

# The role of air contaminants in formulating OXYGEN PLANT SAFETY PRINCIPLES

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Safe operation of air separation equipment is a subject of growing importance because of the vastly increased rates of tonnage oxygen and nitrogen usage by the chemical and metallurgical industries. Much of the large new demand is at locations under heavy and increasing air pollution—conditions requiring fullest application of present technology. Reduction of hazards requires understanding. To this end, past published data provides limited knowledge.

Original data developed at Air Products by controlled explosion tests and solubility studies upon combustible contaminants permit the formulation of new safety principles consistent with historical findings.

The prevention of combustible contaminants (i.e. fuel) accumulation is the first line of defense against hazards. Various fuels have widely different safe limits, and all must be considered jointly for an effective safeguard.

Monitoring air before plant construction aids safe design and plant layout. Continuous monitoring during plant operation is a requirement for safe operation in heavily polluted areas. A new tool—the continuous hydrocarbon analyzer—provides a fresh dimension to the monitoring problem.

This article presents new information on the character of materials and explosions in oxygen plants, and is not intended as a review of design and operating practice.

The accompanying historical review illustrates that the published literature has been mainly concerned with the role of acetylene in the air plant mishaps. Acetylene has been regarded as especially significant for several good reasons. Large numbers of air separation units have been closely associated with acetylene production units; acetylene has a *very* low solubility, is highly reactive chemically (forms ozonides and is oxidized more readily than most other hydrocarbons) and acetylene can be exploded even in the absence of oxygen.

Through the last several decades, these particular characteristics of acetylene have resulted in the adoption of design and operating practices which must have protected many air separating plants from other hazards also. The use of adsorption and purge techniques suitable for avoidance of the acetylene hazard would also simultaneously remove other potentially hazardous contaminants, if present in low concentrations. Historically, acetylene has been responsible in many cases; the possibility of solid acetylene-liquid oxygen explosions has been experimentally established, the accumulation of acetylene in oxygen plant reboilers has been demonstrated; and acetylene has been shown to have been present in plants at the time of explosions.

The actual mode of initiation involved in reported explosions has not been as satisfactorily established.

Recently at least two explosions have occurred in which materials other than acetylene were the primary fuels.

## What Happens to Air Contaminants When They Get Into Oxygen Plants

Air is one of the safest of industrial raw materials, yet, it is, at times, the carrier of contaminants responsible for hazards in air separation plants.

Petrochemical and metallurgical industries, for example, which require the products of air separation, are also producers of by-products in the form of waste gases and vapors whose properties would permit accumulation in cold portions of air plants. The design and operation of such plants takes into consideration the local air contaminant problem.

It is helpful to review the course of a few parts per million of contaminants through an air plant. Specific designs alter cases, but some generalizations are possible:

Optimum air intake location is assumed. Pre-purification systems play a strong role in contaminant removal, often beyond those impurities for which the systems are specifically designed. Moisture removal in traps associated

with compressor intercoolers and aftercoolers is often accompanied by removal of substantial fractions of soluble compounds such as ammonia acetone, ethyl alcohol and others condensable with water.

Caustic scrubbers remove substantially all acidic compounds, such as H<sub>2</sub>S, HCN, and most of the NO<sub>2</sub>.

Adsorptive driers remove heavy hydrocarbons including residual compressor oil along with water. Medium hydrocarbons such as pentane, hexane, and other organic vapors are largely removed.

Still other residuals in the air feed can pass into the main exchange system. Compounds that boil above 90° F. and freeze above -270° F. (see Table 1) should theoretically be effectively condensed and remain in the exchanger until defrost. In practice, small quantities are often carried on as suspended particles in the air stream. Propane and propylene, which remain liquid below -280° F., are normally carried through the main exchanger. Butanes and butenes, if present as mixtures, are probably also carried (as liquids) beyond the main heat exchange system.

In some plants reversing heat exchangers, or reversing regenerators, are employed instead of shell-and-tube heat exchangers for all or part of the air feed. The air feed goes directly to the reversing equipment without removal of moisture or carbon dioxide and other acidic components. These freeze out in cooling but are, in turn, evaporated on reversal by return oxygen or nitrogen product. The only difference is that a slightly greater fraction of acid gases will go beyond reversing equipment into the high pressure column.

To generalize, nearly all hydrocarbons up through butane and butylene (excluding butadiene and methyl acetylene) would enter the high pressure column, as would NO, N<sub>2</sub>O, CO, ozone and hydrogen. Of these, hydrogen and some of the CO would leave the high pressure column with the relatively pure nitrogen overhead and the remainder leave in the crude oxygen bottoms which proceed to the low pressure column.

Carbon monoxide and hydrogen leave the top of the low pressure column with the nitrogen, and all other components must be disposed of via the oxygen.

#### How Contaminants in Liquid Oxygen Are Removed

In plants where the product oxygen is withdrawn from the reboiler as a liquid, such as in liquid oxygen plants and pumped oxygen plants, the materials remaining in the liquid oxygen are continuously withdrawn. In the former, they are removed from the plant in the liquid while, in the latter, they are vaporized homogeneously with the oxygen at the elevated pressure and correspondingly higher boiling point of oxygen.

#### Why Absorbers Are Included

Complete vaporization of contaminants with oxygen can be expected for some plant locations, but not relied upon in all instances. Accordingly, hydrocarbon adsorbers are provided to remove contaminants. Effectiveness of removal is high for acetylene and  $C_3+$  hydrocarbons, intermediate for ethane and ethylene. In addition, the adsorbers are effective for removal of organic compounds and virtually all inorganic contaminants except carbon monoxide. Inorganics removed definitely include oxides of nitrogen. The lowest boiling of these is nitric oxide, but this material is said to form nitrogen peroxide ( $NO_2$ ) with oxygen at these low temperatures (17). Any NO

