FLAMMABLE AND TOXIC MATERIALS IN THE OXYGEN ATMOSPHERE OF MANNED SPACECRAFT

by John H. Kimzey

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Houston, Texas

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ABSTRACT

A preliminary study of the considerations necessary in selecting materials for use in an oxygen-rich atmosphere revealed that a major design effort must be directed toward reducing the toxic and flammable contaminants of the atmosphere. The effect of zero gravity in preventing convection is one aspect of research that deserves considerable effort since heat transfer and flammability are two major fields directly affected. Other research is needed in human tolerances, static electricity, removal of low-molecular-weight gas, fire extinguishment, overall characteristics of materials exposed for long periods in pure oxygen, and in the development of adequate test procedures.
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SUMMARY

A preliminary study of the considerations necessary in selecting materials for use in an oxygen-rich atmosphere revealed that a major design effort must be directed toward reducing the toxic and flammable contaminants of the atmosphere. The effect of zero gravity in preventing natural convection is one aspect of research that deserves considerable effort since heat transfer and flammability are two of the major fields directly affected. Other research is needed in human tolerances to gaseous contaminants, static electricity effects, removal of low-molecular-weight gases, fire extinguishment, characteristics of materials exposed for long periods in pure oxygen; and in the development of adequate test procedures.

INTRODUCTION

The Mercury spacecraft used an atmosphere of 100 percent oxygen at a pressure of approximately 5 psi. The same atmosphere is considered satisfactory for the Gemini and the Apollo spacecraft. The selection of this composition and pressure primarily involved crew inflight safety. In view of the oxygen atmosphere, the materials chosen for use in a spacecraft must be proved safe from the standpoint of contamination from both toxic and flammable gases.

The purpose of this paper is to define problem areas to be considered in the selection of materials for use in an oxygen-rich spacecraft atmosphere, and to indicate research areas requiring further investigation.

ATMOSPHERE SELECTION

Consideration is first given to the selection of an atmosphere in which man must live. Man is acclimated to a mixture of gases, including 21 percent oxygen and 78 percent nitrogen at a total pressure of 760 mm Hg. For a manned spacecraft, a different mixture may be found which will be more advantageous.
Some of the basic considerations for atmospheric selection for manned spacecraft are:

(1) The partial pressure of oxygen must be greater than 144 mm Hg to prevent hypoxia and less than 380 mm Hg to prevent oxygen toxicity (refs. 1 to 4). Other investigations (refs. 5 and 6) have given wider ranges in pressure, such as a minimum of 100 mm Hg to a maximum of 425 mm Hg.

(2) The total pressure must be such that during an accidental rapid decompression, a maximum pressure-change ratio of 2 to 1 should not be exceeded. This change can be tolerated in most gas mixtures without danger of decompression sickness, or bends, if the man is quickly subjected to the change from cabin atmosphere to pressure-suit atmosphere in the event of an emergency.

(3) Present pressure suits cannot be worn when a pressure differential greater than 3.5 psi exists without placing severe restrictions on the mobility of the man in the suit. The atmosphere used in the Mercury and in the Gemini spacecraft is 100 percent oxygen at 5 ± 0.2 psia. The same specification will probably be used in the Apollo Command Module and in the lunar excursion module. The minimum oxygen partial pressure will be 3.6 psia (185 mm Hg), regulated at 160 to 190 mm Hg. The use of this atmosphere, together with the many other restrictions on man in a spacecraft, reduces still further the freedom in material selection and requires maximum control from the standpoint of material atmosphere compatibility.

Pure oxygen imposes more stringent limitations on materials if spontaneous combustion is to be prevented. Man-rating such an atmosphere further limits materials when considerations of toxic contamination and flammability are required.

The use of an inert gas has been considered (refs. 2, 5, 7, and 8) as a means of suppressing flammability and eliminating some possible physiological disadvantages believed to exist. Reference 9 indicates that inert additives are not only unnecessary, but also increasingly complicated. The selection of an inert additive and the amount used involves several considerations. Reference 5 states that an additive (1) should be relatively inert chemically, (2) should be either insoluble in blood or retained in the blood like oxygen to prevent bubbles when environmental pressure is reduced, (3) should be trouble free from the standpoint of vocal communication, (4) should have a small diffusive leak rate through seals and gaskets, and (5) should suppress combustion.

Helium does not fulfill requirements (3) and (4). Nitrogen is poor from the standpoint of requirement (2); and argon, according to the U.S. Navy tests, is considerably worse. Nitrogen is listed in reference 4 as an inert gas, which is probably better than any other gas. Neon, or possibly sulfur hexafluoride, may be suitable for this purpose (ref. 8). Relative values have been assigned (ref. 8) to mathematically compute a habitability index.

The classification of materials as either acceptable or unsuitable for use in a spacecraft atmosphere of pure oxygen is no simple task. Quantity, temperature, outgassing products, and physical state (solid, liquid, or gaseous) must all be considered as well as radiation resistance, particle size, processing, and contacting materials.
TOXIC CONTAMINATION

Guidelines are necessary for the selection of materials for use in a spacecraft atmosphere. Acceptable contamination levels must be established. The determination of these safe levels is the duty of a toxicologist whose decision will undoubtedly be based on observation and past experience with animals and humans. Impurities enter the body in various ways. Reference 1 describes irritants, dusts, and asphyxiants as toxic materials entering the lungs; narcotics and systemic poisons as affecting the nervous systems; asphyxiants affecting the blood; and systemic poisons affecting the tissue. Results of such an entry can vary with the individual, depending on health, exposure time, and, probably, mental state of the individual. Zero gravity may alter tolerances. Also, each combination of toxic material can, according to references 6 and 7, present a new picture.

The degree of irritation is a factor. For example, a contaminant which is a lachrymator; a headache or vomiting producer; an impairment to hearing; or something that generally reduces performance would be less tolerable for an astronaut than for a person who can readily modify ventilation by dilution with safe air, or who can leave the contaminated area. Data presented in reference 10 provide a possible starting point if the data are modified for the new environment. These values, however, are based on a 40-hour work week. Revised values suitable for 2 weeks of continuous exposure are found in table I. The industrial values may be exactly the proper limit for some contaminants as shown for carbon dioxide, beryllium dust, and mercury. Many investigators have agreed (refs. 5, 6, and 11) that the values for most contaminants may be far too high. Reference 5 suggests that one-fifth of the maximum acceptable concentration be used as a design figure for continuous exposure; but reference 11 asserts that no formula can be used to convert these standards to continuous exposure limits. Reference 12 presents the following objections to publishing maximum acceptable concentrations because of (1) legal connotations; (2) indefinite data; (3) concentrations which are morally indefensible and easily misinterpreted; (4) lack of stimulus to operate at the ideal (zero); and (5) little indication of the dangers which may be incurred if the concentrations are exceeded.

