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Wire Chamber Aging

J.A. Kadyk

March 1990

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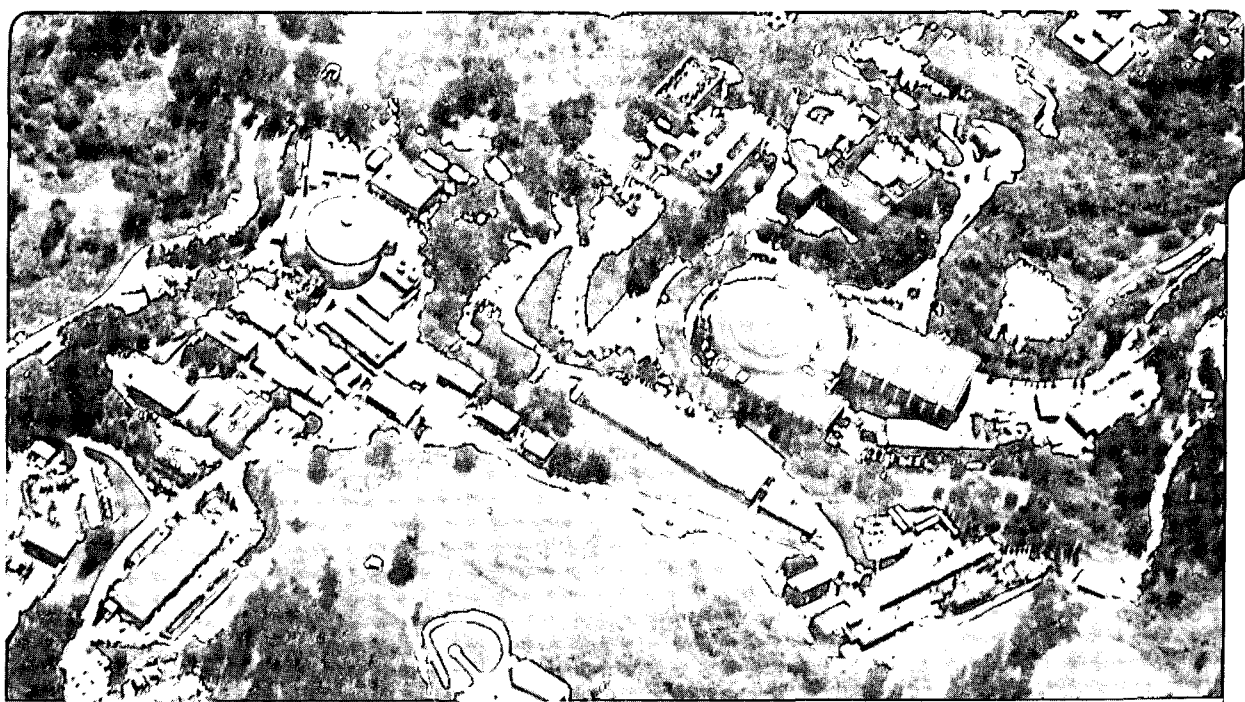

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John A. Kadyk

Physics Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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Table of Contents

	Page
I. Introduction	1
A. Orientation and Scope	1
B. Brief History	3
II. Wire Aging Phenomena and Empirical Results	4
A. Some Fundamental Concepts	4
A.1. Ions and Radicals	4
A.2. The Nature of the Plasma	5
A.3. Quenching Gases	6
A.4. Cathode Wire Coatings	6
A.5. Anode Wire Coatings	7
B. Early Studies of Counters	7
B.1. Studies of G-M Counters	7
B.2. Development of Proportional Counters, Multi-Wire Proportional Chambers and Drift Chambers	8
C. Results From Wire Chamber Operation	10
C.1. Trace Impurities and Influence of Materials Used in Chamber and Plumbing	11
Table I. Some Commonly Used Materials in Wire Chamber Systems	12
C.2. Experiences from Detectors In Experiments	14
Table II. Results From Experiments	15
C.3. Rejuvenation of Damaged Chambers	18
C.4. Results from Laboratory Tests	19
Table III. Results From Laboratory Tests	21
D. Dependence of Wire Aging on Certain Physical Parameters	29
D.1. Gain	29
D.2. Gas Flow Rate	30
D.3. Gas Density	31
Table IV. Gas Flow Rate Dependence	31
D.4. Radiation Intensity	31
E. Observations and Analysis of Wire Deposits	32
E.1. Methods of Analysis:	33
Scanning Electron Microscope/X-ray Emission Spectroscopy	33
Auger Electron Spectroscopy/Ion Etching	33
Mass Spectrometry	33
Table V. Surface Analysis Techniques	33
E.2. Silicon Deposits	33
E.3. Phthalates	34
E.4. Sulfur and Halogens	34
E.5. TMAE	35
E.6. Other Examples	37
F. Effects of Wire Material	37

III. Interpretation and Models: Plasma Chemistry 39
A. Simple Examples of Plasma Reactions 39
Table VI. Average Bond Energies 41
Table VII. Dissociation Energies and Ionization Energies 42
B. Reaction Kinetics and Controlling Parameters 45
Table VIII. Physical Parameters of a Plasma 46
Table IX. Electron Affinity and Permanent Dipole Moment 49
C. Catalytic Behavior 51
D. Plasma Chemistry Studies at Atmospheric Pressure 52
Table X. Effect of Oxygen Additions on Effluent Yields for AC Discharges in N_2/CH_4 53

IV. Further Investigations 53
A. Current Activities 53
B. For the Future 54

V. Principles and Guidelines 57
Table XI. Recommendations: Materials and Procedures 58

VI. Conclusions and Summary 60
Acknowledgments 60
Glossary 61
Bibliography 65
References
Table II 66
Table III 67
Text 67
Appendix A 72

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John A. Kadyk
Lawrence Berkeley Laboratory
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Abstract

An overview of wire-chamber aging is presented. A history of wire aging studies and the manifestations of wire aging are reviewed. Fundamental chemical principles relating to wire-chamber operation are presented, and the dependences of wire aging on certain wire-chmaber operating parameters are discussed. Aging results from experimental detectors and laboratory experiments are summarized. Techniques for analysis of wire deposits and compositions of such deposits are discussed. Some effects of wire material and gas additives on wire aging are interpreted in chemical terms. A chemical model of wire aging is developed, and similarities of wire-chamber plasmas to low-pressure rf-discharge plasmas are suggested. Procedures recommended for reducing wire aging effects are summarized.

I. Introduction

A. Orientation and Scope

Since the advent of wire chambers as highly sophisticated and expensive instruments for particle measurement, the study of the problems limiting their useful lifetime has become increasingly important. These problems are generically combined under the term "aging" even though there are several different manifestations of this term. Typically there may be loss of gain, reduction of plateau, loss of energy resolution, excessive currents, self-sustained current discharge, sparking, etc. Any or all of these effects may result from the use of the detector in a radiation environment. These deleterious effects can all be caused by coating or other degradation of the cathode and anode wire surfaces. The detection of radiation is the purpose for which the wire chambers are intended, and it is ironic that the operation of the chambers can result in their own destruction. However, over the past decade or so it has become evident that there are in fact certain examples of wire chambers which have been operated with little or no deterioration, even after having been exposed to relatively high radiation levels. This observation has encouraged searches for still other gases and conditions that are resistant to aging. These searches have been partially successful, and there are some choices of gas mixtures and operating parameters which have given demonstrably low aging rates. On the other hand, there are examples of very rapid aging. The fact that more than a single solution to the aging problem is needed is a consequence of the different requirements for different chambers: particle tracking over large volumes, vertex detection, pulse height resolution, high event rate, etc. There is presently no unique set of operating conditions that optimizes all of these objectives, and therefore there is the need for different "solutions" to wire aging.

