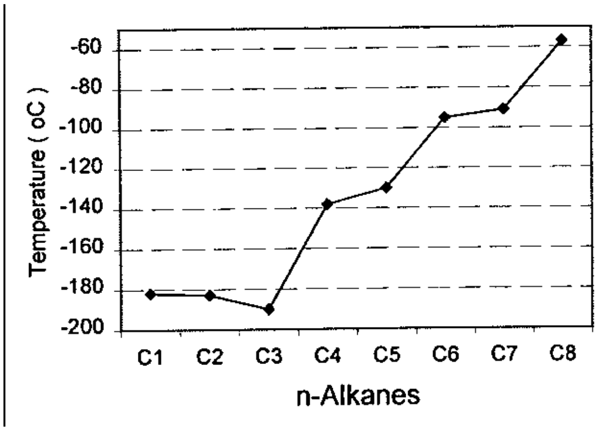


Figure 5. Melting points of alkanes.

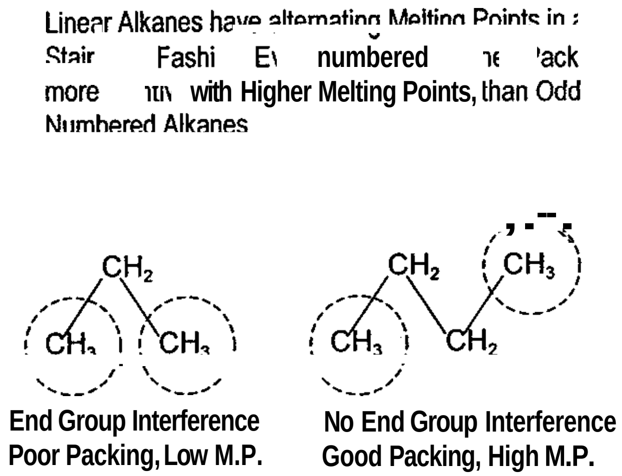
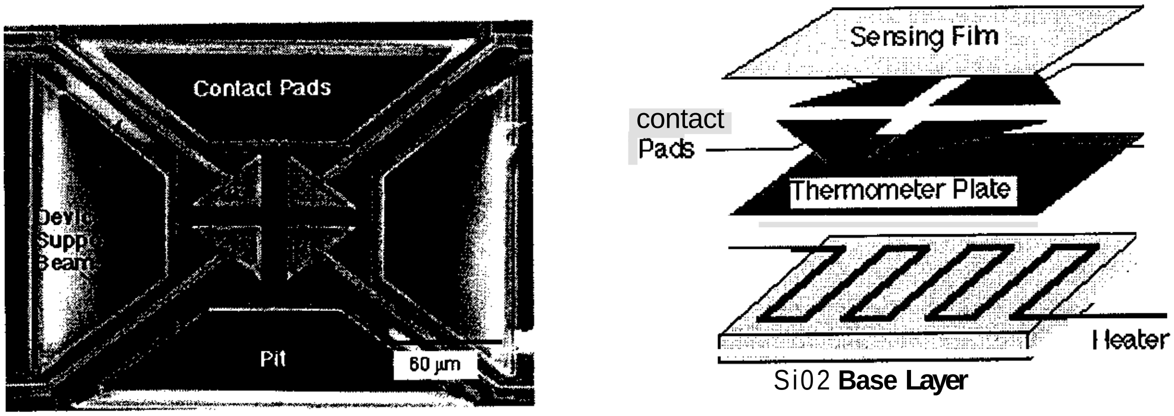

Linear Alkanes have alternating Melting Points in a Stair Fashi Ev numbered ne 'ack more with Higher Melting Points, than Odd Numbered Alkanes

Figure 6. Packing effects and melting points.



(a)

(b)

Figure 7. NIST MicroHotPlate (a) and its layout (b).