Table 1.—Properties of Some Air Contaminants

Name	Formula	Normal boiling point, ° F.	Freezing point, ° F.
Carbon Monoxide	CO	-312.6	-337.1
Methane	CH <sub>4</sub>	-258.6	-296.4
Nitric Oxide	NO	-241.0	-262.6
Ozone	O <sub>3</sub>	-169.6	-420
Ethylene	C <sub>2</sub> H <sub>4</sub>	-154.8	-272.5
Ethane	C <sub>2</sub> H <sub>6</sub>	-127.6	-297.9
Nitrous Oxide	N <sub>2</sub> O	-127.2	-131.6
Acetylene	C <sub>2</sub> H <sub>2</sub>	-119 (sublimes)	-114.6
Hydrogen Sulfide	H <sub>2</sub> S	-75.4	-122.0
Carbonyl Sulfide	COS	-58.3	-217.8
Propylene	C <sub>3</sub> H <sub>6</sub>	-53.8	-301
Propane	C <sub>3</sub> H <sub>8</sub>	-43.7	-305.8
Formaldehyde	H <sub>2</sub> CO	-5	-180
iso-Butane	C <sub>4</sub> H <sub>10</sub>	10.9	-255.3
iso-Butylene	C <sub>4</sub> H <sub>8</sub>	19.6	-220.5
1,3 Butadiene	C <sub>4</sub> H <sub>6</sub>	24.1	-164
n-Butane	C <sub>4</sub> H <sub>10</sub>	31.2	-217.0
Ethylene Oxide	C <sub>2</sub> H <sub>4</sub> O	51.01	-170.4
Acetaldehyde	CH <sub>3</sub> CHO	68.4	-190.3
Nitrogen Dioxide	NO <sub>2</sub>	70.3	15.3
n-Pentane	C <sub>5</sub> H <sub>12</sub>	97.1	-204
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	133.7	-139.0
Methanol	CH <sub>3</sub> OH	148.4	-144.0
Hexane	C <sub>6</sub> H <sub>14</sub>	156.2	-137.7
Benzol	C <sub>6</sub> H <sub>6</sub>	176.0	41.9
n-Decane	C <sub>10</sub> H <sub>22</sub>	345.2	-23.8

In low pressure "gas" plants, where the product is withdrawn from the low-pressure column as a gas, methane builds up to an equilibrium value in the reboiler condenser (also called "vaporizer") and is thereafter vaporized with the oxygen. As hydrocarbon chain length increases (and vapor pressure decreases), the equilibrium concentrations necessary to maintain hydrocarbon balance via vaporization are sharply increased. At high rate of hydrocarbon input, these concentrations can exceed the solubility limit or the lower explosive limit, resulting in hazardous conditions. Burbo and Ishkin (12, 13) have discussed the maximum level of acetylene which can be carried off without exceeding the solubility limit.

not so converted would then be converted to nitrogen tetroxide and adsorbed as such due to the catalytic action of the silica gel; indeed, silica gel has been employed for this purpose at much higher temperatures (18).

Methane is the only contaminant that can reach the reboiler unaffected by scrubbing and drying, freeze-out, or hydrocarbon adsorbers. Small fractions of many other components may run the gamut, but the original quantities will have been greatly reduced.

#### Catalytic Oxidation Offers Promise

Kinder suggested (19) in 1924 catalytic combustion of flammable impurities in air to render them in-

**safety**

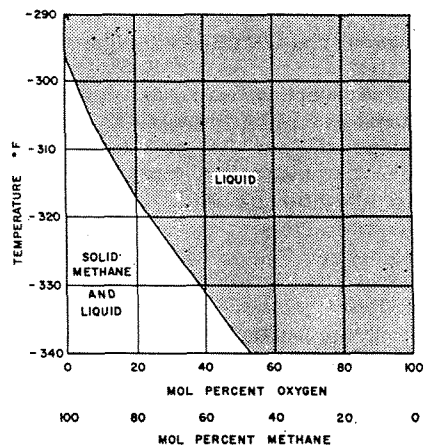


Fig. 1. Methane—liquid oxygen phase system.

Table 2.—Solubility of Various Materials in Liquid Oxygen at -320° F. (22)

Substance	Solubility in ppm
Methane	740,000
Ethane	92,000
Propane	45,000
n-Butane	150
n-Pentane	20
n-Hexane	2
n-Decane	0.6
Acetylene	1.7
Ethylene	1,800
Propylene	2,500
Acetone	1.5
Methanol	12
Ethanol	15
Acetaldehyde	0.4
Benzene	4
Hydrogen Sulfide	50
Nitrous Oxide	70 *
Carbonyl Sulfide	28 *
Nitrogen Tetroxide (N <sub>2</sub> O <sub>4</sub> )	15 *
1-3 Butadiene	20 *

\* at -297° F.

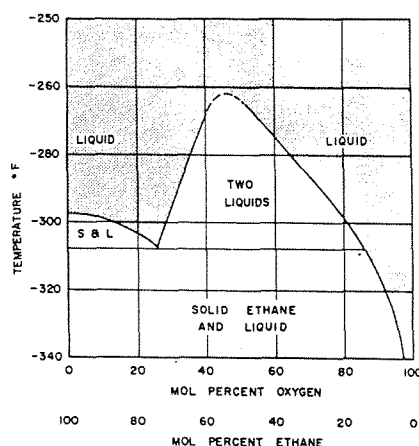


Fig. 2. Ethane—liquid oxygen phase system.

nocuous. Until recently this has been considered to be an uneconomic procedure, but we can envisage that air contaminations will, in some localities, reach levels justifying this method. Kerry (16) has again advanced this proposal and discussed development of catalysts.

One supplier (20), and probably others, can now offer a catalytic unit for virtually complete removal of acetylene by oxidation to carbon dioxide and is continuing work on other hydrocarbons. For acetylene, this apparatus operates in the range of compressor discharge temperatures.

Higher catalyst temperatures (20, 21, 22) are required for oxidation of hydrocarbons other than acetylene. Experimental data are available for methane, ethane, ethylene, propane, propylene, butene, and benzene. This

information indicates that complete oxidation of all hydrocarbons can be secured at a temperature of 800 to 900° F., a more costly temperature level to maintain. However, all but one hydrocarbon, methane, can probably be substantially oxidized at lower temperature, perhaps between 500 to 600° F.

In the material that is presented in this paper it will be shown that oxygen plant tolerance for methane is high indeed, since oxygen containing as much as several per cent of methane is not explosive. This means that methane removal as a contaminant, up to quite high concentrations, is not required for safe operation. The catalytic treatment of air for hydrocarbon oxidation is therefore effective somewhat below 100 per cent oxidation, as oxygen plants have some tolerance to

contaminants. Monitoring permits a new freedom in the use of catalytic air treatment.

#### Explosion Characteristics

Predictability of the effects of liquid oxygen-fuel explosions is frequently difficult or impossible. The combustion phenomena are far out of the ordinary due to the high density of reactants, the liquid phase containing hundreds of times as much material per unit volume as would be present in the gas phase. Acetylene explosions in liquid oxygen are highly brisant (shattering in effect).

There is much literature (23) relating to combustion and explosion of gases and solids, but very little which treats of the same phenomena in liquids. Some generalizations, how-

#### HISTORY

Thousands of air separation plants have been operated in many different industrial atmospheres during the past decades and have achieved a creditable safety record. Infrequent explosions have taken place in a few of these plants; some of these have been described and discussed in published articles.

Brankamp, in 1914 (1), summarized the character of several explosions which had occurred up to that time, ascribing them to mixtures of oxygen with combustible insulation or acetylene. His paper included speculation upon the role of copper acetylide, compressor oil (and its decomposition products), hydrogen and methane atmosphere contaminants, electrical phenomena, ozone, ozonides, and peroxides.