For the reader who would like a quick reference to previous experiences and tests, the Tables II (experiments) and III (controlled tests) are provided, while Tables I and X and Appendix A give some information on materials and guidelines on procedures that are recommended in connection with chamber construction and operation, along with comments regarding their effects upon wire aging. The results are discussed mainly in sections II.C., II.E, II.F, and V, and a Glossary is provided for quick reference to some technical terms used. For the reader who wishes to learn somewhat more of the basic processes leading to wire

aging, the Sections II.A, II.D., III., and IV. may be of interest. The historical development of wire aging studies is traced briefly in this Section (I), and in Section II.B.

In most general terms, the undesirable effects experienced by users of wire chambers fall into one of two categories: (1) loss of gain or loss of gain uniformity (the latter results in shortening of the plateau region and degradation of ionization measurements) or (2) electrical breakdown usually manifested by a self-sustaining dark current discharge, i.e. a large current not induced by a radiation source. As we shall see, the effects of (1) are usually due to anode wire coating, while that of (2) is usually due to a coating of the cathode. Chambers may fall victim to the discharge mode even when less than 0.01 Coulombs of charge per centimeter of wire has been accumulated. When this effect occurs, the chamber operation is either permanently terminated or seriously impaired, unless a remedy can be found (which is possible in some cases, as we shall see). By exercising care in manufacture and operation of chambers, a value in excess of 0.1 C/cm can now be considered to be a reasonable goal, and integrated charge densities considerably higher than this value have been achieved in aging tests. At existing high energy physics experimental facilities, the radiation levels near the beams of storage ring colliders may result in integrated charge levels of ~0.1 C/cm after several years of operation. However, at facilities proposed for future experiments, such as the Superconducting Supercollider (SSC), at least an order of magnitude more in radiation hardness will probably be required. It is clear that the future application of wire chambers will need higher levels of radiation hardness than have presently been achieved in actual experiments.

The purpose of this article is to summarize the current experience with wire chamber aging. The goal is to provide the reader with what is felt to be well-founded advice, although occasionally there may be somewhat conflicting results from different reports. This is particularly the case when information is derived from experiments, as distinct from controlled tests in the laboratory (hereafter called laboratory tests), since in experiments there is usually rather incomplete knowledge of the operating conditions under which the results were obtained. On the whole, however, a reasonable agreement exists about the operation with certain gases and conditions, and these will be emphasized and summarized in tabular form. An earlier review of wire aging may be found in the Proceedings of the Workshop on Radiation Damage to Wire Chambers (1986)[1]. In his summary talk J. Va'vra presents an excellent summary of phenomena and results [2], and the present review will refer often to the material given there.

It is important to point out that the chemistry of wire chamber aging has not yet been investigated systematically or in depth, and so the explanation of why certain examples of chamber operation are successful in avoiding wire aging effects, while others are not, cannot be discussed with any certainty at present. The information derived from actual experiments on a beam line over an extended period is classified and analyzed separately from information derived from accelerated aging tests done in the laboratory. As indicated above, the parameters of wire chamber operation in an experiment, especially the presence or absence of potentially important trace impurities in the chamber gas, are generally much less well understood and documented than in the case of laboratory tests. Another reason for separate classification is the question whether or not aging scales with the radiation dose: laboratory tests are being done with much greater dose rates than normally encountered in actual experiments, and the results are usually interpreted as if they could be scaled to an experiment, an assumption not yet proven.

It has been commonly experienced that the aging effects are the result of a wire surface degradation of the anode ("sense") wire or cathode ("field") wire, and that this occurs frequently, but not always, in the form of an organic "deposit" that usually is a solid ("whiskers", thin films, etc.) [1], but may also be liquid (oily or grease-like)[3]. The solid deposits are generally some form of cross-linked polymer having good electrical insulating qualities, but in certain cases may be elemental carbon. Another form of degradation is chemical attack of a wire surface by active species produced in the avalanche. This is expected to occur only for wires which have chemically active elements in the wire surface material, and

hence are not gold plated.[4,5]. The effects of these degradations in producing the aging symptoms described above will be discussed.

It may be possible to gain a heuristic understanding of the mechanisms of formation of deposits on wires by reference to plasma chemistry investigations made at low pressure (~0.1 to 1.0 Torr) with radio frequency glow discharges, even though our interest is in chambers operated at atmospheric pressure (or above) with direct current discharges. In the former operating regime, the formation of polymer films under a variety of conditions has been extensively studied by scientists and engineers interested in applications of plasma chemistry, and a vast literature exists (see for example under Plasma Chemistry in the bibliography of this paper). Even though the chemical reactions may be complex, and generated under conditions of pressure and discharge that are very different from those used for wire chambers, certain qualitative aspects are expected to be similar and there is already evidence that this is so. We are, however, some distance from the goal of an accurate model with which the presence or absence, and the rate of wire coating can be predicted. A brief discussion is given here of certain aspects of plasma chemistry which are observed in the low pressure regime and are expected to be applicable to wire chamber operation at pressures of one atmosphere and higher.

B. Brief History

Studies of aging effects in counters were made at least as early as the 1940-1950 decade [6-9], with the observation of effects of dissociation of quenching vapor in Geiger tubes. These tubes were sealed and contained a gas mixture of argon, plus a quenching gas: methane, ethanol, or ethyl acetate. After approximately 10^8 counts, the plateau would disappear, and multiple pulsing and after-pulsing were observed. The spurious pulses were shown to result from the lack of quenching gas (see Glossary, or II.A.3), which was ultimately depleted by the molecular dissociation processes occurring in the electrical discharge plasma along the length of the anode wire. The plateau reduction was caused by solid deposits, which were a result of the discharge, and which could be removed by cleaning or heating the wire [8,9]. Analysis of the remaining gas inside a Geiger tube having ethyl acetate quenching gas showed that methane and water vapor were among the dissociation products [9]. Methane was known to be capable of producing polymeric deposits.

Beginning in the late 1960's and by 1970, the aging effects in proportional counters were under investigation [10-16], proportional counters and multiwire proportional chambers had come into widespread use, largely replacing Geiger counters, and their aging problems were receiving much more attention. A commonly used gas was argon mixed with 10-20% methane. Deterioration occurred after a limited number of particle counts (~10^8), as observed by a loss of gain and of pulse height resolution, and again the effects were attributed to deposits on, or coating of, the anode wires [10,12-14,16]. These deposits were usually, but not always, visible under an optical microscope. Moreover, the composition of the deposits was not well understood because the techniques used to analyze them, such as X-ray fluorescence [10,14], have difficulty in detecting the light elements that are expected to be in the polymeric wire coating. It was established that these deposits originated from the gas. Tests in argon/methane (90/10) mixtures [12,14,16] showed that the gain loss depended upon the total accumulated charge, the operating gain, and the wire material. Furthermore, it was shown that in certain cases at least, the gain loss could be explained by an increase in the effective anode wire diameter caused by the coating, resulting in a reduction of the surface electric field intensity [10,12,16]. Variations in gain along the wire were then the result of variations in coating thickness, and were the cause of the observed plateau reduction and loss of pulse height resolution. Later (section II.A.5), we will see that there is yet another surface mechanism for gain loss.