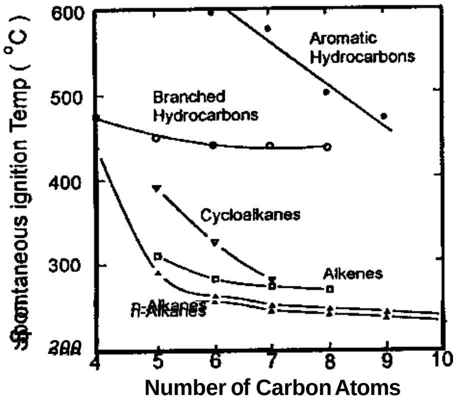


Figure Sa. Ignition temperatures for various hydrocarbons [1, 14, 15, 16].

Ease of Ignition	Carbanion	Free Radical	Carbocation
Arenes MOST Difficult	Easy / 379	Easy / 88	Easy / 239
Very Difficult *	Difficult / 419	Difficult / 93	Easy / 231
CvcloAlkanes Difficult	Difficult / 420	More Difficult / 97	Difficult / 250 **
Alkenes / Easy	Easy / 391	Easy / 86	Difficult / 255
Alkanes / Easiest	Difficult / 420	More Difficult / 98	Difficult / 250

* Comparisons are within types of intermediate

** Estimated

Figure Sb. Ease of formation of gas phase intermediates (Unit: Kcal/Mole) [17].

cyclopentane is more reactive to free radicals than cyclohexane [18, 19]. There is better agreement with ease of formation of carbanions for these species. Thus, oxidative attack on alkanes occurs most readily at primary C-H bonds, with secondary **C-H** bonds favored more than tertiary C-H bonds [14, 15]. This is precisely the order of stabilizing effects for carbanions [13].

At first glance, the much lower energies of formation (Figure 8b), for free radical intermediates than for carbanions, would imply that free radical intermediacies would have to be operational in **all** phases of a fire. However, it must be emphasized that these data are valid only for *gas phase* considerations, which should not be expected to apply to surface chemistry. For example, it is very evident that the free radical process is favored for the free radical reaction (1) over the ionic gas phase dissociation (2) of HCl [17]:

$$\mathrm{HCI} \longrightarrow \mathrm{H\cdot\ Cl\cdot} \qquad \mathbf{AD} = 103\ \mathrm{kcal/mole} \tag{1}$$

$$\mathrm{HCI} \longrightarrow \mathrm{H^{+}\ Cl^{-}} \qquad \Delta H_{f} = 186\ \mathrm{kcal/mole} \tag{2}$$

On the other hand, impingement of gaseous HCI onto a basic surface such **as** NaOH obviously results in an exothermic ionization process. We now suggest that hot surfaces can function **as** superbases in flame initiation, and that these participate through ionic pathways in the pre-flame chemistry to form alkyl hydroperoxide intermediates (ROOH), which then quickly break down through thermal pathways to form propagating free radicals. Other workers [8] have postulated that alkyl hydroperoxides are central to the build-up of concentrations of radicals such **as** OH, H·and·O, which are important species for fire propagation mechanisms.

Important considerations based on polarizing influences may be exerted by the nature of the hot surface itself and by the ambient atmosphere over the hot surface. In Figure 9, the hot surface seems most important in governing the ignition temperature; there can be very large variations (more than 100 °C) in these values that can be attributed only to this factor. Many workers (e.g., Pfefferle [20] have found important concentrations of hydroxyl, oxygen, and hydrogen free radicals on catalytic hot surfaces. Any theory involving mechanistic pathways to ignition must certainly address this phenomenon.