In 1923 Pollitzer (2) published a comprehensive paper describing a number of explosions and presented experimental work which sought to elucidate the explosion mechanism. His survey disclosed that air plant explosions invariably took place in the oxygen evaporating equipment, that is, in the reboiler or in the oxygen evaporating coils; that the plant on-stream time could not be evaluated as a factor; that explosions occurred generally during operation, some after a few hours only, some after many weeks; that still others took place after shutdown. He considered ozone, acetylene, and lubricating oil as sources of energy and considered mechanical agitation as a source of ignition, either directly or through augmentation. He carried out experiments in which solid acetylene was suspended in liquid air or oxygen, demonstrating that such mixtures could explode. Pollitzer further studied specific air plant explosions

and found either proof or strong evidence that acetylene was present at the time of each explosion. His work resulted in a clear understanding that acetylene is a hazard.

Fyleman, in 1923 (3), emphatically concluded that acetylene caused air plant explosions. He produced acetylene experimentally from oil in simulated air compression, showing that the air compressor itself can be a source of acetylene entry into an air plant, even in an uncontaminated atmosphere. The precautions of avoiding hot spots in the compressors, of using suitable oil, and of banning carbide from the neighborhood of the plant are listed as being proven through experience to provide adequate protection. In a large Norwegian plant liquefying about 100 tons of air per day, where the air was always contaminated with acetylene and where effects of explosions had previously been serious, it was found that explosions were eliminated by withdrawing (from the reboiler) a bucketful of liquid oxygen every hour and throwing it away.

Some discussion and review papers, such as that by Berger (4), appeared in subsequent years, but significant and pertinent new experimental evidence was not added to the literature until the 1940's. A publication by Strizhevskii (5) was one of the first papers in a series of several valuable contributions appearing in the Russian literature. These papers, taken as a group, treat the solubility of several hydrocarbons in liquid air, the adsorption of hydrocarbons upon silica gel, and the use of this information in air plant design. Strizhevskii's review is a good summary of the state of the art in 1939.

Ishkin, Burbo, Tsin, Fedorova, Fastovskii, and Krestinskii, jointly and

individually, have reported upon the solubility of acetylene (6, 8), of carbon dioxide (6, 8), of ethylene (7), of propylene (7), and of methane (9) in liquid oxygen and in liquid nitrogen, and upon the vapor pressure of solid acetylene (10). In 1940, Ishkin and Burbo (11) reported experimental data for the adsorption of acetylene upon silica gel from a flowing stream of liquid air. Burbo (12) and Ishkin and Burbo (13) round out the Russian contributions with a discussion of acetylene accumulation and distribution in an air plant and with a description of the use of silica gel adsorbers for removal of acetylene from operating plants.

Cox and DeVries (14) reported experimental work from Purdue University upon the solubility of solid ethane, ethylene, and propylene in liquid nitrogen and oxygen.

Until the last decade, the literature has cited acetylene as the chief culprit or suspect. This view has been remarkably and demonstratively successful in reducing and eliminating hazards. The actual initiating mechanism has remained substantially unknown. Many factors have been recognized as having potential roles as initiators, but basic experimental work has not been reported until recently. Nomura and Kanda (15), working in the Research Institute for Iron, Steel, and Other Metals, Tohoku University, have demonstrated that an explosion occurs when ozone is contacted with ethylene or acetylene at low temperatures. An understanding of the mechanism of the reaction of ozone with unsaturated hydrocarbons was their objective.

Recently, Kerry (16) summarized many aspects of air plant contamination and discussed safe design and operating practices.

ever, may be tentatively made, subject to experimental evaluation. In the gas phase, a distinction between *combustion waves* and *detonation waves* may be drawn. A combustion wave is propagated through the combustible mixture by heat transfer and diffusion. A detonation wave is propagated by the energy of the chemical reaction taking place in the highly compressed shock wave; the shock wave raises the energy level of the reactants, preparing them for the chemical energy release which, in turn, provides the energy for continuation of the shock wave. Combustion waves are slow, of the order of several feet per second; detonation waves are faster than the speed of sound, of the order of several thousand feet per second. Either type of combustion may take place in an explosive mixture, depending upon many factors such as mixture composition, mixture density, and confinement. A detonable mixture may be made richer or leaner in fuel until the upper and lower limits of detonability are reached. As the mixture is made still richer or leaner beyond these limits, upper and lower limits of inflammability are reached. The detonation phenomena are dependent upon factors such as volume and shape of container and type of initiation.

The foregoing generalizations apply to homogeneous gas fuel-oxidant mixtures. Much of the above general understanding of combustion in gases may be directly used in describing combustion phenomena in liquid oxygen. In liquid oxygen-fuel mixtures which are single phase, we may expect to observe experimentally upper and lower limits of detonability and inflammability, as is the case with single phase gaseous mixtures of air or oxygen with fuel.

Similar to gas phase combustion, the predictability of the character of combustion becomes less certain as the liquid system becomes two-phase. Dusts and mists suspended in air are uncertain in behavior due to the lack of uniformity of dispersion and to the variation in particle size. Likewise, suspensions of solid or liquid combustibles in liquid oxygen are non-uniform and their behavior as combustibles is uncertain.

#### Explosion Prevention

Pure oxygen—gas and liquid—can be handled and processed without fear of combustion. Explosive mixtures of combustibles with oxygen do not automatically explode. Some source of ignition energy is required. This does not imply that fuel-oxygen mixtures should be permitted to accumulate or persist in air plants, for given suffi-

cient time, the source of ignition may well appear.

The oxygen-fuel-initiator combination must be avoided. Oxygen, of necessity, is present; possible initiator mechanisms are many, and positive control extremely difficult; control of fuel accumulation controls the situation and avoids the hazard. Prevention of fuel accumulation is the safest solution of the air plant hazard potential. The avoidance of fuels does not mean that initiators are to be ignored; it is merely a recognition that in the absence of fuels, the initiators become impotent.

Plant safety may be maintained through sound design and operational principles by the recognition of the following:

1. Explosiveness is predictable from mixture composition.
2. Composition of plant streams can be monitored during operation.
3. Careful design and operating techniques based on experience and appraisal of the problem can anticipate and prevent explosive concentrations.

Let us now consider in more detail some of the implications involved in avoidance of oxygen plant hazard through contaminant control. The three elements listed above will be examined in turn. First, what are the conditions which determine explosiveness; what are the conditions which allow explosiveness to be predicted and, hence, avoided?

#### Conditions of Hazard

For any combustible there is some level of concentration in liquid oxygen above which the mixture is hazardous and below which it is not. For the highly soluble ones this is the flammable limit; for the less soluble ones the limit is, to all practical purposes, the solubility.