The concepts should be stated in more realistic toxicological terms. Reference 13 includes information on the nature of the toxic action of the substances and defines whether the limit has been established, on the basis of discomfort, irritation, or injury. Reference 14 suggests the following categories (table II) to describe the physiological effect of some combustion products: (1) least detectable odor, (2) least amount causing throat irritation, (3) safe for several hours, (4) safe for 1 hour, (5) dangerous 1/2 to 1 hour, (6) fatal in 1/2 hour, and (7) rapidly fatal. Thus, seven different concentrations of the same irritants are classified as appropriate, with consideration given to both the degree of danger and the effect of time. This is certainly more practical than a single go-no-go value which could produce an intolerable atmosphere if several contaminants were present in combination, with each value slightly below the maximum allowed. Such qualifications could allow water vapor to be classified along with other additives when a humidity in excess of 90 percent becomes intolerable in some conditions where a temperature above the normal body temperature of 98.6° F is encountered (ref. 15).
TABLE I.- TENTATIVE LIMITS FOR ATMOSPHERIC CONTAMINANTS FOR 2 WEEKS EXPOSURE

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Maximum average level for continuous exposure 2 weeks, ( \text{mg/m}^3 ) ( (b) )</th>
<th>Industrial maximum levels, ( \text{mg/m}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>110</td>
<td>360</td>
</tr>
<tr>
<td>Acetone</td>
<td>240</td>
<td>2400</td>
</tr>
<tr>
<td>Acetylene</td>
<td>2.5 percent lower limit of flammability in air</td>
<td>None</td>
</tr>
<tr>
<td>Aerosols</td>
<td>0.1</td>
<td>None</td>
</tr>
<tr>
<td>Ammonia</td>
<td>17</td>
<td>70</td>
</tr>
<tr>
<td>Benzene</td>
<td>32</td>
<td>80</td>
</tr>
<tr>
<td>Beryllium dust</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>9000</td>
<td>9000</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>29</td>
<td>110</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>63</td>
<td>160</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.58</td>
<td>3</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>50</td>
<td>None</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>190</td>
<td>1900</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>250</td>
<td>None</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>45</td>
<td>90</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.00 percent lower limit of flammability in air</td>
<td>None</td>
</tr>
<tr>
<td>Isobutyraldehyde</td>
<td>290</td>
<td>None</td>
</tr>
<tr>
<td>Isoprene</td>
<td>140</td>
<td>None</td>
</tr>
<tr>
<td>Lithium hydroxide dust</td>
<td>0.03</td>
<td>None</td>
</tr>
<tr>
<td>Methane</td>
<td>5.00 percent lower limit of flammability in air</td>
<td>None</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>65</td>
<td>260</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>290</td>
<td>590</td>
</tr>
<tr>
<td>Methyl isobutyl ketone</td>
<td>200</td>
<td>410</td>
</tr>
<tr>
<td>Methyl propyl ketone</td>
<td>350</td>
<td>700</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>350</td>
<td>1750</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>59</td>
<td>None</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>Toluene</td>
<td>375</td>
<td>750</td>
</tr>
</tbody>
</table>

\(^a\)Source: Reference 11.
\(^b\)Since the values expressed in parts per million will change with total barometric pressure, space cabin values are given in milligrams per cubic meter.
TABLE II. - THE PHYSIOLOGICAL EFFECTS OF SOME GASES WHICH MAY OCCUR IN FIRES

<table>
<thead>
<tr>
<th>Effect</th>
<th>Carbon monoxide, CO</th>
<th>Chlorine, Cl₂</th>
<th>Hydrogen chloride, HCl</th>
<th>Carbonyl chloride, COCl₂</th>
<th>Hydrogen fluoride, HF</th>
<th>Hydrogen cyanide, HCN</th>
<th>Ammonia, NH₃</th>
<th>Hydrogen sulphide, H₂S</th>
<th>Nitrous fumes as NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Least detectable odor</td>
<td>3.5</td>
<td>--</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
<td>53</td>
<td>b¹⁰</td>
<td></td>
</tr>
<tr>
<td>Least amount causing throat irritation</td>
<td>15</td>
<td>35</td>
<td>3.1</td>
<td>10</td>
<td>1.0</td>
<td>15-3.0</td>
<td>400</td>
<td>100</td>
<td>62</td>
</tr>
<tr>
<td>Safe for several hours</td>
<td>100</td>
<td>0.35-1.0</td>
<td>10</td>
<td>1.0</td>
<td>1.5-3.0</td>
<td>20</td>
<td>100</td>
<td>20</td>
<td>10-40</td>
</tr>
<tr>
<td>Safe for 1 hour</td>
<td>400-500</td>
<td>4</td>
<td>50-100</td>
<td>10</td>
<td>50-60</td>
<td>100</td>
<td>2500-4500</td>
<td>200</td>
<td>100-150</td>
</tr>
<tr>
<td>Dangerous 1/2 to 1 hour</td>
<td>1500-2000</td>
<td>40-60</td>
<td>1000-2000</td>
<td>25</td>
<td>50-250</td>
<td>100-240</td>
<td>2500-4500</td>
<td>200</td>
<td>100-150</td>
</tr>
<tr>
<td>Fatal in 1/2 hour</td>
<td>4000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>200-450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapidly fatal</td>
<td>1000</td>
<td>1300-2000</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>3000</td>
<td>5000-10 000</td>
<td>1000</td>
</tr>
</tbody>
</table>

¹Source: Reference 14.
²Sense of smell lost after 2 to 15 minutes exposure to 100 to 150 ppm.
FLAMMABLE CONTAMINATION

The flammability effect of materials in various environments may be compared by several means. The ignition requirements and flame characteristics are considered along with fire extinguishment.

Ignition Requirements

The conditions to initiate combustion are far more complex than are generally believed. For example, it is misleading to refer to the ignition temperature of a material as if it were a chemical property. The following factors must all be considered in determining whether ignition will occur:

1. Composition and physical state of fuel
2. Composition and physical state of the oxidizer
3. Pressure, stress, or other internal forces
4. Gravitational force field
5. Temperature and enthalpy of container, fuel, and oxidizer
6. Energy media
7. System restraints
8. Surface area, texture, and particle size
9. Degree of mixing or stratification
10. Stability or degrees of self-degradation
11. Catalyst
12. Thermal conductivity
13. Time

The above items should be considered in terms of changing conditions as well as the rate of change. This list is not intended to imply that all of the factors are separate effects, nor that all of the factors can even occur, to a greater or lesser degree, at the same time. In some cases, many of these factors are negligible to the extent that their values are not measurable.