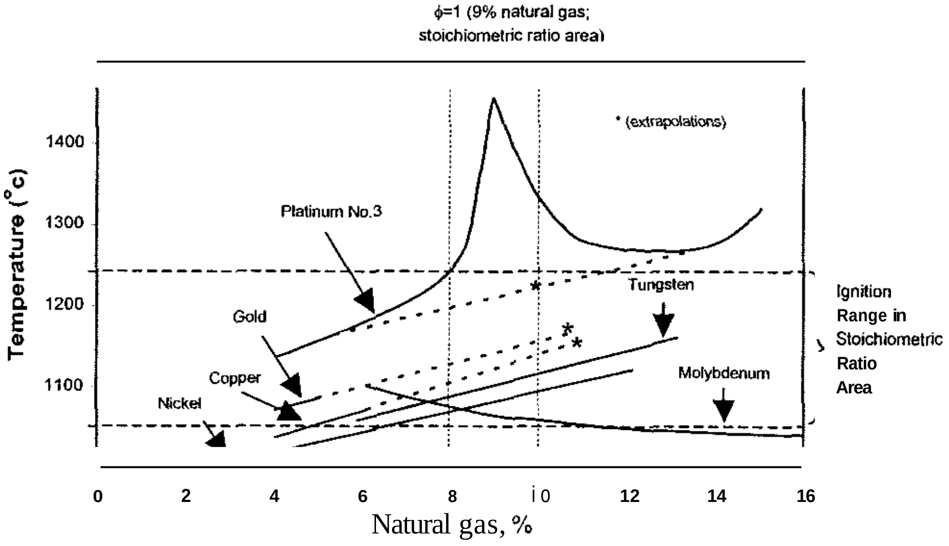


Figure 9. Ignition of natural gas mixtures (methane. ca. 80%: ethane ca. 20%) by hot metal surfaces [6]. (See also Figure 13 and accompanying text for related remarks. Note that considerable flameless combustion occurs below ignition temperatures, **as** seen in Table 1; and that Pfefferle and co-workers found that "the sharp maximum in surface temperature required for gas phase ignition (for platinum) is an artifact caused by transient heating of the surface **as** ignition occurs" [21]).

There are important effects that promote negative charge effects at hot surfaces and ionizing influences in the surface ambience. Seebeck [22, 23, 24] and Hall current [25] effects induce charge transfers in heated metals, with electron diffusion from hot to cooler metal surfaces (Figure 10). For a hot surface, there must be a hotter heat surface transferring heat to the surface, and a corresponding drift of electrons with a partial negative charge build up on the surface. The magnitude of charge (typically microvolts/°C change in temperature) may appear miniscule, but it would be anticipated that the effect for millivolt potentials for hundreds of degree temperature changes would be sufficient to promote significant polarization by interaction of partially negatively charged surfaces with thermally excited oxygen and fuel molecules adsorbed to the surface.

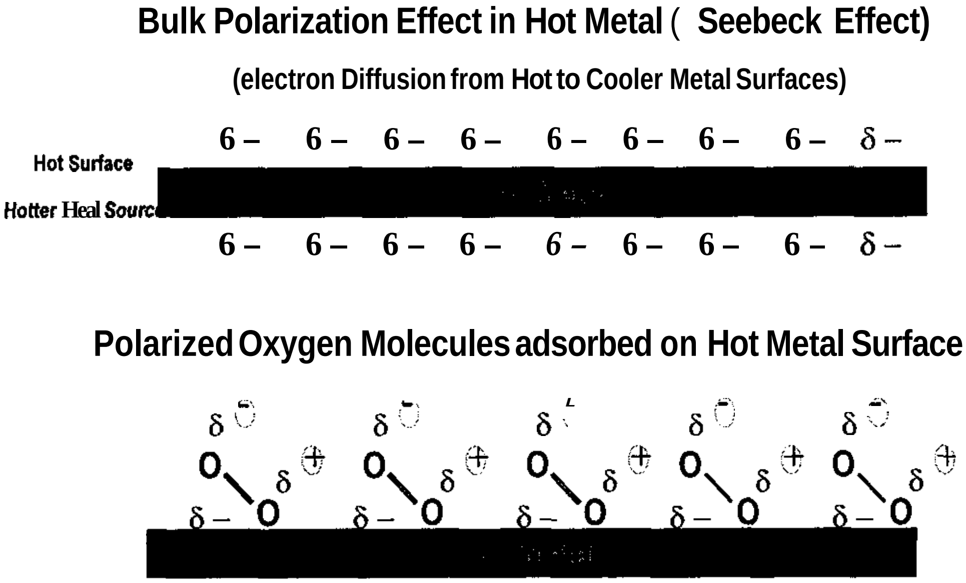


Figure 10. The Seebeck effect and resulting polarization of adsorbed oxygen on hot surfaces.