The flammable limit is self-evidently to be avoided. The significance of solubility becomes evident when one considers that levels above the solubility limit can result in localized concentrations of fuels above the lower explosive limit. This is possible even though the total quantity of fuel with respect to the total quantity of oxygen is below the flammable limit. Thus, if either the explosive limit or the solubility limit is exceeded, a hazardous condition exists. Accordingly, if either of these limits are approached, corrective measures are indicated. Solubility values for a number of materials in liquid oxygen at  $-320^{\circ}$  F. are given in Table 2, and in Figures 1 and 2. Discussion of these data appears later.

The lower explosive limits of hydrocarbons can be expressed as methane equivalent. When this is done, the numerical values lie within a comparatively narrow range. This permits a

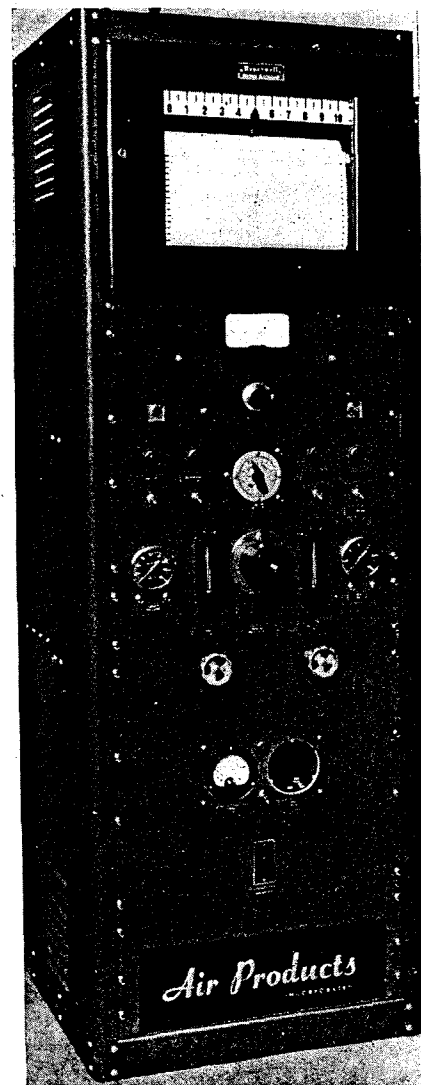


Fig. 5. Continuous Total Hydrocarbon Analyzer.

first approximation of explosive limits for mixtures, which is useful since the energy release per unit mass at the lower flammable limit is roughly the same for all hydrocarbons. In Table 3, a comparison is drawn among several hydrocarbons, of lower gas phase flammable limit, energy release per gram mole of mixture, and lower flammable limit expressed as methane (approximated by multiplying the lower explosion limit by the number of carbon atoms in the molecule). It will be seen from experimental explosion test data presented in the following section that the lower explosive limit for gas phase mixtures of hydrocarbons and oxygen is useful for liquid mixtures of the soluble hydrocarbons.

#### Experimental Explosion Test Data

In Table 4 are summarized some representative data from Lewis and von Elbe (23) which relate detonability and flammability limits for certain gaseous single-phase fuel-

oxidant mixtures. Detonability limits are composition-wise within the flammability limits. The lower flammability and detonability limits are roughly the same for the mixture of the fuel with either air or oxygen. This qualitative similarity is due, no doubt, to the fact that excess oxidant is present in either case. The upper limits, however, differ markedly from air to oxygen.

It is of interest to compare the behavior of a liquid oxygen-methane mixture with the corresponding gaseous data. Oxygen and methane form a single-phase liquid system at temperatures above the freezing point of methane, as is shown in Figure 1, and at much lower temperatures it is still possible to prepare very concentrated single-phase mixtures. Due to this great solubility, it is possible to observe experimentally both the lower explosive limit and the upper one. Following the technique described in another section of this paper, it has been found (22) that the lower explosive limit in the liquid oxygen-methane system of 11

mole per cent methane and the upper explosive limit of 50 mole per cent methane fall within the gas phase limits of 5.4% and 59.2%. The lower explosive limit of ethane has been observed, using flash bulb initiation with the unprotected bulb directly immersed in the ethane-liquid oxygen mixture, and found to be about 4 mole per cent ethane. This system has an upper explosive limit which can be observed only at such elevated system pressures as those which permit a single liquid phase to exist. The liquid phase explosion limits for methane and for ethane are thus seen to be consistent with the gas phase data for the same systems.

Selected data from a comprehensive experimental explosion testing program under way at Air Products (see Experimental Explosion Testing Techniques) are presented in Table 5.

The first eleven tests encompass both the high and low explosion limits for the  $\text{CH}_4\text{-O}_2$  liquid system. The same results are obtained at both liquid nitrogen and liquid oxygen temperatures. The lower explosion limit