Composition and state of fuel and oxidizer. - Generally, solids and liquids do not burn by themselves. Except for a few materials such as carbon and some metals, a change of state is necessary. Only gases burn, whether in the free state or released from solids or liquids by an evaporation process. In order for solids or liquids to
perform as fuels, the first step is for energy, frequently in the form of heat, to evaporate some of the material to a gas. This energy can be generated by compression or friction with adjacent materials; or supplied by a high-temperature source in conjunction with radiation, convection, or conduction; or some combination of these. Exact processes may be very complicated. For example, surface effects of metallic titanium in oxygen are still unknown. This metal has ignited in pure oxygen spontaneously at 350 psia and, under flow conditions, at a pressure as low as 50 psia (ref. 16).

The flammability limits of combustible gases in air are compared with the flammability limit of pure oxygen in figure 1. The similarity of the lower limits is

\[
\begin{align*}
\text{Hydrogen} & \quad \text{Air} \quad \text{Oxygen} \\
* \text{Carbon monoxide} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Divinyl ether} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Diethyl ether} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Ethylene} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Ammonia} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Ethane} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Methane} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Cyclopropane} & \quad \text{Air} \quad \text{Oxygen} \\
\text{Propylene} & \quad \text{Air} \quad \text{Oxygen}
\end{align*}
\]

*This is not listed in reference 19. (Water was added to catalyze the reaction.)

Figure 1. - Flammability limits of various combustible gases in air and in oxygen. (From ref. 19.)
striking, and shows, from this standpoint, that the pure oxygen atmosphere is no different from a 21-percent mixture. Only carbon monoxide is outside the typical difference of 0.1 or 0.2 percent. The reason that some lower limits increase slightly from air to oxygen, while other limits decrease, is not clear unless the values represent various experimental conditions such as the amount of water vapor. All values are for a pressure of one atmosphere. Reference 17 compares differences in flammability of solids in air and in oxygen.

Reference 18 asserts that, in the absence of gravity, the flammable mixture ranges will be narrowed to "approach those obtained with horizontal propagation of flame. For example, the flammable range of hydrogen in the air would be approximately 6.5 to 71 instead of 4 to 75 volume percent."

Pressure, stress, or other internal forces. - The effect of pressure, according to reference 19, is that the ignition for mixtures of natural gas and air becomes more difficult as pressure is reduced below atmospheric pressure; however, the pressure limits of mixtures which will burn are as wide at 155 mm Hg pressure as at one atmosphere (fig. 2). Only by decreasing the pressure to 52 mm Hg for this gas mixture, is flame propagation impossible.

The testing of aircraft fuels at various pressures, using nitrogen and carbon dioxide as inert gases, showed that the percent of oxygen necessary for ignition increases as pressure decreases (ref. 20). This testing also showed that, as a diluent, carbon dioxide was better than nitrogen on a volumetric basis (fig. 3). Reference 18 indicates the minimum pressure necessary to support combustion was a function of the "quenching limit" of the mixture. Other considerations complicate generalization. For example, small diameter tubing required greater pressures to sustain combustion than large diameter tubing. Equally significant, flames have been found to propagate at pressures down to 0.01 psia (0.5 mm Hg) in large diameter tubes, although energy requirements for ignition were quite large at such low pressures. Both low and high rates-of-pressure change were investigated (ref. 21) on a candle flame and burning pools of liquid fuel (JP-6) and unsymmetrical dimethyl hydrazine (UDMH). No abnormal behavior was noticed.
The stoichiometric mixture of hydrogen and oxygen tested for ignition in a sphere (7.4 centimeters in diameter and lined with potassium chloride) shows the dependence of temperature on pressure (fig. 4). The plot in figure 4 shows how a gas, such as hydrogen, can be reported to have ignition temperatures ranging from 410° to 930° C; and how several ignition factors are necessary to define an atmosphere that provides reproducible data. Changing the salt coating on the inside of the container, the diameter, and the heating technique gives slightly different results expressed as a rate of change of pressure over a period of time (ref. 19). Cotton twill was ignited in pure oxygen at various pressures and showed that burning rates increased rapidly with pressure (ref. 3).

Reference 5 shows "on a highly qualitative basis" (fig. 5) that the fire hazard increases markedly as total pressure is reduced, if the partial pressure of oxygen remains constant.
Figure 4. - Ignition conditions for hydrogen-oxygen stoichiometric mixture heated in a potassium chloride sphere. (From ref. 19.)

Figure 5. - Relative fire hazard as a function of atmospheric pressure. (From ref. 5.)

A more complete view of the effects of pressure and inert gases is given in reference 22 for the "slow oxidation phase in the autoignition process of certain oils and other organics." In this type of combustion process the partial pressure of oxygen is a governing factor, and the presence of an inert gas is not necessarily beneficial. Reference 22 states that such an inert gas... impedes the dissipation of combustible gases and vapors that are formed from, say, the plastic insulation of an overheated electric wire, or from the lube oil in an overheated bearing, etc. The effect is noted in tests in which oils or other organic fluids are dropped on a heated surface. The temperature of the surface at which ignition occurs is found to be generally higher in undiluted oxygen than in an oxygen-nitrogen atmosphere with equivalent oxygen partial pressure. In this respect the rarefied atmosphere in a space vehicle has an advantage over the ordinary atmosphere."

For combustion processes in which oxygen is rapidly consumed, an inert gas can suppress burning by reducing the flammability and combustion rate, by absorbing some of the heat, and by restricting the oxygen mobility by reducing the oxygen molecular mean free path (ref. 22). Thus, ignition of plastics, fabrics, oils, et cetera, requires less contact time and less contact surface with incandescent bodies when nitrogen is removed.
The presence of inerts in contact with flammable material has been investigated for explosives. Reference 23 reports a study of incompatibility of components of explosive systems. When new mixtures are compounded, it is often observed that the addition of an ingredient considered to be inert will lower the thermal stability of the major components. The properties of a mixture cannot yet be inferred from the properties of the components.

Potential energy in the form of internal stresses can be difficult to identify. If loads inside the solid material change because of external heat or mechanical forces, the net result may lower the internal temperature if relieving the stress, or increase the internal temperature if the external energy increases the internal stress. Thus, combinations of events may contribute to ignition. In all cases, increasing the load on a solid, whether by tension or by compression, raises the temperature. Releasing a tensile or compressive load lowers the temperature. The net temperature change is dependent upon the rate of loading and the mass of material as well as the inherent thermodynamic properties.