Suggestions were made to replace the methane quenching gas by some other gas that would not result in the formation of wire deposits [17]. Since the anode wire coatings were thought to arise through polymerization processes involving ions and free radicals from the disrupted methane molecules, searches concentrated on gases which did not produce polymerizable

molecular fragments. Carbon dioxide was tested [13,17-19], but also seemed to result in deposits, this time principally on the cathode wires, and consisting of elemental carbon. Moreover, carbon dioxide is not as good a quenching gas as methane.

Another aging effect, different from those discussed above, is the electrical breakdown of the chamber resulting in heavy current in the absence of any radiation (particle) sources. This spontaneous or self-sustained current discharge has been ascribed generally to a thin insulating layer being formed on the cathode, and is frequently called the "Malter effect"[20]. A method used to avoid this coating was developed at CERN for use in high-gain multiwire chambers [21], where large number of ions are formed with each particle detected. The technique consisted of adding to the wire chamber gas a small amount (~ 4%) of the vapor of methylal [$(CH_3O)_2CH_2$], which has a low ionization potential and does not polymerize [22]. The positive ions produced in the avalanche are neutralized by charge exchange collisions with methylal before they reach the cathode; the resulting ionized methylal molecule subsequently drifts to the cathode and is neutralized without causing polymerization. The ions initially produced at the anode wire would otherwise result in a deposit of an insulating hydrocarbon film on the cathode wires. The addition of methylal was shown to give about a factor of 10^3 reduction in aging from the Malter effect, but gives little or no protection against coating of the anode wire.

More recently, it has been shown that certain other "additives", i.e. gases or vapors added at approximately the $\lesssim 1\%$ level, can give dramatic improvements in the lifetime of wire chambers. Especially noteworthy is the use of ethanol [23] or isopropanol [5] vapor, especially when used in argon/ethane gas mixtures. Water vapor as an additive has also been demonstrated to be very effective [24-29]. The basis for this lifetime improvement is not yet established, but may be at least partly associated with the presence of the oxygen in each of these particular additives. This point and other possible factors will be further discussed. Other additives, such as hydrogen in argon/methane also are claimed to extend the lifetime of sealed proportional counters [30]. Moreover, it has been shown in laboratory tests that with very pure gases and under otherwise clean conditions, very low aging rates are obtained using the same primary gas mixtures which have not given very good results when gas purity was not carefully controlled [4]. These observations show that very small amounts of certain constituents of the gas mixture can have important effects on aging processes.

Some of these results, and others, will be summarized in tables and will be discussed with a view to understanding the results in terms of the basic chemical processes involved, and how this may help to find more general solutions to the problems of wire aging. A Glossary has been included to help explain some terms that may not be familiar to all readers.

II. Wire Aging Phenomena and Empirical Results

A. Some Fundamental Concepts

A.1. Ions and Radicals

Studies of chemical reactions occurring in electrical discharges date to the beginning of this century. Some early work, which is relevant for our interest in wire aging, was done on the breakup of methane (CH_4) in a.c. and d.c. discharges at low pressure (see plasma chemistry references in Bibliography of this paper). It was at first thought that the methane molecule was broken up in the discharge, and that the fragments then recombined into just ethylene (C_2H_4) and hydrogen [31]:

$$2\ CH_4 \rightarrow C_2H_4 + 2H_2 \qquad (1)$$

However, an experiment to test this theory was done in a sealed tube and the expected 50% rise in pressure (from the increase in density of molecules) did not occur. Instead a more modest pressure rise was observed [32]. This led to more detailed investigations which showed the

chemistry to be much more complex [7-9]. Many reactions other than (1) occur, and, in particular, there are some that lead to non-volatile products which condense upon the electrodes and therefore do not contribute to a pressure rise. It was soon realized that many active atomic and molecular species are involved. The bombarding electron energies in the discharge are generally more than enough to produce the singly ionized states: CH_4^+,CH_3^+,CH_2^+, CH^+, C^+ and H^+; more highly ionized states can also be produced. Furthermore, corresponding to these ions, there are chemically active but electrically neutral species called free radicals, which have unpaired valence electrons that are not participating in a chemical bond but are available to do so: $CH_3\cdot$, CH_2:, etc. The presence of an available electron is indicated by "·", and ":" represents two electrons, etc. In the simplest case, a chemical bond between two molecules or fragments is formed when one electron from each species participates in a "single bond" involving just those two electrons. Reactions between all these species can produce additional neutral radicals* and ionized species, and these processes can ultimately result in the formation of polymers. To take one simple example, the $CH_3\cdot$ radical can propagate in the presence of ethylene (C_2H_4) to form a polyethylene-like polymer, in the following fashion:

$$CH_3\cdot + C_2H_4 \rightarrow C_3H_7\cdot \ , \ C_3H_7\cdot + C_2H_4 \rightarrow C_5H_{11}\cdot \ , \text{etc} \qquad (2)$$

$$\begin{array}{ccccc} H & H & H & & HHH \\ HC\cdot & + & C= & C & \rightarrow HC\text{-}C\text{-}C\cdot \ , \text{etc.} \\ H & H & H & & HHH \end{array}$$

This formation of a polymer chain can begin in the gas plasma, or on an electrode surface, or begin in the gas and migrate to the surface. In any case the molecular weight soon becomes so large that the polymer condenses from the gas phase and is deposited as a solid or liquid on the chamber electrodes or walls. Similar reactions can occur between ions, or between ions and radicals, but there are two reasons why radicals dominate: (1) radicals occur in far higher concentrations than ions, at least for the types of discharge with which we are concerned, because it takes much less energy to break a chemical bond than to form an ion; (2) ion-ion reactions are suppressed due to the repulsive electric force (assuming here only positive ions).

A.2. The Nature of the Plasma

The general mixture of positive ions, neutral species including radicals, and negative ions (electrons mostly) has no net charge when initially produced: it is called a plasma. We will be concerned primarily with reactions occurring in the plasma at the anode wire of wire chambers or proportional counters. It is here that a high concentration of radicals and ions are produced, and where the principal reactions occur leading to wire deposits.