Table 5.—Experimental Explosion Test Data

Test No.	Composition of test mixture, mole %	Vol. of condensed sample, cu.cm.	Test container	Initiation	Remarks
1	4 $\text{CH}_4$ —96 $\text{O}_2$	15	$\frac{5}{8}$ " O.D. $\times$ 6" long copper tube	Blasting cap	No explosion
2	5 $\text{CH}_4$ —95 $\text{O}_2$	200	250 cc. glass flask	Blasting cap	No explosion
3	7 $\text{CH}_4$ —93 $\text{O}_2$	30	1" O.D. $\times$ 4" long copper tube	Blasting cap	No explosion
4	10 $\text{CH}_4$ —90 $\text{O}_2$	90	$\frac{1}{4}$ " O.D. $\times$ 7" long copper tube	Blasting cap	No explosion
5	12 $\text{CH}_4$ —88 $\text{O}_2$	30	1" O.D. $\times$ 4" long copper tube	Blasting cap	Exploded
6	15 $\text{CH}_4$ —85 $\text{O}_2$	30	1" O.D. $\times$ 4" long copper tube	Blasting cap	Exploded
7	33.3 $\text{CH}_4$ —66.7 $\text{O}_2$	30	1" O.D. $\times$ 4" long copper tube	Blasting cap	Exploded
8	50 $\text{CH}_4$ —50 $\text{O}_2$	14.5	$\frac{5}{8}$ " O.D. $\times$ 6" long copper tube	Blasting cap	No explosion
9	50 $\text{CH}_4$ —50 $\text{O}_2$	16	$\frac{5}{8}$ " O.D. $\times$ 6" long copper tube	Blasting cap	Exploded
10	55 $\text{CH}_4$ —45 $\text{O}_2$	30	1" O.D. $\times$ 4" long copper tube	Blasting cap	No explosion
11	69 $\text{CH}_4$ —31 $\text{O}_2$	15	$\frac{5}{8}$ " O.D. $\times$ 6" long copper tube	Blasting cap	No explosion
12	100 $\text{N}_2\text{O}$ slurrified in liquid oxygen	Solid	50 cc. test tube	Blasting cap	No explosion
13	100 $\text{N}_2\text{O}$	Gas at 70° F.	1 gallon can	Blasting cap	Exploded
14	100 $\text{N}_2\text{O}$	Gas at 70° F.	1 gallon can	M-2 flash bulb, plastic removed	Exploded
15	100 $\text{NO}_2$	Gas at 70° F.	1 gallon can	M-2 flash bulb, plastic removed	Exploded
16	100 $\text{NO}_2$	Solid	50 cc. test tube	M-2 flash bulb, plastic removed	Slurrified in liquid oxygen, no explosion
17	50 $\text{C}_2\text{H}_6$ —50 $\text{O}_2$	10	20 cc. test tube	Ozone	$\text{O}_2$ with 0.1% $\text{O}_3$ was bubbled through test mixture while applying mechanical shock, no explosion
18	Solid $\text{C}_2\text{H}_6$ floating in liquid oxygen	10	22 cc. test tube	Ozone	$\text{O}_2$ with 0.1% $\text{O}_3$ bubbled into test mixture. Immediately exploded.
19	Solid $\text{C}_2\text{H}_6$ floating in liquid oxygen	30	1" O.D. $\times$ 4" long copper tube	Blasting cap	Exploded
20	Solid oil slurrified in liquid oxygen	135	250 cc. round bottom flask	Blasting cap	Exploded. Much oil unreacted.
21	Tricresyl phosphate lubricant, slurrified in liquid oxygen	100	250 cc. round bottom flask	Blasting cap	Exploded
22	Polyethylene glycol lubricant, slurrified in liquid oxygen	100	250 cc. round bottom flask	Blasting cap	Exploded
23	3.1 $\text{C}_2\text{H}_6$ —96.9 $\text{O}_2$	10	1" O.D. $\times$ 4" long copper tube	M-2 flash bulb	No explosion
24	4.4 $\text{C}_2\text{H}_6$ —95.6 $\text{O}_2$	10	1" O.D. $\times$ 4" long copper tube	M-2 flash bulb	Exploded
25	3.1 $\text{C}_2\text{H}_6$ —96.7 $\text{O}_2$ + 0.2 $\text{NO}_2$	10	1" O.D. $\times$ 4" long copper tube	M-2 flash bulb	No explosion
26	Solid $\text{C}_2\text{H}_6$ in liquid oxygen	10	10 mm. glass test tube	Ozone	$\text{O}_2$ with 0.1% $\text{O}_3$ bubbled into test mixture. No explosion.

**Table 3.—Gas Phase Flammable Limit—Carbon Atom Approximation**

Compound	Formula	Lower limit, mole %	Lower limit, as methane, mole %	Heat of combustion, K cal./mole	Energy release at lower limit, K cal./gm mole of mixture
Methane	CH <sub>4</sub>	5.00	5.00	213	10.16
Ethane	C <sub>2</sub> H <sub>6</sub>	3.00	6.00	373	11.2
Propane	C <sub>3</sub> H <sub>8</sub>	2.12	6.36	531	11.3
Butane	C <sub>4</sub> H <sub>10</sub>	1.86	7.44	688	12.8
Pentane	C <sub>5</sub> H <sub>12</sub>	1.40	7.0	845	11.8
Hexane	C <sub>6</sub> H <sub>14</sub>	1.18	7.08	1002	11.8
Nonane	C <sub>9</sub> H <sub>20</sub>	0.83	7.47	1473	12.2
Decane	C <sub>10</sub> H <sub>22</sub>	0.77	7.7	1630	12.6
Ethylene	C <sub>2</sub> H <sub>4</sub>	2.75	5.5	337	9.2
Propylene	C <sub>3</sub> H <sub>6</sub>	2.0	6.0	492	9.8
Butene-1	C <sub>4</sub> H <sub>8</sub>	1.65	6.6	650	10.4
Acetylene	C <sub>2</sub> H <sub>2</sub>	2.50	5.0	311	7.6
Toluene	C <sub>7</sub> H <sub>8</sub>	1.27	8.9	944	12.0
Benzene	C <sub>6</sub> H <sub>6</sub>	1.4	6.4	789	11.0

**Table 4.—Flammability and Detonability Limits—Gases (17)**

Mixture	Lower limit, mole %		Upper limit, mole %	
	flammability	detonability	detonability	flammability
H <sub>2</sub> —O <sub>2</sub>	4.65	15	90	94
H <sub>2</sub> —air	4.0	18.3	59	74
CO—O <sub>2</sub> (moist)	15.5	38	90	93.9
CO—air	12.5	....	....	74.2
CH <sub>4</sub> —O <sub>2</sub>	5.4	....	....	59.2
CH <sub>4</sub> —air	5.0	....	....	15.0
C <sub>2</sub> H <sub>2</sub> —air	2.5	4.2	50	80
C <sub>2</sub> H <sub>4</sub> O (ether)—O <sub>2</sub>	2.1	2.6	>40	82
C <sub>2</sub> H <sub>4</sub> O—air	1.85	2.8	4.5	36.5
C <sub>2</sub> H <sub>6</sub> —O <sub>2</sub>	4.10	....	....	50.5
C <sub>2</sub> H <sub>6</sub> —air	3.0	....	....	12.5

is about 11 mole per cent methane and the upper 50 mole per cent methane, with the confinement and initiation indicated in Table 5. It is expected that more powerful initiation than provided by a blasting cap would extend these limits slightly.

Nitrous oxide, N<sub>2</sub>O, which has an endothermic heat of formation, is exploded by a blasting cap, as an atmospheric pressure gas at 70° F., but is not explosively decomposed by such initiation when frozen solid and at liquid oxygen temperatures.

Oils and other insoluble hydrocarbons, slurried in liquid oxygen, may be exploded by a blasting cap. Explosions involving dissolved fuels under identical conditions have a higher combustion efficiency and are more brisant due to the greater intimacy of fuel-oxygen contact.

Addition of 2,000 ppm of NO<sub>2</sub> to an ethane-oxygen liquid system just below the lower explosive limit of ethane produces no explosion.

Ozone, at a low concentration in oxygen, when introduced into a slurry of acetylene in liquid oxygen, immediately produced an explosion. When introduced into a slurry of ethylene in liquid oxygen it did not produce an explosion.

**Explosion Initiators**

Only meager knowledge of the forces which initiate explosions in oxygen plants is available. Despite this handicap, constructive recommendations can be made to minimize some modes of ignition. Because of this handicap, we have no assurance that there may not be unknown mechanisms of ignition not covered by the recommendations.

It is well known that discharges of either static electricity or mechanical

shock can initiate explosion of a sensitive material. To minimize these, excessive impingement velocities and vibration should be avoided.