Gravitational force field. - The effect of gravity is the least investigated consideration of ignition. If gases are stratified according to density, either from different temperatures or composition, the gases will shift to some extent as gravity forces change. The heavier gases will drift in a direction opposite to the applied acceleration, and may compress slightly as the gravity forces increase, causing adiabatic heating. Conversely, the low density gases in the same system will flow in the direction of the applied acceleration and will be cooled slightly. This latter effect is obvious from meteorological experience with rising air. Thus, convection processes increase in an increased gravity environment proportional to the induced field strength.

Reference 21 shows the effect of changing the gravitational field on the autoignition characteristics of fuels. Tests made at 1g and 10g indicate a possible dependence of the autoignition on the acceleration field strength.

In a reduced gravitational field, a gas or a liquid will experience some important effects (refs. 18, and 24 to 29). A study of ignition was made (ref. 30) using both paraffin and representative spacecraft materials. Atmospheres included a total pressure of 5, 10, and 15 psia and oxygen content ranging from 100 percent (which was used most frequently) down to 21 percent. Intervals of weightlessness as long as 12 seconds were achieved in a KC-135B aircraft. Ignition was provided by an electrical resistance wire. Most fuels ignited readily. Results were documented in both high-speed color and infrared motion pictures. A few tests failed to ignite due to separation of the wire from the fuel during handling techniques, and characteristics of the fuel making the fuel difficult to ignite under any conditions. Teflon insulation and glass-filled phenolic resins were in this category. Teflon would burn only while the heat of ignition was maintained, but the small tubing that was used did not always sustain combustion. The phenolic did not ignite when a few turns of wire spaced at intervals in excess of 1/4 inch were used; but the phenolic did ignite when tested a second time with many more turns of wire of a smaller diameter spaced closer together.

Convection ceases to exist at zero gravity, and diffusion became the major factor for mixing. Convective flow affects cooling rate and may result in excessive heating. This, plus the resulting three-dimensional stratification or pocketing of gases of different composition, makes the use of a circulating fan far more than a comfort item.
Loss of power to such a fan not only upsets the heat balance, but also tends to cause an individual's breath to form a cloud surrounding him which has an increasing concentration of carbon dioxide and water.

Aerosols, whether liquid droplet or solids (dust, lint, hair, food, ceramic, or metal particles), become increasingly important considerations in an ignition process at zero gravity. The effects of zero gravity on flame characteristics need considerable investigation; these effects will be discussed in a following section. Reference 18 shows the increase in the likelihood of ignition from a constant energy source that is not cooled by convection.

Temperature and enthalpy of container, fuel, and oxidizer. - The overall system, consisting of fuel, oxidizer, and container, will vary in susceptibility to ignition according to the heat conduction of the component materials. If the container is above the temperature of the fuel or oxidizer, the container will contribute energy to the system. If below, the container will remove energy. Likewise, the composition, specific heat, and coatings of the container will be a measure of the heat content and, consequently, the ability to act as a heat sink.

Based upon the temperature and other physical and chemical properties, various types of ignition may occur. Reference 31 distinguishes flash-ignition temperatures of solids from self-ignition temperatures. Reference 31 also describes work with plastics using a hot-air ignition furnace. Reference 19 describes cool flames as a type of combustion that proceeds at speeds as low as 10 cps. Reference 32 distinguishes between a combustion wave and a detonation wave.

Energy media. - Solar intensity outside the atmosphere of the earth may create unforeseen problems. The viewing ports of manned spacecraft may be coated or of such a composition to protect human occupants from short ultraviolet and longer infrared wavelengths, but consideration should be given to the conversion of oxygen to ozone, as well as ionization of other gases and materials exposed. If the requirements of some experiments specify windows that are ultraviolet transparent, the situation previously mentioned is particularly applicable. The opening of hatches for extravehicular activity may change the surface properties of interior materials from vacuum exposure as well as from exposure to the intense radiation levels. A classical example (not directly applicable to spacecraft) of how ultraviolet radiation can initiate an explosion is the case of a mixture of hydrogen and chlorine gas. The system is dormant under artificial illumination. Direct sunlight, however, quickly triggers ignition by converting molecular chlorine to chlorine atoms which react with molecular hydrogen, leaving hydrogen ions to react with molecular chlorine. Mixtures of hydrogen and oxygen gas in the presence of organic materials also react spontaneously if initiated by ultraviolet radiation. Thus, a first-order chain reaction is established. The kinetics of other reactions are not so straightforward. Intermediate unstable compounds frequently complicate the process. Even the simple hydrogen-oxygen reaction can take 19 possible routes.

The extent and effect of static charges resulting from two spacecraft conducting a rendezvous may present complications. If one or both spacecraft operate a chemical propulsion system while maneuvering in a high solar-intensity field, a strong electrostatic charge may result. When contact is made between the bodies, as in docking maneuvers, energy will be released to balance the charge. Part of this energy could
be transmitted by secondary arcing and heating within each spacecraft. An antenna
could provide the high voltage input and damage the communication equipment. The
high voltage could exceed operating limits of electronic parts and cause overheating.
Or, if a structural part of the spacecraft received the energy at contact, the dissipa-
tion path could still cause trouble.

Reference 19 states that a strong electric field presents a number of complicated
disturbances in a flame. The effect generally results from migration of the charged
gas particles toward the negative electrode causing an electric wind which distorts the
flame in various ways, which, in turn, causes the flame to be speeded up, slowed
down, or even extinguished.

System restraints. - Aircraft fuels were tested (ref. 20) in a large container
having a volume of 12.5 cubic feet, and it was concluded that the high and low ignition
limits are wider than hitherto reported in the literature. The values from this test
varied mostly on the rich side (approximately 2 percent) with the lean values differing
approximately 0.25 percent. The geometry of the confining surface, the reflective
nature, and whether baffles or screens are present, all have an effect on ignition,
however subtle. The container size is related, in reference 18, to the minimum pres-
sure necessary to support combustion, as described previously.

Surface area, texture, and particle size. - Many items classed as nonflammable
in air, and even in gaseous oxygen, are pyrophoric if the particle size is small enough.
Condensed metal vapor evaporated in an ultrahigh vacuum (ref. 33) blazed promptly
when released in the air. With a high-surface-mass ratio (particle mean diameters
from 200 to 600 angstroms), the heat sink is lost, and surface oxidation can result in
a temperature sufficient to reach the melting point. Oxidation then becomes continu-
ous and rapid and results in ignition. Recent findings are discussed in reference 34.