As shown in Figure 11, repulsion of pi bonds (such as exist in arenes and olefins) can occur by the partially negatively charged character of the hot surface [26, 27].

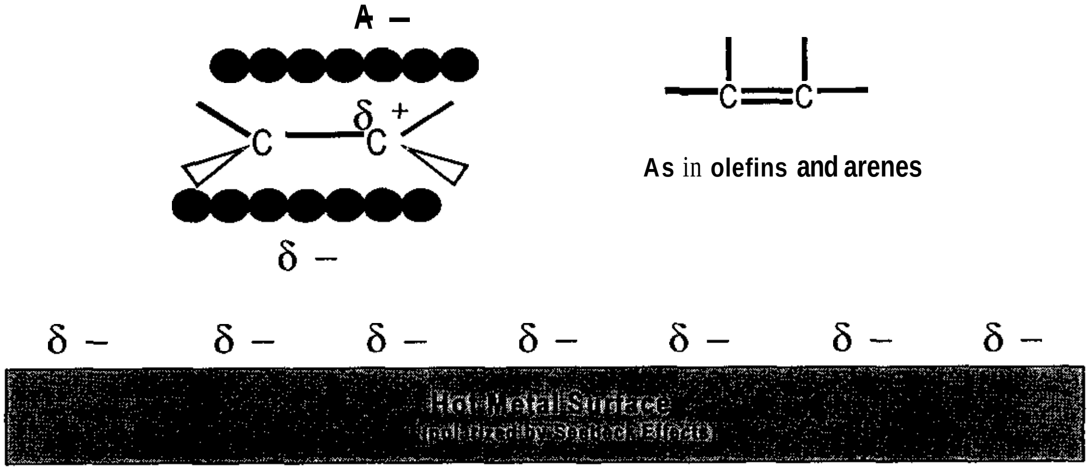


Figure 11. Anomalously high ignition temperature of arenes and olefins, caused by repulsion of pi bonds by partially negatively charged hot surfaces.

Oxyanionic surfaces such **as** quartz also can facilitate hot surface ignition by the strong polarization of adsorbed oxygen molecules, due to very high negative charge of oxygen atoms which comprise the entire surface of the silica matrix [28] (Figure 12).

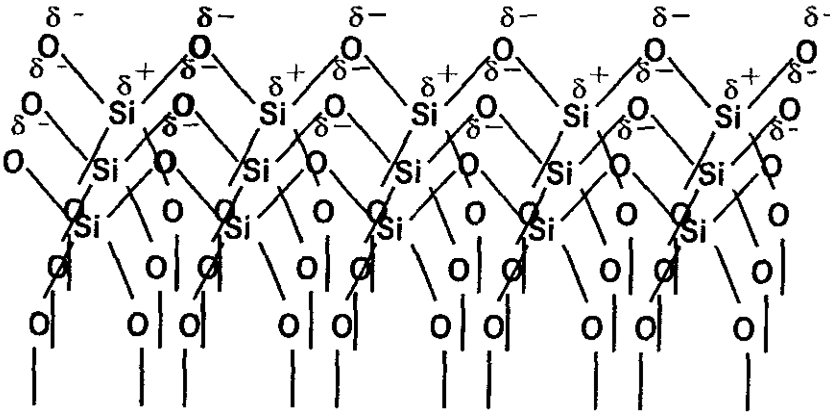


Figure 12. Polarization of quartz, **glass,** and similar silica surfaces.