The plasma surrounding a wire extends to only a short distance from the wire surface, perhaps a small number of wire radii, due to the decreasing electric field (~ 1/radius). Electrons are attracted to the anode with average drift velocities of typically ~ 5 cm/μsec, while the positive ions drift toward the cathode at a much lower velocity, both due to their much higher mass than that of electrons, and due to their lower kinetic energies. This is called a non-equilibrium plasma because the kinetic energies of the electrons and ions are quite different: E(electron) ~ 1-10 eV, E_{ion} ~ 0.03-0.09 eV (equivalent ion temperature ~ 300°–1000°K). By contrast, an arc discharge, where ions also have energies > 1eV, is an example of an equilibrium plasma. The breaking of bonds to form radicals and the production of ions are determined primarily by the electron energy spectrum and its relationship to the bond and ionization energies. The energy spectrum, in turn, is a function of the electric field strength, the energy loss per collision, and the mean free path between collisions, the latter being determined by the cross section and the density of the gas. A typical collision rate of a molecule may be 10^9-10^{10} Hz. Active species will therefore react very quickly, and the "soup"

of the anode wire plasma provides a suitable environment for complex chemical phenomena to occur, characterized by electron energies of a few eV.

A.3. Quenching Gases

Recombination of ions and de-excitation of atoms typically results in UV photon emission, which can cause secondary electron emission if the emitted photon excites other atoms or strikes the cathode surface; this then may result in subsequent avalanches. For this reason, quenching gases, typically hydrocarbon in nature, are introduced. These gases are polyatomic, and therefore have many vibrational and rotational degrees of freedom, giving them large cross sections for absorbing UV photons. However, a good quenching gas does not readily ionize or emit photons as a result, but rather de-excites by fragmentation or collision processes.

A.4. Cathode Wire Coatings

Another process can result in secondary electrons being emitted from the cathode: A drifting positive ion is neutralized when it reaches the cathode, and is thereby left in an excited state. Upon collision with the cathode, it can then use part of this excitation energy to overcome the work function at the cathode surface causing a secondary electron to be emitted. We will see evidence for this process from certain phenomena occurring in wire chambers (e.g. "dark currents"). As mentioned above, the quenching gas will minimize this effect by de-exciting in such a way as not to produce more secondary electrons, for example by fragmentation.

A more serious problem is that of the so-called "Malter effect" [20]. A thin insulating coating may be deposited on the cathode by a mechanism involving polymerization. Here at the cathode, the effects of such a coating can be much more devastating than at the anode: a current run-away process can ensue, resulting in continuous electrical breakdown of the wire chamber and permanent damage. This is all too common an experience for users of large and expensive wire chambers in the field of high energy physics. In the Malter effect, an electric dipole layer forms across the insulating film at the cathode due to the positive ions drifting from avalanches at the anode. Because the layer is a good insulator, the positive charges do not readily reach the cathode, and since the layer is very thin, the positively charged layer, together with the induced image charge on the cathode, produces a very large electric dipole field. The result is that the threshold for field emission is exceeded, and electrons are "pulled" from the cathode by the electric field. This generally occurs at a field strength of about 10^7 V/cm. These electrons can more successfully penetrate the Malter layer than can the positive ions, and some will neutralize the positive charge. Many electrons, however, will enter the gas, drift to the anode, and produce more positive ions, which then drift to the cathode and enhance the strength of the dipole field and the field emission of electrons. This positive feedback can result in large standing currents and the demise of the chamber. Onset of this phenomenon is usually noted during and after periods of intense radiation of a wire chamber, when excessive noise or "dark" currents appear in addition to those normally associated with the radiation. This large dark current is an indication of "enhanced sensitivity" of the cathode to low-energy photons (or ions), due to an incipient insulating layer and charge build-up, causing a reduction of work function at the cathode surface, but where the effect has not yet reached the threshold for the Malter discharge. At this stage, there may be a significant dark current or noise which will disappear when the radiation source is removed though it may take a substantial time to decay. When the problem has progressed to a very serious level, the dark currents persist after the source of radiation (e.g. the particle beam) has gone away. At this point, only turning off the chamber high voltage for some time will restore the normal chamber operation. The large dark currents subsequently return, however, when a threshold radiation value (or chamber current) is exceeded.

There exists some evidence that effects similar to those described above can be caused by metal oxide coatings on the cathode [33]. Most notably, aluminum oxide is a very good insulator, and forms quickly when aluminum is exposed to air. Wire chambers or proportional tube counters using aluminum cathodes may exhibit large dark currents or Malter-like breakdown effects even before any polymerized coating is deposited by plasma polymerization. Symptoms resemble those described above, except the onset may be almost immediate, since the insulating metal oxide layer is already present, while polymerization processes require some time interval during which the insulating layer is formed.

A.5. Anode Wire Coatings

The other general category of aging effects is due to anode wire coatings. Anode wire coatings can occur in many physical forms, can be liquid or solid, and can be insulating or conducting. The increase in diameter of the anode wire due to the coating will result in lower surface fields, hence lower gain, even for a conductive coating. As an example, a 0.5 μm thick coating, or only about one wavelength of light, on a 25 μm diameter anode wire, can cause a large reduction in the avalanche gain, perhaps ~20% - 40%. This coating is presumably deposited non-uniformly, since gain variations are usually observed along the wire length. This would be a serious problem if a chamber used energy loss resolution as a means of particle identification, where the pulse height is used to determine the primary ionization. This is also a problem when counting particles with a pulse height threshold, since the high voltage plateau length for satisfactory operation is diminished by gain non-uniformity. Finally, if the layer is insulating, then another mechanism for gain loss can be the reduction of surface fields due to the influence of the electrons collected on the layer, and furthermore this effect will also be generally non-uniform. Worse yet, the gain may be rate dependent, the collected charge depending on a balance between charge leakage away from the layer and accumulation of additional charge [34].

B. Early Studies of Counters

B.1. Studies of Geiger-Mueller Counters

Some of the first studies of counter lifetimes were done on Geiger-Mueller (G-M) counters. These are sealed tubes containing an inert gas, usually argon, and a quenching gas, such as methane, ethanol, or ethyl acetate. In a G-M counter, the discharge begins with an avalanche in the gas, and then it spreads along the entire length of anode wire, resulting in a large amount of ionization and a very large pulse. It was learned, through carefully contrived experiments (see next paragraph), that an observed increase in "noise" or dark current was due to the quenching gas being "used up" after about 10^{10} pulses, while the shortening of HV plateau was due to deposits on the anode wire [8,9]. Since a much larger charge transfer per pulse is involved in a G-M counter discharge than that of a "proportional" counter, it is a common experience to reach the end of the useful life of the G-M counter by the nature of the quenching process: fragmentation of the quench gas molecules due to the discharge, and the ultimate exhaustion of the quenching gas. However, the polymerization processes which result from the formation of these molecular fragments cause additional problems through their non-uniform coating of the anode wire: this causes a plateau reduction because of a fixed threshold gain required for the detection of the G-M discharge, but varying gain along the wire. Fig. 1 shows examples of plateau curves for a G-M counter after various levels of exposure to radiation [8]. A good quench gas not only absorbs UV photons resulting from argon de-excitation, but will also charge exchange with Ar^+ ions to prevent these ions from releasing secondary electrons at the cathode upon striking the surface. The work function at the cathode metal is typically ~4 eV, while Ar^+ has an excitation energy of 15.8 eV. The ionization potential of the quench gas must be less than that of Ar for the charge exchange to be possible