Energy added by micrometeoroid impact can ignite pyrophoric materials in the
presence of oxygen. Titanium in gaseous oxygen may be ignited by impact if many
cracks develop in some confined area. The heat of chemisorption (ref. 35) is approx-
imately 225 000 cal/mole of titanium, or 50 000 Btu/lb reacted. Heat applied in any
way, including an electrical short, results in combustion if the surface becomes mol-
ten; and the oxides which are formed can wash away, continuously exposing new mate-
rial for additional reaction.

Heats of reaction (ref. 36) are known for virtually all oxidation reactions; there-
fore, the heat evolved can be calculated for known materials. To determine whether
the heat will result in ignition is more complicated. The rate of heat evolution is
apparently the key, and this in turn is dependent on the surface characteristics.

Degree of mixing or stratification. - Gases having different densities in a field
of unit gravity may stratify and mix only by diffusion. In a field of zero gravity strat-
ification may be more of a problem. The addition of a flammable gas to an atmosphere
by any means, such as a leak or by outgassing of an overheated material, will create
a chemically unstable condition.

Stability or degree of self-degradation. - The stability of materials is a broad
category which could cover loss of solvents or entrapped gases from surface coating,
compounds, and foamed or solid polymers to such things as depolymerization and
spontaneous combustion. A study of self-heating reactions (spontaneous combustion), reported in reference 37, produced kinetic constants for various cellulosic and polymeric materials and natural oils from which, assuming a first-order reaction, critical radii of spherical piles of materials at storage temperatures ranging from 20° to 100° C are given. When considering a spacecraft atmosphere, the outgassing products in the new environment and the thermodynamic effects of zero gravity are pertinent, as well as the relative efficiencies of removing impurities by the environmental control system. A summary of decomposition products of various materials is given in reference 14 (table III). The amount of carbon monoxide is considerable. A test of the same fuels in oxygen rather than air would undoubtedly show more complete combustion and correspondingly different products of combustion. The higher flame temperatures add one further variable but the toxicity products would, in general, be the same. None of the nitrogen products such as cyanides or ammonia are due to atmospheric ammonia. The ratio of carbon dioxide to carbon monoxide may go up and carbonyls may also increase, although whether the environment is weightless or one g, or more, makes a difference as to whether a reaction goes to completion.

Catalysts. - The use of radiant energy to catalyze a reaction was mentioned previously for the hydrogen-chlorine reaction. Other catalysts include contacting solids and liquids. Materials added to catalyze polymerization of plastics can catalyze depolymerization as well. Coatings including unwanted soils may provide the media for initiating a reaction. The interaction of various materials complicates the ability to predict ignition. Even under laboratory conditions, the kinetics are extremely complex, with many different chemical mechanisms possible. The nonpredictability of inerts added to explosives was discussed earlier.

Thermal conductivity. - Localized energy from mechanical friction, electrical resistance, or chemical reaction will be dissipated over a large mass of material or leak away at such a slow rate as to give a high temperature. Thus the heat rate can be relatively low and result in the temperature increasing until ignition is reached. Efforts have been made to improve electrical potting compounds by improving their heat dissipation without a loss of electrical resistivity. The objective is to improve performance by maintaining lower temperatures rather than prevent ignition; but the effect is the same. Structural plastics are becoming more useful in spacecraft design. Their use should incorporate enough thermal paths to avoid thermal overloads.

Time. - A tabulation of ignition requirements must necessarily list time as one of the variables. Rates have been discussed in many of the other requirements. Something goes from a stable, safe condition to an unsafe condition where ignition takes place according to a combination of things that are rate-controlled. The rate of heat input, the time of exposure, the rate of evaporation or melting, the rate of applying or relieving a pressure or force, the rate of adding inerts, the rate of conducting heat and radiant energy away, the rate of oxidizer flow, and the gravitational acceleration are all time-controlled.

Flame Characteristics

The significant flame properties are the rate of burning, the flame temperature, and the emission spectra. For any chemical reaction, the heats of combustion are predictable from the recorded heats of reaction. For a given reaction with a known
TABLE III.- SUMMARY OF DECOMPOSITION PRODUCTS OF PLASTICS²

<table>
<thead>
<tr>
<th>Investigation and references</th>
<th>Material</th>
<th>Method of testing</th>
<th>Analyses, percent volume</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oxygen, O₂</td>
<td>Carbon dioxide, CO₂</td>
</tr>
<tr>
<td>F. D. Snell</td>
<td>Melamine resin, paper, or wool</td>
<td>Heated in a current of air and products passed over rats in cages</td>
<td>9.8</td>
<td>6.2</td>
</tr>
<tr>
<td>J. C. Olsen</td>
<td>Wood</td>
<td>5 lb burned in 110 ft³ air</td>
<td>6.6 to 6.6 to 3.4 to 13.4</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>Rubber</td>
<td>Insulation on cable in 5-liter flask</td>
<td>6.6 to 6.6 to 0.5 to 14.2</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>Wool</td>
<td>Heated in silica tube with a current of air</td>
<td>4.0 to 8.0 to 3.0 to 8.0</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>Silk</td>
<td>Burning house</td>
<td>19.9</td>
<td>.7</td>
</tr>
<tr>
<td>F. E. T. Kingman, et al</td>
<td>Timber and fiber insulating board</td>
<td>1.6</td>
<td>17.8</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3</td>
<td>9.2</td>
<td>16.7</td>
</tr>
<tr>
<td>E. H. Coleman and</td>
<td>Chlorinated methacrylate resin 27 percent chlorine</td>
<td>0.3 g at 550°C in 5 liters air</td>
<td>(b)</td>
<td>2.6</td>
</tr>
<tr>
<td>C. H. Thomas</td>
<td>Polyvinyl chloride 17 percent chlorine</td>
<td>0.25 g at 550°C in 5 liters air</td>
<td>(b)</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>Polyvinyl chloride</td>
<td>0.25 g at 550°C in 5 liters air</td>
<td>(b)</td>
<td>2.0</td>
</tr>
<tr>
<td>A. Schlesheim</td>
<td>Plywood</td>
<td>Heated at 550°C in 5 liters air</td>
<td>2.8</td>
<td>17.1</td>
</tr>
</tbody>
</table>

²Source: Reference 14.