Charge densities due to electronegativies: Si, **40%** positive; **O, 20%** negative [28]

Polyakov et al. [29] have shown dependence of corona discharges during adsorption of oxygen on various metals; with lower discharge potentials in moist air than in dry air. In studies of mixtures of hydrocarbon gases with water, hydrogen bromide, and even hydrochlorofluorocarbons (all highly efficient extinguishing agents, and all highly **polar** species that would appreciably polarize ambient air in the vicinity of the bot surface), it was discovered that instead of inhibiting ignition, these actually were ignition promoters **[30, 3**1]! This is a further argument for an ionic rather than free radical pathway in facilitating ionic ignition initiation processes in surface ignitions.

Figure **13** shows possible Seebeck effects in ignitions, particularly when compared to relative ignition temperatures for the same metals (cf. Figure 9). Except for nickel, all other metals have an inverse relationship of thermoelectric power to ignition temperature: the more positive the thermopower of a given metal, resulting in a greater thermoelectric shift of electron density, the more general the trend is for a decreased ignition temperature. Anomalously, nickel, with an extremely negative thermoelectric power, has a very low ignition temperature. This may be due to the ferromagnetism of nickel, though the ignition temperature here is far in excess of its Curie temperature (ca. **357** °C, or **630** K), above which the metal loses its spontaneous ferromagnetism [22]. More likely, this behavior could be attributed to oxide formations that readily occur with this **as** well **as** with many other metal surfaces at elevated temperatures.

Metal oxides profoundly adsorb polarized molecular oxygen [32]; this molecular oxygen facilitates catalytic oxidations [33]. Even clean metal surfaces profoundly adsorb atomic oxygen, polarization of which would result from Seebeck effects, with partially negative charge character on these adsorbed oxygen atoms. This would thereby provide a propensity for catalytic oxidations. Even metals such **as** titanium, which does not oxidize significantly at normal temperatures, when heated above **250** °C (as **0** would occur when heat treating takes place to increase metal strength), very significant oxidation does occur **[34].**

Thus, existing evidence implicates thermal polarization of adsorbed oxygen (either in molecular form over oxidized surfaces, or **as** atomic adatoms on non-corroded surfaces) and of fuel molecules (induced by polarizing effects of the hot surface), as shown in Figures **14** and 15. The high gas phase Bronsted Basicity [13] of the negative dipole of the excited oxygen molecule, or of the oxygen atom, on the hot surface abstracts a proton from the thermally excited fuel molecule. **A** synchronized S_Ni type mechanism

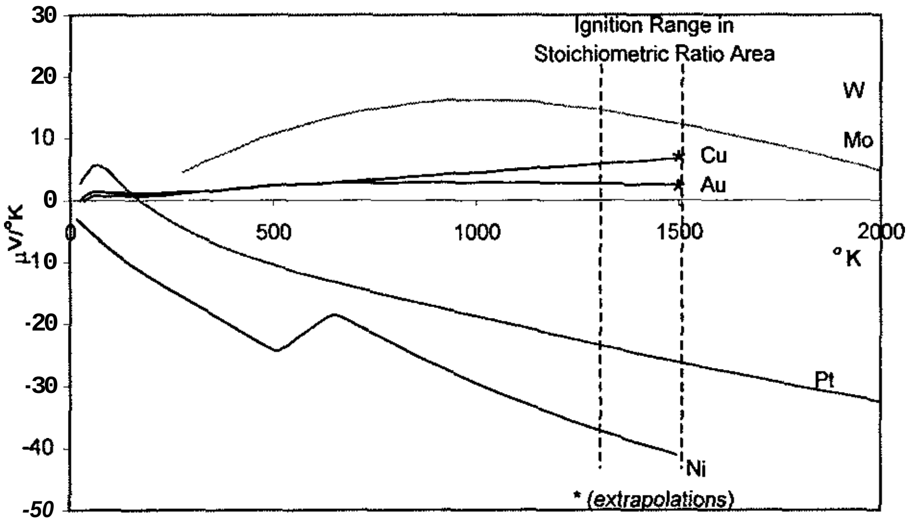


Figure 13. Thermoelectric power of metals, showing possible relationship with ignition temperature trends [29].