It is quite possible that some oxygen plant explosions have been initiated by obscure chemical reactions. Ozone has been under suspicion in this regard. Experimentally, gaseous mixtures of oxygen and acetylene or ethylene have been ignited by addition of ozone (15). A slurry of solid acetylene in liquid oxygen has also been ignited by ozone (22). It is probable that the initiator in this particular case is a highly shock-sensitive ozonide of acetylene.

Oxides of nitrogen are atmospheric pollutants that have been under suspicion. Accordingly, attempts have been made to ignite hydrocarbon-liquid oxygen mixtures by addition of nitrous oxide, nitric oxide, and nitrogen dioxide. To cite one experiment, an explosive mixture of methane, acetylene, ethylene, and butadiene was added to liquid oxygen and then both nitric oxide and nitrogen dioxide added. This mixture boiled for several hours without event, until detonated by a blasting cap. Such findings, together with an observation that at least one plant has operated safely at a high level of nitrogen oxide contamination (24), are interesting but are by no means conclusive.

Nitrogen tetroxide, N<sub>2</sub>O<sub>4</sub>, does react with unsaturated hydrocarbons (25) and explosive compounds can result (26). This tetroxide is readily formed from either nitric oxide or nitrogen dioxide by the reactions:

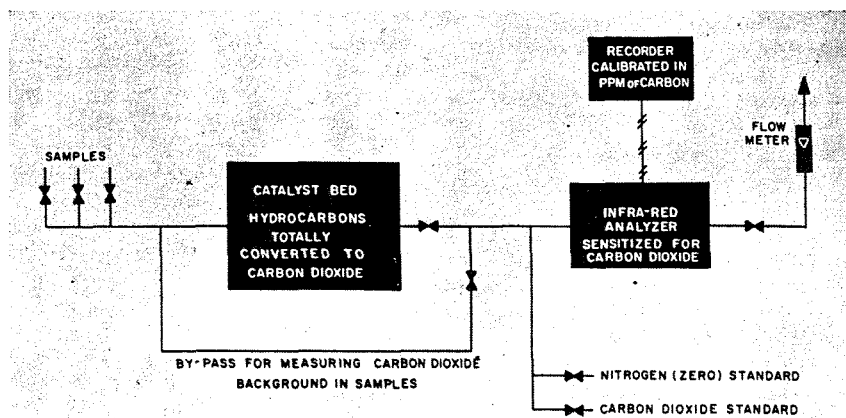
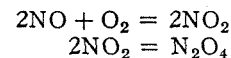


Fig. 4. Schematic diagram of Continuous Total Hydrocarbon Analyzer.

When coke oven gas is cooled, a resin is deposited, which has occasionally exploded in main heat exchangers. These resins are believed (27) to be formed from nitric oxide or nitrogen dioxide and olefins which are present at a level over one per cent. Neither these resins nor anything resembling the same type of explosion is known to have occurred in an air plant. Indeed, such an occurrence is unlikely because even a refinery atmosphere could contain little more than a minute fraction of the olefin concentrations in coke-oven gas.

The possibility of such intermediates acting as initiators is not completely excluded.

Thus, we see that ozone is a plausible initiator of oxygen plant explosions, but two oxides of nitrogen (NO and NO<sub>2</sub>) remain subjects of conjecture. There may well be other manners of ignition of which we have no knowledge.

It would be desirable to remove all components that could possibly become a source of ignition. The obvious method of removal is to install an adsorber in the crude oxygen line to remove material more strongly adsorbed than oxygen, nitrogen, and argon. Since nearly all air contaminants boil well above these, such a method should work. In case the adsorbers do not control the offenders, the next obvious step is to drain liquid oxygen and discard it until the level of contamination is again reduced to a safe level.

Regardless of the method of initiation, no explosion can occur without fuel. This means we must emphasize prevention of hazardous fuel levels as the first line of safety defense. As we learn more about initiators, monitoring means may be applied.

Due to the lack of fuller knowledge on initiation, our second line of defense—preventing ignition—is a weak and unreliable one.

From a recent paper by Lewis entitled "Industrial Explosion Hazards Detection" (28) we quote:

"Knowing that potentially hazardous conditions are likely to exist, one may accept them and attempt to prevent their activation. Obviously, some idea of the ease of initiation of violent phenomena is needed. . . . Usually a more realistic approach, when the difficulty of identifying all possible means of initiation is thought out, is to prevent the conditions which permit the development of propagation of explosive reactions."

#### Monitoring

Plant streams can be monitored during operation and the level of con-

tamination so determined. This level measures the approach to a hazardous condition. Monitoring techniques vary with the particular situation. Process cycle, design features, atmospheric environment, and onstream requirements all affect the monitoring procedures which are selected. Relatively stringent standards may prudently be set for plant startup. These may be modified as permanent "ground rules" are established through on-site plant experience.

The air separation plant in which the entire oxygen product is withdrawn from the reboiler as a liquid combines a minimum of process design and operating precautions. The liquid may be the final product or it may be pumped to elevated pressure and vaporized by heat exchange. In such plants, the opportunities for accumulations of contaminants are minimized, reducing hazards. If plants produce some or all of their oxygen as a low pressure gas taken from the column, both plant design and plant operation become more critical. If these plants, in addition, are located in industrial areas where the concentration level of contaminants may be unusually high, the need for monitoring is increased.

The variable nature of air pollution must be considered in the formulation of sound design and operating procedures. Allowance must be made for temporary surges in contamination greatly exceeding the typical values. Thus, on rare occasions, the pollution levels may override the design safety factors and corrective procedures such as drainage of liquid oxygen, shortening the hydrocarbon adsorber cycle, and emergency shutdown may be required. Continuous monitoring affords necessary guidance in such contingencies.

Safety through monitoring requires the establishment of safe operating limits of concentration. Using the approximation that the lower flammable limit, expressed as methane or carbon atom equivalent, is reasonably constant and above 5 mole per cent, a value such as 500 ppm (safety factor—100:1) may be adopted as a tolerable level for soluble contaminants. The value used in a particular situation is dependent upon appraisal of the individual plant contamination spectrum, this appraisal being typically a cooperative effort of the air separation plant supplier with the future plant operator. The utility of the carbon atom equivalents approximation as a measure of hazard and the possibility of sudden variation in atmospheric contamination support continuous total hydrocarbon analysis as a basic feature of the monitoring program.

#### Continuous Hydrocarbon Analysis

A continuous total hydrocarbon analyzer has been developed (22) which is sensitive to any hydrocarbon (or other organic combustible) without discrimination. (See Figures 4 and 5).

The apparatus provides a means for continuously analyzing air plant streams for very low concentrations of carbon-containing impurities. In principle, the apparatus parallels classical carbon analysis by oxidation of combustible material to carbon dioxide and determining the latter. In this apparatus, the hydrocarbons in the sample stream are completely oxidized over a catalyst, and the resultant carbon dioxide analyzed by a sensitive infra-red analyzer.