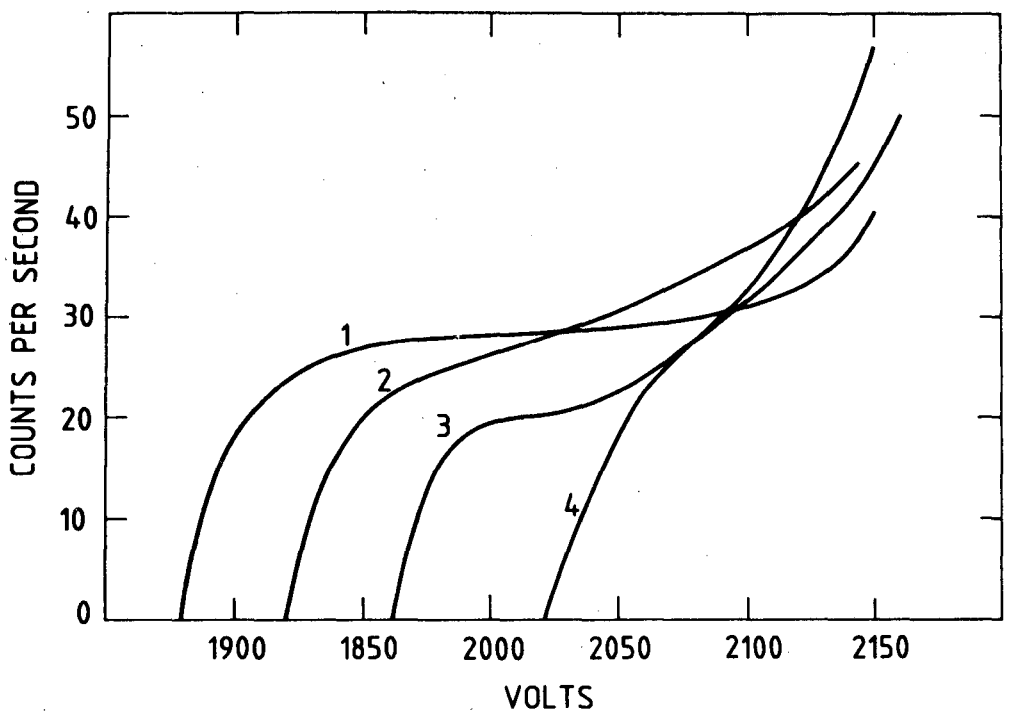

Fig. 1. Operating characteristics of a methane-filled Geiger-Muller tube of various ages. Curve 1 was measured after 10^7 counts, curve 4 after 10^8 counts [8].

(for CH_4 it is 12.6 eV; for C_2H_5OH it is 10.5 eV). The ionized quench molecule does not emit a secondary electron at the cathode, but instead is neutralized and dissociates [6,13]. Unfortunately, the dissociation products of most quench gases can and do coat the cathode to produce the Malter effect.

These interpretations of cathode and anode coatings have been verified many times. A classical experiment is to replace the gas in an "aged" counter with new gas, whereupon the dark current goes away, but the plateau is still very narrow[9]. The gas taken from the aged counter is used to fill a counter having a new anode wire, and this counter is observed to have a normal plateau, but the dark current is large. Similarly, counters suffering from Malter breakdown recover when the cathode is "cleaned", but not when the anode wire is replaced. This seems to clearly separate the aging problems we have discussed into those distinctly associated with either the anode or cathode. However, there is at least one effect, gain loss, which could be due to charged insulating coatings on either the anode or cathode.

B.2. Development of Proportional Counters, Multiwire Proportional Chambers and Drift Chambers

For the detection of charged particles, the G-M counter was replaced for most purposes during the 1960-1970 period by a counter operating in the avalanche mode. This was called the "proportional counter", because the response at lower gains is quite proportional to the ionization deposited in the counter.* This is in contrast to the G-M counter where, in the plateau region, the pulse amplitude is essentially independent of the initially deposited

* The name proportional counter is used here, since it is traditional. Modern higher gain usage of the same device is frequently not in the proportional region, due to space charge effects, and a more accurate and descriptive name perhaps should be "avalanche" counter.

ionization. This is fine for counting particles, but useless for making measurements of particle ionization (e.g. in determining particle velocity, or distinguishing one from more than one particle striking the counter simultaneously). Other disadvantages of the G-M counter are the very long recovery time (~100 msec) compared to the proportional counter, and the comparatively short counter lifetime. The proportional counter has shorter recovery time (~few μsec), and although it produces relatively small pulses compared to the Geiger-Mueller counter, this can be compensated for, within certain limitations, by increasing the electronic gain.

The development of the multiwire proportional chamber (MWPC)[35] for particle tracking was a natural and very useful extension of the proportional counter, and brought with it the same problems of aging. Later, the development of drift chambers introduced another, still more powerful, particle tracking device. Very large drift chambers, containing many tens of thousands of wires, are now in common use, each representing an investment of millions of dollars. More recently, high resolution drift chambers have been developed for operation very close to beams and the point of particle production to identify very short-lived particles. Such "vertex detectors" are subjected to relatively high radiation levels due to their proximity to the beams, and are operated at high gains to achieve the desired spatial resolution. On both of these accounts are these chambers especially vulnerable to aging effects. Aging problems became more difficult for another reason: proportional counters and some multiwire chambers use a continuous cathode (tubular or flat foil walls), while the drift chambers use a cell structure defined by cathode wires, and perhaps also by potential wires. This means that the same amount of polymerizing material is deposited in higher concentrations on wires than would be the case for the continuous cathode, just due to the smaller cathode area, making the drift chamber vulnerable to the Malter breakdown at a much earlier stage, by even a factor of 10-100 [22]. On the other hand, photon quenching was not quite so important, since the cathode wires represented a much smaller "target" for UV photons than did the continuous cathode.

The aging problems associated with the early wire chambers are well summarized by F. Sauli [36]. Permanent damage to wire chambers was directly traced to visible thin layers of material coated on electrodes, and this was presumed to arise from the ions and/or radicals produced in the avalanche from the hydrocarbon quenching gas. Removal of these layers by careful cleaning would eliminate the problems temporarily. Soon, there was the idea of addition of a non-polymerizing quenching gas, one that would have the lowest ionization potential of any gas in the mixture [22]. Due to charge exchange, ions of only this buffering quencher would be attracted to the cathode, where, after neutralization they would not polymerize. The principle hydrocarbon quencher would still exist in such a gas mixture, but the easily ionized buffer gas would keep ions of the quencher from reaching the cathode. Alcohols were known to have the desired buffering properties, and indeed they perform as expected. In the classic example using "Magic Gas" [21], consisting of 75% argon, 24.5% isobutane, and 0.5% Freon 13B1, the chamber lifetime was extended by about three orders of magnitude by the addition of 4% methylal [$(CH_3O)_2CH_2$]. However, the actual situation is not quite so simple as this model suggests, since radicals, not ions, are thought to be mainly responsible for polymeric coatings, and certain gases which are known not to polymerize, nevertheless cause aging problems (e.g. CO_2).