¹Not determined.
<table>
<thead>
<tr>
<th>Investigation and references</th>
<th>Material</th>
<th>Method of testing</th>
<th>Analyses, percent volume</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oxygen, $O_2$</td>
<td>Carbon dioxide, $CO_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plywood polyvinyl chloride and flame-retardant paint</td>
<td>Heated at 550°C in 5 liters air</td>
<td>2.1</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td>Plywood with polyester resin and flame-retardant paint</td>
<td>Heated at 550°C in 5 liters air</td>
<td>2.5</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>Polyvinyl chloride coating only</td>
<td>Heated at 550°C in 5 liters air</td>
<td>0.3</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>Vinylidene coating only</td>
<td>Heated at 550°C in 5 liters air</td>
<td>17.0</td>
<td>4.0</td>
</tr>
<tr>
<td>H. A. Watson</td>
<td>Foamed polyvinyl chloride</td>
<td>2 to 3 g heated electrically, in 270 liters air</td>
<td>20.7</td>
<td>0.16 to 0.35</td>
</tr>
<tr>
<td></td>
<td>Foamed acrylonitrile</td>
<td>20.7</td>
<td>0.16 to 0.35</td>
<td>0.023 to 0.040</td>
</tr>
<tr>
<td>L. B. Berger</td>
<td>Phenolic resin with fillers</td>
<td>2 to 3 g heated electrically, in 270 liters air</td>
<td>(b)</td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td>Melamine resin with fillers</td>
<td>2 to 3 g heated electrically, in 270 liters air</td>
<td>(b)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

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*Source: Reference 14.

*Not determined.
heat quantity, therefore, the temperature is related to the combustion rate. In pure oxygen a solid or liquid will produce a flame which will burn faster and hotter without the dilution of atmospheric nitrogen to absorb some of the heat or otherwise interfere with the reaction. Gases, on the other hand, may or may not burn hotter in pure oxygen. If the additional oxygen available provides for more thorough combustion, such as in the case where carbon dioxide rather than carbon monoxide is the end product, more heat is liberated. Furthermore, the heat of evaporation required for solid or liquid fuel can reduce end temperatures compared with gaseous reactions. The rate of combustion is affected by particle size, initial temperature, effects of confinement (which change a system pressure, composition, and temperature of surrounding material), heat capacity and conductivity of appropriate compounds, and whether ignition conditions are maintained throughout combustion or removed as soon as the fire starts.

**FIRE EXTINGUISHMENT**

Most materials used in spacecraft construction are flammable. Materials that are virtually fireproof include some oxides, nitrides, sulfides, fluorides, borides, and the variety of materials generally classed as ceramics. Certainly magnesium, titanium, aluminum, and iron alloys, as well as organic materials, would ignite far more readily in pure oxygen and may continue to burn.

Efforts are being made to make various materials more fireproof (ref. 38). Such research may result in reducing the likelihood of ignition and limiting the spread of fire, or causing materials to be self-extinguishing. The need for a research program to acquire more knowledge of the toxic gases resulting from burning various plastics is indicated in reference 39. Reference 40 shows that concepts of fire and fire extinguishment must be revamped and that a fourth consideration needs to be added to the familiar triangle of heat, fuel, and oxygen. This consideration is the chemical chain reaction in the flame itself. If the flame-chain reaction is interrupted, extinguishment will start. A surface for attachment for the free radicals in the flame zone must be provided. This is apparently one of the advantages of dry chemicals such as potassium bicarbonate.

Reference 41 gives four categories for mechanisms of flame extinguishment. They are (1) isolation of combustible and air, (2) removal of heat, (3) disturbance of the flame zone, and (4) radiation blockage. These categories are also discussed in reference 18. Fluorinated hydrocarbon compounds are recommended (ref. 15) for fire extinguishment in spacecraft since these compounds require less material to extinguish the fire; the compounds are excellent on fuel-oxidizer fires; and the compounds have relatively low toxicity. Reference 42 discusses halogenated extinguishing agents. It is noted that tests in air are described in detail with the primary effectiveness being for oil and electrical fires. Nothing could be found on the use of these compounds in oxygen-rich atmospheres.

The use of distilled water as a fire-extinguishing agent is being evaluated, as reported in reference 43. Perhaps distilled water is the best available substance; but, wetting a surface in zero gravity may be difficult.
The operational procedure for extinguishing a fire in the Mercury spacecraft and the early Gemini spacecraft called for removing the oxygen by opening a vent valve. Fortunately, this procedure was never evaluated since 30 to 90 seconds would probably be needed to be effective. This procedure is obviously inappropriate if the crew were in shirt sleeve garments, as 5 or more minutes are needed for the crew to don their suits.

It is believed that the best approach to fire extinguishment is to provide a gas blanket around the flaming parts to reduce the oxygen concentration while reducing the total pressure. The use of 100 percent oxygen as a start requires considerable gas for necessary dilution. The requirements for a gas that can extinguish fires in a spacecraft include (1) lightweight, (2) nontoxic, (3) chemically inert, and (4) high heat capacity. A review of the state-of-the-art in flame extinguishment by chemical and physical agents in a one-g environment is given in reference 43. Emphasis here is on mechanisms involved.

Possible candidates for fire-extinguishing gases include carbon dioxide, helium, argon, neon, nitrogen, water vapor, bromotrifluoromethane, and other halogenated compounds. Bromotrifluoromethane should also be considered. Helium is already carried on board and may be satisfactory for this purpose. A low-pressure system (100 to 200 psi) could be piped around the spacecraft cabin. Should a fire start, a sensor could operate a valve to release the gas and dilute the oxygen. The reduction of the helium pressure could be used to operate a switch to turn off the circulating fan. The pilot could then have a longer time to pressurize his suit and vent the cabin.