The sample introduction may conveniently be sequence-timed to assure uniformly repetitive examination of several different sample streams. This, in effect, affords, with the one instrument, a substantially continuous trace for each sample. A typical strip chart record from the analyzer is shown in Figure 6.

The choice of samples for monitoring is somewhat dependent on the air plant cycle, but a sample which is representative of reboiler conditions usually affords the most useful information for effective fuel control. The air feed, after compression and drying, is often sampled to indicate the level of fuel entering the plant. Air feed sampling is more significant in liquid oxygen or liquid pump plants where the reboiler concentration does not exceed five times that of the incoming air. In plants producing low pressure gaseous oxygen, of course, the reboiler accumulations will be dependent upon the vapor pressures of each contaminant and the amount of liquid oxygen withdrawn as a purge.

For additional information, occasional samples are taken from exchanger defrosts, from adsorber reactivation gas, from liquid purges and other points—some of which are unique with specific cycles. These samples are generally not essential in fuel control but provide supplementary information for diagnostic purposes.

It is evident that, although continuous total hydrocarbon analysis is an invaluable aid, an understanding of the relative amounts of the individual contaminants is also needed. A total hydrocarbon level of 200 ppm is safe only if no hydrocarbons with a solubility limit below 200 ppm are present in excess of their individual solubility limits.

Acetylene is one of the few troublesome hydrocarbon contaminants having a very low solubility. Because of

its low solubility and its reactive character it must be monitored separately. Usually this is done by a special Ilosvay test made at scheduled times. Such scheduled tests for acetylene are adequate so long as results remain convincingly low. A set of typical rules employed in many well-run plants over the years is as follows:

- Above 0.2 ppm, tests should be frequent.
- Above 0.5 ppm, corrective measures should be taken.
- Above 2 ppm, the plant should be shut down.

The adequacy of this approach is reflected in the excellent safety record enjoyed by producers of cylinder gases. Acetylene is also detectible by infrared techniques; such instruments are commercially available for continuous monitoring.

Individual analyses also serve in diagnosis of exact causes of "peaks" or "high plateaus" in the total combustible trace. To this end, the gas chromatograph using the adsorption or partition column, or both simultaneously, is a very convenient tool. Following concentration, samples as small as 0.05% of a component can be analyzed in a positive and quantitatively reproducible manner in a few minutes. The mass spectrometer, infrared spectroscopy, distillation, and other standard techniques of gas analysis also serve. Some specific tests for non-hydrocarbon contaminants are indicated in Table 6.

Extension of some of these analytical methods in the ppm or even into the ppb (parts per billion) range is facilitated by sample concentration using a low temperature adsorption technique. Atmospheric samples, for example, can be concentrated in a train consisting of a dry pump, a CO<sub>2</sub> scrubber, a drier, an adsorption cell containing silica gel at liquid oxygen temperatures, and a wet test meter. After passing the necessary quantity of air through the sampling system, the adsorbed sample is quantitatively transferred into a gas measuring burette in preparation for analysis.

Some plant operators conduct scheduled total hydrocarbon or individual hydrocarbon analyses on a batch sampling basis to provide assurance of safe operation in their particular environment. Others employ continuous observation as their best solution.

Primary concern for protection and, hence, most extensive monitoring, must be applied where the most susceptible cycle is being operated in the most unpredictable atmosphere. Least extensive monitoring is necessary where the liquid pump plant is oper-

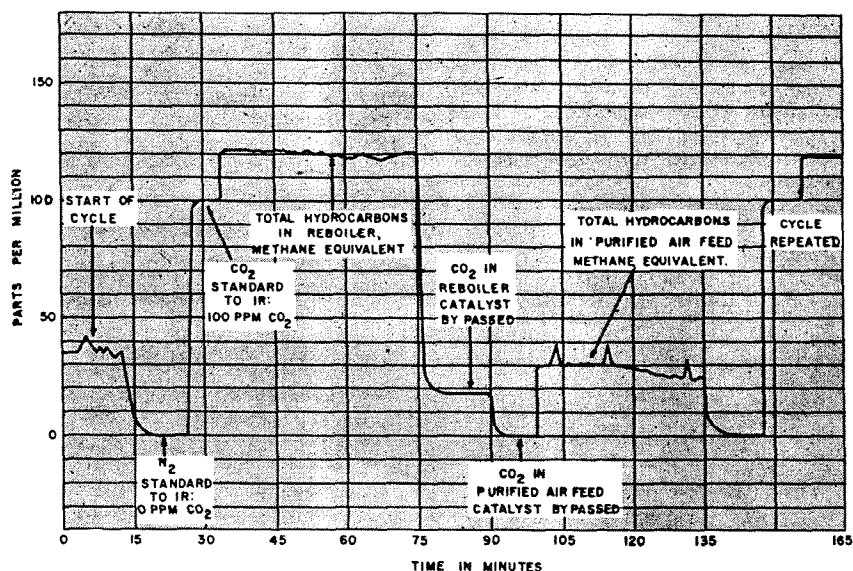


Fig. 6. Sample strip chart from Analyzer showing operating cycle.

Table 6.—Type of Contaminant Analyses

Compound	Method of Analysis
Acetylene	After concentration by low temperature freezeout, detect colorimetrically with Ilosvay solution (30).
Carbon dioxide	After low temperature concentration and absorption in excess barium hydroxide, back-titrate with acid (31).
Carbon monoxide	a) After CO <sub>2</sub> removal, concentrate at low temperatures, oxidize to CO <sub>2</sub> and proceed as above, for CO <sub>2</sub> . b) Colorimetric analysis by palladous sulfate and ammonium molybdate (32).
Hydrogen sulfide	Following absorption by zinc acetate, convert into methylene blue in solution, measure colorimetrically (33).
Nitric oxide	Following permanganate oxidation, detect colorimetrically with Greiss-Saltzman reagent (34).
Nitrogen dioxide	Colorimetric, with Greiss-Saltzman reagent (34).
Ozone	Numerous methods including use of aldehyde, KI, fluorescein, etc. (35).
General	Following low temperature concentration, methane, individual hydrocarbons, light organics and nitrous oxide may be determined readily by gas chromatography, mass spectrometry, infrared spectroscopy, or Podbielniak distillation.