[13] can occur for attack by polarized oxygen atoms (Figure 14): the electron pair being freed in the C-H moiety can bond to an adjacent adsorbed oxygen atom, with an electron pair from this newly formed alkoxy species bonding with the first (now protonated) oxygen, to form an adsorbed alkyl peroxide. (Metal surfaces are blanketed by oxygen atoms, even at low temperatures [20]; this close proximity of adsorbed oxygen atoms can lead to concerted interatomic reactivities as described above.) Likewise, polarized adsorbed molecular oxygen can directly give rise to alkyl peroxide formation, as shown in Figure 15. In either case, the alkyl peroxide will thermally dissociate to form initially adsorbed free radical species. When enough of these accumulate in a sufficient population, they can desorb and participate with energized fuel molecules in conventional cool and hot flame free radical propagations. (Stabilizing or destabilizing influences in such free radical propagation systems would be entirely operational, and thus conventional free radical chemistry will prevail from this stage on.) This event can thus be construed as the defining moment that ignition occurs.

FUTURE RESEARCH

1. Construction of a miniaturized hot surface temperature apparatus.
2. Use of infrared radiation or lasers to heat the hot surface. This should make the hot surface the hottest part of the heated body, to install a partial positive charge at this surface, and thus would be predicted to promote higher ignition temperatures.
3. Application of direct positive charges to the hot surface. (This could have implications in terms of prevention of fires on hot surfaces.)
4. Examination of polarity fields in vicinity of the hot surface, after onset of preignition but before onset of actual ignition, to determine if there is a field with negative charge character which could be ascribed to Seebeck effect induced polarization.
5. Suggestions for use of isomerized, branched chain analogs of n-alkane (straight chain) jet fuels. These would have considerably higher ignition temperatures, with additional features such as lower viscosity and lower melting points (wiih favorable implications for high altitude refueling operations and for use in Arctic conditions.)
6. Isotope effect studies, with deuterated fuels. High isotope effects would indicate free radical pathways; low values would favor ionic mechanisms.