As previously mentioned, aging effects at the anode wire cause loss of gain and/or non-uniformity of gain, which results from a coating of the wire or possibly a chemical attack of a wire that is not chemically inert. The characteristic behavior of degradation is dramatically exhibited by deterioration of the Fe^{55} x-ray spectrum in an argon-based counter gas. Fig. 2 shows the spectral shapes for the gas argon/methane (90/10) at increasing levels of exposure to Fe^{55} [10,16]. Examination of the irradiated part of the anode wire showed a strong carbon signal, suggesting a hydrocarbon polymer (the x-ray flourescence technique used was insensitive to hydrogen).

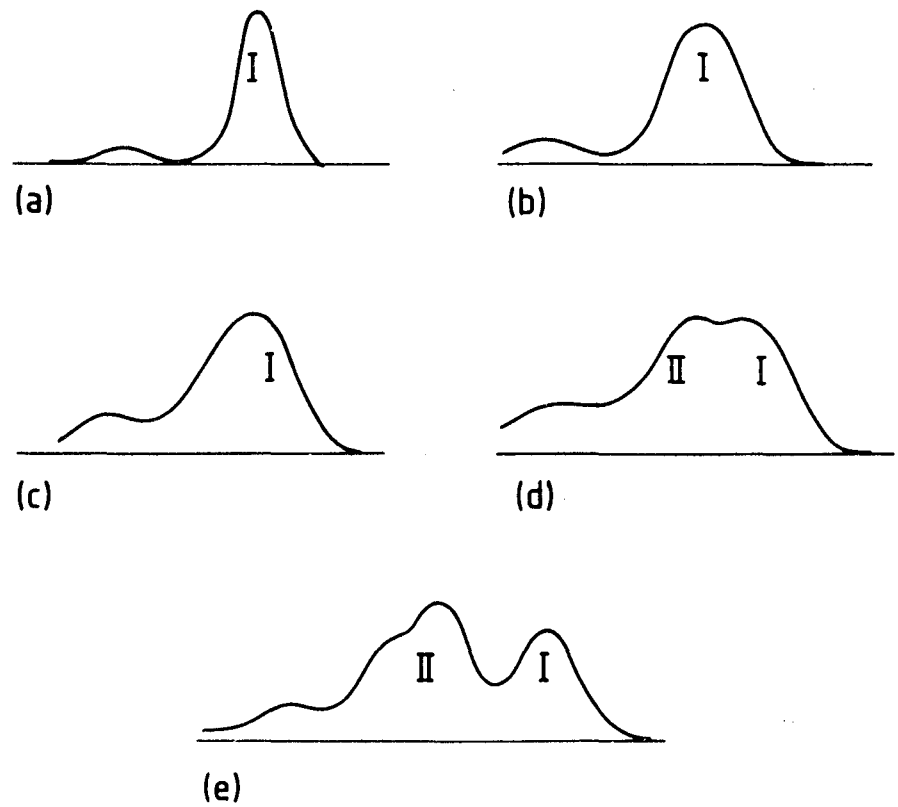

Fig. 2. Five successive pulse-height distributions as they develop during irradiation with a 5.9 keV X-ray source of a proportional counter filled with 10% methane in argon [10].

C. Results From Wire Chamber Operation

Until relatively recently most of the information on wire aging came from installed experiments at major high energy physics facilities. Here the pathologies of the wire chambers bloomed, and it was usually after the fact that evidence was gathered in an attempt to reconstruct the circumstances of a wire chamber's demise. There was little to document the radiation levels of chamber currents versus time, or the "on" and "off" periods for chamber or beam, much less having the analysis of gas used in operating the chamber, and perhaps not even having a record of flow rate or gain. Unfortunately, all of these parameters are important and influential in their effects on wire aging. However, some estimates of these parameters were made, and there are some experiences in common to several different experiments. There are, of course, contradictory experiences as well, which only means that we do not always have a full set of information about the parameters that can affect each result. We will, in section II.C.4., also discuss and summarize results from small-scale, carefully controlled and monitored, laboratory tests. This will represent a very different situation, where essentially a full set of relevant information may be available, but it applies to a more nearly ideal situation, where conditions are much more under control than in a real experiment, particularly with regard to purity and cleanliness in the chamber and its plumbing. Nevertheless, we will find some coherence between the results from experiments and from laboratory tests. Eventually, it will be necessary to succeed on both levels: to achieve a set of conditions and gases in laboratory tests which gives acceptably low aging rates, and also to know what purity and cleanliness are necessary, both qualitatively and quantitatively, to implement successfully these

laboratory results in the field. We are now about at the stage where the latter goal is being approached, though not yet reached. The goal is all the more difficult since not just one set of wire chamber conditions is needed; rather there are many different types of wire chambers built for a variety of different applications, each needing a different solution to the problem of aging: high spatial resolution, good resolution of ionization density, high particle rate or timing resolution, low scattering cross section, etc. We shall now look to see how some of these objectives have been met.

C.1. Trace Impurities and Influence of Materials Used in Chamber and Plumbing

Before examining results from experimental detectors and from laboratory tests, it is important to be aware of the abundant evidence that small concentrations of certain gaseous constituents can have very important and sometimes dramatic effects upon the rate of wire aging. We shall see that this may be due either to the presence of contaminants initially present in the gas, or may result from outgassing of solid materials in contact with the gas. We shall also see the deliberate introduction of small concentrations of "additives" which are found to be effective in reducing wire aging. In Table I are listed certain compounds or materials about which some basis exists for understanding their effect, if any, upon aging. We shall discuss a few of these examples.

It is now well established that commercial grades of PVC are directly associated with aging problems, perhaps due to outgassing of phthalates (and perhaps due to unpolymerized monomers), which show up prominently in wire coatings [37]. Phthlates are plasticizers which are commonly added to many plastics to give them flexibility. Another example is single-part RTV[4], which is a frequently-used silicone sealant. Silicone is a generic name for silicone polymers whose backbone chain consists of alternating silicone and oxygen atoms, with hydrocarbon groups appended to the silicon atoms. Silicone is often detected in analyses of wire deposits, but the source of the silicone is frequently a point of controversy [37]. Low molecular weight silicone residues, originating for example in silicone vacuum grease, or in a silicone oil bubbler, could exist in vapor phase and subsequently undergo reactions in the plasma of the avalanche discharge to produce deposits. It is also notable that although silicon is very commonly found on anode wires, it is not often found on the cathode. The presence of silicon is emphasized here, because it appears in anode wire deposits in astonishing abundance sometimes , even though its source cannot always be identified [24,38,39]. Recent tests of silicone oil and single-part RTV exhibit moderate aging even though the vapor pressure of the oil is only $\sim 1 \times 10^{-8}$ Torr [40] (see Table III and discussion in II.C.4 and II.E.2). Frequently, there are potential silicon sources in RTV,O-ring grease, oil bubblers, and chamber walls made from G10. It is possible that other, unidentified sources existed in these cases (e.g., silicone mold-release agent remaining on G10 walls). Commonly known sources of silicones are listed in Table I. Another suggested source is silane (SiH_4), a gas commonly used in the microelectronics industry to produce silicon coatings: perhaps a gas cylinder containing the gas supply for wire chambers was at one time used to contain silane, and there is still some outgassing of silane from the cylinder walls. An example of a drift chamber which failed due to radiation damage was discussed by Williams [37]. In this case the wire coatings were analyzed using mass spectrometry and Auger electron spectroscopy, and both phthalates and silicones were found to be present.