The effects of zero gravity on combustion may prove very interesting. Very few references to this subject were found in the literature. As reported in reference 44, burning liquid fuels were photographed in a falling chamber at six different gravitational accelerations between zero g and one g. Burning times were 1/3 second and less. Results showed that while droplet diameters decreased with time, flame diameters increased. Reference 30 gives somewhat different conclusions. After the flame corona reached a maximum size in times varying from 0.44 to 1.02 seconds, the corona then darkened gradually as the size diminished. Apparent extinguishment of paraffin was noted after intervals of 0.84 to 1.16 seconds following ignition. This conclusion was reached since nothing was visible after these intervals in motion pictures taken in color at 400 frames per second, or in infrared at 200 frames per second. In all cases, however, the return of an acceleration as from striking an object in the test aircraft or the return to level flight imposing loads varying upward of 2-1/2g caused the flame to appear and the fuels were consumed. Whether total self-extinguishment would occur in fuels enveloped in flame is not yet known. Propagation of a flame occurs at a somewhat reduced rate, compared with one g, as demonstrated in styrene, foam rubber, wood, paper, tygon tubing, nylon fiber, and other structural polymers. Combustion gases apparently envelop the fuel and impede the passage of oxygen by diffusion. The mixture ratio of fuel-to-oxygen can be considered to change continually from lean to rich, and steady-state conditions do not appear to exist. This characteristic can be used to an advantage from the standpoint of extinguishing an accidental fire; however, the propagation along flammable surfaces and time to stop artificial convection can complicate procedures. Burning rates in zero gravity were investigated for tubular fuels and reported in reference 45. These tests showed that, for surface propagation, steady-state burning does take place. After the surface is enveloped, however, and the burning direction is perpendicular to the surface, the fire
tends to be self-extinguishing and steady-state conditions, from this aspect, do not take place. The above distinction could not be verified, however, as all fuels were totally consumed during the high-g pullout of the aircraft providing the zero g. Theoretical considerations of zero gravity, as discussed in reference 46 are remarkably well handled although some minor revisions are now in order. From initial work with a candle it was estimated that the danger of fire under weightlessness is more serious "than has been predicted" (ref. 47).

In zero gravity, a heating element is reported to lose its efficiency to transfer heat to a liquid, thus continuous boiling may be impossible. Only superheated vapor contacts the hot surface and the net effect is a slight increase in pressure, leaving only conduction and radiant heating of the liquid. If an immersion heater is provided to evaporate the cryogenic liquid, an agitator or large conductive surface area is also needed. If the immersion heater is not provided, the element will soon be surrounded by a cloud of gas having a steep temperature profile, with only radiant and conductive heat transfer to the liquid. Thus, the needed gas is not obtained, and the heating element may be damaged by overheating. A leak results if the tubing containing the electrical resistor is opened. Furthermore, the liquid could become contaminated by the material separating the heating element from the surrounding tubing. A similar condition, which may not work during zero gravity, is the external heating of a tube containing a frozen heat-transfer material which must be thawed to resume circulation. A liquid film inside the tube may not conduct the heat, without convection, to assist circulation. If an agitator is needed here, the design could be troublesome.

**SOURCES OF CONTAMINANTS**

Contamination can result from simple evaporation in a reduced pressure, from the effect of overheating causing degradation of materials, or from the products of reaction between materials of the craft. (Materials in electrical equipment must be selected on the basis of not producing contamination, toxic or flammable, if overheated. This may be exceedingly difficult to do.) Mechanical failure from a leak or improper functioning of some device can allow contamination. Failure of valves, location of vents, sequencing or timing of events, whether pilot-operated, ground-operated, or automatic, are all problem areas. In this connection, the backup system must be especially clean because crew tolerances are reduced under emergency conditions.

Ionization of gases is a complicating factor, whether produced deliberately for some physiological purpose by onboard electrical equipment or by external radiation. Ionization can affect the rate at which organic materials deteriorate and can affect reaction products. Radiation can indirectly affect the atmosphere of a spacecraft by changing the emissivity of a radiator surface, by reducing its efficiency, and by upsetting critical thermal balances. The direct effect on optical surfaces and the indirect effect of limiting maneuverability by avoiding exposure of certain surfaces would be undesirable.
Man is one of the major sources of atmospheric contamination. His food, prepared for long storage, is not necessarily adaptable to eating under conditions of zero gravity, as reported by the pilot of the Mercury Atlas 7 flight (ref. 48). The waste products, whether breath, perspiration, or other excretory matter, have to be disposed of efficiently since there are hundreds of byproducts which, in sufficient concentration, are toxic. Aside from carbon dioxide and water vapor, hydrogen and methane are the major gases derived from man (ref. 1).

The survival equipment carried on board for emergency use in flight or after landing must be critically evaluated for hazards. A leaking tube of lotion may have an animal oil which can ignite in pure oxygen. Similar flammables may be present as solvents in syringes, creams in deodorants or dentifrices, cotton in gauze, or wood in splints.

Metal working in space may produce pyrophoric impurities. If cutting, grinding, or welding is done in vacuum as on the exterior of a spacecraft, small particles may be produced. Some of these coated to the gloves or adhered to the surface of the space suit on the arm or shoulder may be troublesome as the man enters an airlock and oxygen is introduced. If the heat of reaction causes the melting point to be reached, the result is total oxidation of the particle. Temperatures are excessive at incandescence and, according to the base material, ignition may result. Nitrogen may be reactive in this respect with some alloys, especially titanium.

Lunar samples, whatever their composition, are other sources of problems. Lunar material may quickly change properties when carried into a pressurized oxygen atmosphere. Even if most are carefully packaged to protect them, some may be carried inside as soils. It would be desirable to measure heats of oxidation at a safe distance from the returning vehicle. Their long dehydrated environment may make water compatibility questionable as well.

Purity of products is important. Analysis specifications for breathing-grade oxygen must be stricter than for aviation use. The fuel-cell manufacturers also require uncontaminated gas. Whatever impurities are present may be accumulative, if leak rates are less than specified. The quantity and identification of impurities must be anticipated for designing the absorber to estimate both the removal of the impurities and the capacity of the impurities to saturate the absorbent bed, or to displace the flammable or toxic gases previously absorbed. Some of the gas products removed from the CO₂ absorber of three Mercury flights, MA-6, MA-7, and MA-8, could have entered the system as an impurity in the oxygen installed for breathing (ref. 49). Many impurities can result from ground-handling techniques. It is important, yet difficult, to anticipate the problem areas sufficiently in advance to take action. For example, one region that has not been thoroughly investigated is the gaseous products emitted from camera film emulsion. Certain gases believed to be attributed to the plasticizer in the cellulose acetate, and still unidentified, are not usually considered harmful. In sufficient quantity the gases can be a hazard, particularly if future programs will require photographic film processing. Protection from ultraviolet, vacuum effects, and temperature extremes, as well as the need for accessibility, requires the film to be inside the cabin. If investigation proves that the gas is harmful, custom-designed film may be required, or an extra safety factor must be included in the gas purification.
It may be well to mention that processing film during flight may be ruled out on the basis of the reducing agents needed to produce the metallic silver, or color, on the exposed emulsions. Pyrogallic acid or catechol are used as developers; both have a strong affinity to oxygen and, even if the developers work, may scavenge an excessive quantity of the gas.