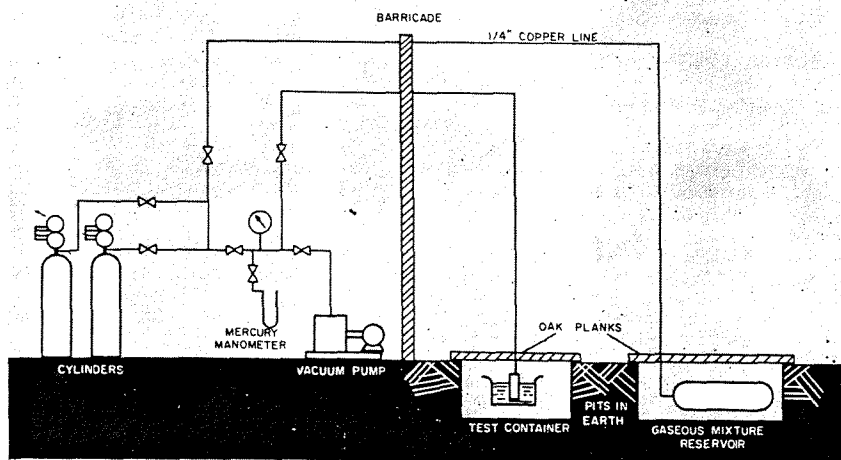


Fig. 3. Explosion testing apparatus.



ated in a continuously clean atmosphere.

In short, the extent of required monitoring practice can be determined only by careful consideration of plant cycle, mode of operation, the atmospheric level of contamination, and knowledge of the properties of the contaminants.

#### Appendix A

##### SOLUBILITIES IN LIQUID OXYGEN

Liquid methane is completely miscible with liquid oxygen and, below its freezing point, solid methane is very soluble in liquid oxygen. Data on this are given in Figure 1. The previously published data of Fastovskii and Krestinskii (9) have been verified and extended. Physical chemists will be interested in the observation that methane solubilities are in fair agreement with values calculated from the laws of ideal solution (29) using the latent heat of fusion of methane corrected for the specific heats of the solid and liquid.

New data on ethane are presented in Figure 2, which is a phase diagram for the ethane and oxygen system. Above about  $-262^{\circ}\text{F}$ . liquid ethane and liquid oxygen are miscible; between this temperature and the freezing point ( $-298^{\circ}\text{F}$ .) these liquids are only partially miscible. Two liquid phases, one rich in ethane, the other in oxygen, can coexist; in fact, this situation persists below the freezing point down to  $-308^{\circ}\text{F}$ . The solid ethane has a high solubility in the ethane-rich phase down to  $-308^{\circ}\text{F}$ ., but the ethane-rich phase is no longer stable below this temperature, and the equilibrium is then with the oxygen-rich phase to the extent of a reduced solubility.

So far as is known, the complex nature of ethane-oxygen phase equilibria has

not been heretofore recognized, although Cox and DeVries (14) previously studied this system, and these same authors did note similar behavior of propane and propylene with liquid oxygen.

The solubilities of a number of materials at a single temperature of  $-320^{\circ}\text{F}$ . are given in Table 2. It may be noted that nearly all of these values represent original data. The solubilities for many of these are limited to a few parts per million. A description of three experimental methods available follows:

(1) *Turbidity Method*. This technique involves preparing a mixture of the desired concentration of hydrocarbon and oxygen and, subsequently, condensing this mixture inside a glass bulb and noting whether the condensate is one- or two-phase. The concentration of hydrocarbon in the mixture may be gradually changed until successive condensed samples result in a sample being clear, if the concentration of hydrocarbon is being decreased, or cloudy, if the concentration of hydrocarbon is being increased. This visual method of determination, if carefully operated, can be accurate even to 1-2 ppm.

(2) *Freeze-out Method*. This technique can be effected by totally evaporating the contaminated liquid oxygen, passing the vapor stream through a freeze-out trap maintained at liquid oxygen temperatures and so collecting the hydrocarbon or other contaminant. The trap is later evacuated to remove the oxygen completely, leaving only the relatively non-volatile hydrocarbon. Finally, the trap is warmed to room temperature. The amount of hydrocarbon so isolated in the trap can be calculated through knowledge of the trap volume and the final temperature and pressure in the freeze-out trap. Care should be taken, however, to remove any moisture or carbon dioxide

during the preparation of the saturated liquid oxygen solution.

(3) *Infra-red Analyzer Method*. A saturated solution is first prepared and then totally vaporized through an infra-red analyzer. The total dissolved material is determined by integrating these analyzer values. This is applicable when infra-red equipment is available for direct monitoring. Hydrocarbon analyzers of the type described in this paper make it possible to apply this method to any hydrocarbon or any organic chemical. This technique is not a rapid one and requires great care, but is capable of high accuracy.

#### Appendix B

##### EXPERIMENTAL EXPLOSION TESTING TECHNIQUE

One experimental approach which has been used (22) in evaluating the explosiveness of hydrocarbon-liquid oxygen mixtures is schematically indicated in Figure 3. The system consists essentially of a gaseous mixture reservoir, a test container in its surroundings, and the necessary lines, valves, etc., for the introduction and purging of gases. Some data obtained with this system are listed in Table 5. The apparatus and technique will be described in more detail by describing Test Number 5 of this table.

A copper tube 1-in. O.D.  $\times$  4-in. long was closed at each end with flat brass stock, soldered into place, and a  $\frac{3}{4}$ -in. copper tube was soldered as a connection to one end. An electric blasting cap was taped to the outside of this tube at the lower end and the assembly centered in the lower part of a gallon can, which in turn was placed in an earthen pit and covered with oak planks. This test container was connected as shown in Figure

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3 to a 2,100 cu. in. gaseous mixture reservoir located in a separate barricaded pit. The system was alternately evacuated and filled with oxygen gas to atmospheric pressure three times. The third time, the exact pressure of oxygen gas in the system as indicated by the mercury manometer was carefully noted. Methane was then added, increasing the total pressure to 1.24 atmospheres. Oxygen, in turn, was added, bringing the total pressure to 2.0 atmospheres, and the mixture allowed to mix by diffusion and convection. The test container portion of the system was then purged three times by evacuation and filling with the 12 CH<sub>4</sub>-88 O<sub>2</sub> mixture. The gallon can in which the test container was situated was at this time filled with liquid oxygen and sufficient gaseous mixture allowed to flow from the 2,100 cu. in. reservoir to result in about 30 cu. cm. of liquid condensate in the test container. No composition change takes place during this transfer as total condensation occurs in the 1-in. X 4-in. tube; the quantity of material transferred is noted by pressure drop in the reservoir.

The circuit to the blasting cap was closed and an explosion occurred, bursting the test container and also the liquid oxygen container. The debris was collected from the walls of the pit and saved for comparison with other tests.

The above procedure was modified somewhat when working with liquids and solids and also was modified when the condensed system would consist of more than one phase. The blasting cap initiation was satisfactorily reproducible at liquid air temperatures; other initiation methods employed were: high energy spark, hot wire, fused wire, dropping weight, air gun pellet, M-2 flash bulb, and ozone.

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