Table I. Some Commonly Used Materials In Wire Chamber Systems
(see Glossary for some abbreviations used)

Material	Common or Trade Name	"Rating"	Comments
Gas Tubing, Plumbing, Bubblers:			
Stainless Steel		Very good	Electropolished SS is best
Copper, hydrogen fired		Very good	
Copper, refrigeration		Perhaps OK	Some Cu tubing is drawn using lubricating oil: bad.
Aluminum		Depends on gas	Al is very active chemically,but forms a protective oxide.Not a very good cathode material
Polyethylene	Poly-flo	Good	
Polyamide 11	Nylon, Rilsan 11	Very good	Works with DME
Polyvinyl chloride (with plasticizer added)	PVC, Tygon	Very bad	Outgases phthalates, halogenated hydrocarbons - causes aging
Polytetrafluoroethylene	PTFE Teflon	Good if "baked"out	
Perfluoroethylene propylene	FEP Teflon		Electron capture in DME("unbaked" FEP)
Perfluoroalkoxy	PFA Teflon		
Trichloroethylene Trichlorotrifluoroethane	Chlorinated Cleaning Solvents	Bad if any residue remains	Can outgas: chlorine probably causes fast aging
Silicone grease		Bad	Silicone often found on anode
Silicone oil (in bubbler)		Bad*	Moderate to severe aging
High-boiling polycyclic petroleum fraction (in bubbler)	Mineral Oil	OK*	
Water (in bubbler)		OK	Beneficial in small concentrations "additive" (deionized water best)
Refined Petroleum Oil (in bubbler)	Mechanical Pump Oil	OK*	
Chamber Materials (see also materials above used for plumbing):			
Fiberglass/epoxy	G10	Probably OK	Must have clean surface: mold-release agent (silicones) may be on surface (very bad).
Methyl methacrylate	Lucite, Plexiglas	OK	
Glass	-	OK	
Polymethacrylimide	Polyfoam	OK	
Polyethylene terephthalate	Mylar	OK	
(?)	Rohacell	Probably OK	
Alumina (Al_2O_3)	Ceramic	OK	Al_2O_3 can accumulate charge

Table I. Commonly Used Materials In Wire Chamber Systems (continued)

Material	Common or Trade Name	"Rating"	Comments
Glass Ceramic (SiO_2,Al_2O_3,MgO, K_2O, B_2O_3, F)	Macor	Probably OK	Bad results reported with DME
Epoxies	Torr-Seal	OK	Good results with all of
	"5-Minute"	OK	these, but the "5 minute" can
	Epon/Versamid	OK	be hygroscopic (surface moisture)
Polyurethane		Probably bad	Report of bad effects from soft urethane adhesive
Silicone Polymers	RTV: 1 part	Bad	Acetic acid smell: causes aging
	RTV: 2 part	?	Probably OK - little data
Polyoxymethylene	Delrin, Hostaform	OK (?)	
Polyphenylene oxide	Noryl	OK (?)	
Fluorinated copolymer	Viton	Good, usually	Bad results reported using DME
Polychlorotrifluoro-ethylene	Kel-F	Good	
Perfluoroelastomer	Kalrez, Chemraz	Good	Works well with DME, but structurally weak
Ethylene-tetrafluoro-ethylene copolymer	Tefzel	Good	
Polyvinylidene fluoride	Kynar	Good	
Polyimide	Kapton	Good	
Higher Molecular weight alkanes	Paraffin	OK (?)	
(Waxes and Resins)	Resin	OK (?)	
	Beeswax	OK (?)	

* Little or no aging observed when argon/ethane (50/50) supply was deliberately bubbled through, mineral oil, or Duo-Seal mechanical pump oil, just upstream of test chamber, but significant aging was observed with silicone oil (Dow 704) even though the concentration in the gas was very low: vapor pressure is quoted by manufacturer as 1.4×10^{-8} Torr. About 0.2 C/cm of charge transfer was achieved during these tests (see Table III).

Table I lists many commonly used materials, and it is only in certain cases that available information directly implicates certain materials. If success has been obtained with a material in some situations it is called "OK", even though it may react adversely with certain other gases, and a comment is made. For example, Teflon is generally regarded as very inert, but appears to be incompatible with dimethyl ether (abbreviated as DME)[41]. Some recent results show that a significant amount of outgassing occurs from "unbaked" Teflon, the exact constituents depending on the type of Teflon (compounds containing halogens are detected) [42]. In general, great care should be taken to avoid compounds containing chlorine in the gas. As we will see later (sections II E.4 and III C.), chlorine is known to accelerate greatly certain polymerization reactions in plasma chemistry research at low pressure (~ 1 torr) and there are reasons to expect that this may also apply to wire chamber aging. (However, see section II.C.4 and and Ref. 44 for recent results contrary to this expectation.) One source of chlorine could be from chlorinated solvents commonly used during manufacture to degrease and clean various pieces of equipment or materials (e.g. gas plumbing components) that later are in contact with the chamber gas supply. Depending on the procedures used, there may still be a solvent residue which can contaminate the gas: a few parts per million may be enough to cause serious problems.

C.2. Experiences from Detectors in Experiments

Table II summarizes some data relating to presence or absence of aging of wire chambers used in actual experiments. Since much of this data has been obtained through an experimenter's estimates of currents, running time, etc., it will of necessity be subject to large uncertainties. This should in no way reflect adversely on the experimenter who has made the effort to collect and report this data. Indeed, it represents a considerable amount of work to reconstruct the quantities and experiences noted in Table II. It is not at all common practice in an experiment to have monitors which will automatically record all of these relevant quantities. Even though care has been exercised to be accurate in assimilating the reports, this author accepts full responsibility and blame for any mis-representations. These results are taken from a variety of sources, but especially from the contributed talks, "Result Summaries", and the summary talk by J. Va'vra, all found given in the Proceedings of the Workshop on Radiation Damage to Wire Chambers [1]. The general idea for Table II was due to J. Va'vra and the present table includes more experiments than found in his summary talk. This is partly due to some newer results, and partly because the criterion on the minimum amount of charge collected per cm of anode wire has been relaxed. Table II also includes experiments with detectors which failed due to severe wire aging after a relatively mild beam exposure. Whenever it is known, the surface field at the cathode, or in lieu of that, the cathode diameter, will be given; this quantity is important in determining the propensity for sustained dark current discharges. There may be other quantities which are expected to affect aging, but they are either not known or very difficult to put into a meaningful context (such as gas flow rate). In any case there is not room in the table for everything, and additional relevant information may be found under the "Comments" column or by looking up the reference. We will now discuss the table and try to extract from it some important lessons .

In Table II we have attempted to include as many pieces of information as possible that are thought to influence the aging, and give the type of aging if it occurred. The detectors listed usually made use of an argon-based gas, plus a hydrocarbon, and perhaps some other "additive". The result are grouped roughly according to the type of gas mixture: Ar/C_2H_6, Ar/CH_4, Ar/CO_2, or "Magic Gas". Although essentially no information is available on the trace impurities of the gases, there is frequently some information about materials used for the gas plumbing system and for the chamber.