GAS CONTAMINANT DETECTION AND REMOVAL

The use of lithium hydroxide and activated charcoal as a gas absorber for Mercury spacecraft has proven adequate. Other gases, it is noted, are in the absorber from preflight systems, including solvents and refrigerants, as well as those added during flight. Future flights of longer duration that use a completely closed system will present far more sophisticated procedures (both from the standpoint of ground handling and gas product removal) which, in recycling, could build up to dangerous concentrations. It may prove worthwhile to take gas and aerosol samples periodically during spacecraft flights to analyze the atmosphere for impurities not absorbed. Detection equipment (other than for carbon dioxide) could identify traces of fuel, oxidizer, hydrogen, ozone, and carbon monoxide before these impurities cause trouble. Different gases are absorbed with various efficiencies. Hydrogen, specifically, is not absorbed easily and could build up in a closed system. In addition to the fuel cells and human waste products, hydrogen may result from lunar materials reacting with moist air.

Toxic concentrations, which are corrected by utilizing the suit systems, may be tolerated for the necessary short periods in which the crew must eat and drink. Flammable overloads can be corrected only by dumping valuable oxygen overboard.

PROHIBITED AND PERMITTED MATERIALS

In Project Mercury, various materials were prohibited. These included, originally, metallic mercury and teflon. Later zinc chromate, generally used as a primer, was prohibited from use on a heated surface because of the possibility of liberating acidic chromium trioxide gas. Still later the use of zinc chromate was prohibited on any surface. Teflon has been restricted by default since even the manufacturer was unsure of the toxic effects. Recently, however, the material has been reinstated for use in spacecraft unqualifiedly in unpressurized regions and in pressurized regions provided temperatures would be expected to remain below 200° C. When studying teflon, investigators pointed out (ref. 50) that a "polymer fume fever resembling influenza is possible from most overheated plastics if sufficient quantity is inhaled, [but they] are not as toxic as the acrolein emitted from overheated animal fat."

Many starch or carbohydrate foods in dehydrated, powdered form could react explosively if spilled into a pure oxygen atmosphere. Packaging, water content, and particle size are therefore important. Tests are necessary but expensive. Something more specific than odors alone (ref. 51) must be measured. One proposal gives three possible approaches, including a simulated 14-day mission using several animals to detect a composite effect.
The American Society for Testing Materials (ASTM) is studying various aerospace problems, such as lubricants. Testing standards for flammability and toxicity, which can be used universally, are also needed. Existing ASTM's are not adequate for testing either ignition or flame characteristics of materials used in a spacecraft. Nothing could be found that was an acceptable test for toxicity from gases released in a closed, pure oxygen atmosphere at a reduced pressure.

It is believed that, as knowledge of the new environment increases, various materials will be used with greater confidence and others will be found to have disadvantages that should eliminate them. Here, again, it may be best to qualify usage of some materials according to location, temperature, and quantity. A list of prohibited items could include the following: (1) those items which were prohibited in the past and are still believed harmful; (2) halides in oxygen provided for breathing; (3) metals generally classed as toxic or having a high vapor pressure at 150° F; (4) metals in a dry powdered form, or having less than a specified particle size; (5) foods in a dehydrated, powdered form packaged in such a manner that they might be exposed to oxygen; (6) untreated cellulosic materials such as wood or cotton; (7) materials having a high outgassing rate in a reduced pressure atmosphere; (8) materials processed with organic solvents which have not been adequately aged; and (9) materials used in sufficient quantity to produce gases in excess of the least amount causing throat irritation when in the spacecraft cabin.

EXPLOSION PROOFING

The design philosophy of explosion proofing is a consideration for all phases of spacecraft, including gaseous oxygen or areas where fuel and oxidizer may be present such as during ground preparation. Electric contacts which might arc in use should certainly be enclosed in containers filled with an inert gas or be exposed to the space vacuum.

CONCLUSIONS

A preliminary study of problems associated with the selection of materials for use in the inhabited regions of manned spacecraft led to the following conclusions:

(1) Pure oxygen at a pressure of 5 psi appears to be a suitable atmosphere for manned spacecraft flights lasting upward of 2 weeks, provided flammability problems can be tolerated.

(2) The lower flammability limits in pure oxygen are virtually the same as in a 20-percent air mixture.

(3) The effect of zero gravity on combustion may prove to be an advantage in extinguishing fires.

(4) Adequate standardized testing procedures for evaluating materials to be used in a habitable oxygen-rich spacecraft atmosphere are needed.
(5) Acceptable concentrations of various contaminants that man can tolerate in a spacecraft are needed as a guide in the selection of materials.

(6) Information is needed on many factors affecting ignition and flammability, such as:

(a) Flame temperatures and velocity for various fuel mixtures in pure oxygen and in various mixtures of oxygen and inert gases.

(b) The effect of air circulation, acoustics, ultrasonics, and other wave propagation during zero-gravity conditions.

(c) The effect of various gravity forces, including zero gravity, on flame propagation of liquid and solid fuels not containing oxidizers.

(d) The effect of zero gravity, including the loss of convective currents, on diffusion, evaporation, solubility, and heat transfer.

(e) Improved techniques to detect and extinguish fires.

(f) Coatings to suppress ignition.

(g) The detection and removal of flammable gases and aerosols accumulating in flight, including hydrogen, methane, carbon monoxide, and other low molecular-weight gases.

(h) The relationship between oxygen partial pressure and the effectiveness of various extinguishing agents.

(i) The rate of pressure buildup inside a spacecraft due to an accidental fire, and due to operating various fire extinguishers.

(7) Information is needed on metals, such as titanium alloys, including:

(a) Heating from chemisorption of oxygen released in flight against metals previously exposed to ultrahigh vacuum.

(b) Micrometeoroid impact damage to pressurized containers of gaseous oxygen and fuels.

(c) The effect of electrical overloads in an oxygen atmosphere.

(8) Information is needed about gases produced from photographic material or any other material which may prove toxic or otherwise harmful if used in a spacecraft atmosphere.
(9) Information is needed on the possible large static electricity buildup on spacecraft, including:

(a) The effect of operating various onboard equipment, including communications and propulsion devices.

(b) Ways to detect charges quantitatively, how to control or change their values, and how to suppress or absorb energy differentials during docking of spacecraft, including transport craft, space stations, and men in space suits maneuvering outside their parent vehicles.

(10) Information is needed on the outgassing products of materials exposed to oxygen at various temperatures and radiation levels.

Manned Spacecraft Center
National Aeronautics and Space Administration
Houston, Texas, March 1, 1966
914-50-70-07-72
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44. Kumagai, Seiichiro; and Isoda, Hiroshi: Combustion of Fuel Droplets in a Falling Chamber. Sixth International Symposium on Combustion, 1956, pp. 726-731.


"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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