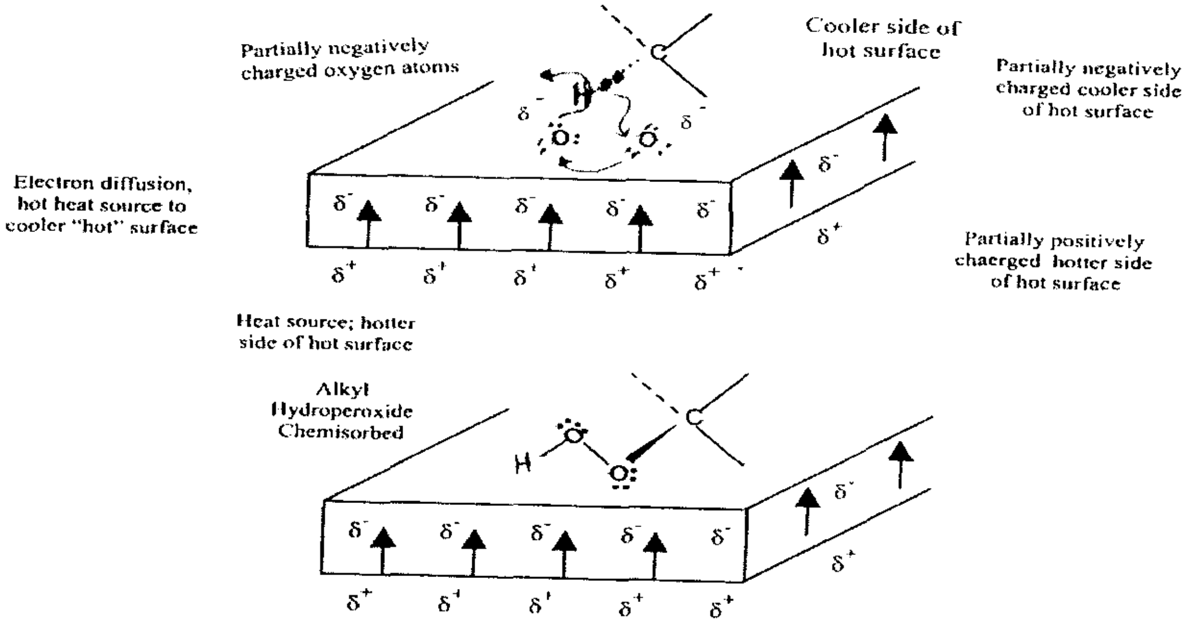


Figure 14. Polar effects in hot surface ignition: Polarized adsorbed oxygen atoms.

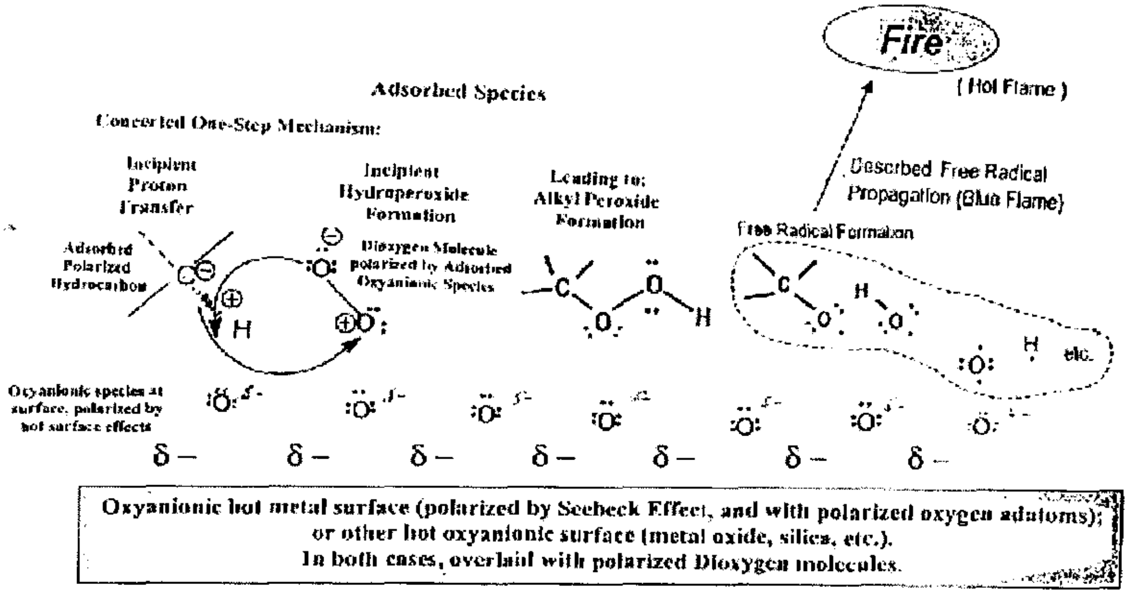


Figure 15. Polar effects in hot surfaced ignition: Polarized oxygen molecules.

7. Investigation of cationic (positively charged), rather than anionic firefighting agents such as AFFF. Cationic agents may be useful in mitigating reignition or other ignition phenomenon.
8. Suggestions of use of metals or alloys with hot temperature ignition characteristics for hot surface ignition problem areas, as in aircraft engines and dry bays; or with low hot surface ignition characteristics for use in cold-start Diesel engines.
9. Suggestions for application of these principles of polar effects **in** hot surface ignition to industrial applications of catalytic oxidations (e.g., in chemical oxidations of hydrocarbons to aldehydes or alcohols; and in hydrocarbon fuel cell research.)

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