Table II Results From Experiments

Gas	Aging Observed[1]	Gain	Charge (C/cm)	Cathode Field or Wire Diam.	Plumbing[2]	Other Materials[2]	Running Time or Other Information	Ref.
$Ar/C_2H_6(40/60)$	None	10^5	0.01	35 kV/cm	SS(100 m) + Nylon (10 m)		35 μm Ni-Cr anode	II-1
$Ar/C_2H_6(50/50)$	G.L., D.C.	$3x10^4$	0.01	(planar low field)	No PVC	Paraffin, resin beeswax; soft urethane adhesive; G10 coated with epoxy	1 year	-2
$Ar/C_2H_6(50/50)$	None	$4x10^4$	0.02	10 kV/cm	Metal		Deposits only on anode (silicon)	-3
$Ar/C_2H_6(50/50)$	G.L., D.C., S.C.	10^4 - $2x10^5$	0.02	50 μm	50 m PVC + Cu	SS, Mylar polyethylene & silicone oil & vacuum grease	Silicon on anode; 2 years	-4
$Ar/C_2H_6(60/40)$ + 0.1% iC_3H_7OH	None	"	0.01-0.02	"	"		2 years	-4
$Ar/C_2H_6(50/50)$	S.C.	$2x10^5$	0.05	75 μm	>100 m Cu	Al-Mylar, G10, RTV, epoxy		-5
$Ar/C_2H_6(50/50)$ + 1.5% C_2H_5OH	G.L.	$2x10^5$	0.3	75 μm	>100 m Cu	Al, Mylar, G10, RTV, epoxy	Rate-related efficiency due to anode deposits	-5
$Ar/C_2H_6(50/50)$ +2% C_2H_5OH	G.L.	$5x10^4$	0.2-0.4	18-20 $\frac{kV}{cm}$	70m Cu 10m"non-PVC"	vacuum oil, Al, epoxy	5 years; oil found in gas; no aging after gas filter added.	-6

Table II, continued

Gas	Aging Observed[1]	Gain	Charge (C/cm)	Cathode Field or Wire Diam.	Plumbing[2]	Other Materials[2]	Running Time or Other Information	Ref.
$Ar/C_2H_6(50/50)$ +0.3% C_2H_5OH	None	$4\text{-}8\times10^4$	0.035 - 0.04	10-15 $\frac{kV}{cm}$	30m Cu	G10, Delrin epoxies, Al-Mylar Teflon, vacuum grease	Also Viton O-rings. Vertex detector. 1.5 yrs. Stablohm 800 anode wire (40μm diam.)	-7
$Ar/CH_4(80/20)$	S.C.	2×10^5	0.03	100 μm		Plastic insulation including phthalates	8.5 Atm. pressure. Failure after 3.5 months Deposits in both electrodes	-8
$Ar/CH_4/H_2$ (79.5/19.5/1)	G.L.	?	0.25	100 μm		Mylar, Aclar	Silicon on anode. Failure after 100 days	-3
$Ar/CH_4/iC_4H_{10}$ (88.5/8.9/2.6)	G.L.	$3\text{-}4\times10^4$	0.02	0.94 $\frac{kV}{cm}$	50 m steel, Cu	G10, cables; Rohacell	4 bar pressure, sealed; 300-1000 ppm H_2O 6 years	-9
$Ar/CO_2(95/5)$	None	?	0.22	35 kV/cm	70m Cu, non-PVC plastic	O-rings	3 bar pressure vertex detector	-10
$Ar/CO_2/CH_4$ (89/10/1)	None	7×10^4	0.01	20-26 $\frac{kV}{cm}$	90 m Cu	SS, glass, brass, Teflon, Kapton	1.15 bar pressure; no oils or greases; vertex detector	-11
$Ar/CO_2/CH_4$ (49.5/49.5/1)	None	3×10^6	0.025	1.6 $\frac{kV}{cm}$	Polyethlene	Al-Mylar, Delrin epoxy, Teflon, Lucite, vac. grease	Straw chamber, vertex detector, 4 Atm., 2 years	-12
$Ar/CO_2/CF_3Br$ (65/35/0.5)	G.L.	10^4	0.1-0.2	6.7 $\frac{kV}{cm}$	PVC, polyethylene	Al-Mylar, RTV	Silicon on both electrodes; research grade gas; flourine on cathode foil. MWPC, $(\Delta G/G)\sim-10\%$ at 0.4 -4.0 mC/cm	-13

Table II, continued

Gas	Aging Observed[1]	Gain	Charge (C/cm)	Cathode Field or Wire Diam.	Plumbing[2]	Other Materials[2]	Running Time or Other Information	Ref.
$Ar/iC_4H_{10}/iC_3H_7OH$ (65/35/1.5)	None	$6x10^4$	>0.03	(planar; low field)	50 m Cu 10 m Rilsan	Mylar, epoxy	3-year; No deposits on anode wires, MWPC	-14
Ar/iC_4H_{10}/methylal (53/40/7)	G.L.	10^5	0.3	4.4 $\frac{kV}{cm}$	60 m SS 25 m Rilsan	epoxy, Polyfoam	4 years; MWPC; ~1μm anode deposit	-14
Ar/iC_4H_{10}/methylal (75/20/5)	None	$3x10^4$	0.2	5 $\frac{kV}{cm}$		epoxy, G10 paraffin, resin, beeswax	2 years; soft urethane adhesive covered up with 5-min. epoxy: now OK.	-2
Ar/iC_4H_{10}/Methylal/ CF_3Br(66/30/4/0.25)	G.L.	10^8	0.2	1.5 $\frac{kV}{cm}$		Al	Straw tubes, SS anode, vertex detector	-15
C_3H_8/methylal (97/3)	G.L., D.C.		0.008				Dark current cured by adding H_20(2000 ppm) or oxygen filter.	-16

[1] G.L. = Gain Loss; D.C. = Dark Current (excessive); S.C. = Self Sustained Current (Malter Discharge), N.C. = No Change in gain.
[2] PVC = polyvinyl chloride (Tygon or equivalent); SS = stainless steel ; Cu = copper, Polyfoam = polymethacrylimide; Rilsan = Nylon = polyamide 11, RTV = silicone-based Room Temperature Vulcanizate. Also see Table I for list of names and compostions of commonly used plastics.

All of these gases probably incur aging problems at some level of collected charge, though they may not have reached that level in the reported results, which is never greater than a few tenths C/cm. We see that in certain cases a dark current breakdown has occurred at a low level of collected charge, and the chamber has been restored to normal operation by the addition of a small amount of an alcohol, such as ethanol, or of water vapor. A combination which works very well (with gold-plated wire) is $Ar/C_2H_6(50/50)$ with ~1.5% of ethanol added, by bubbling the gas through the ethanol at 0°C [23].

It has been known for some time that alcohols, methylal, and certain other compounds containing oxygen are effective in suppressing or stopping polymerization. Yasuda, in his discussion of polymer growth, illustrates the blocking of one mechanism of chain growth by water, and states that "...most organic compounds with oxygen-containing groups, such as -COOH, -CO-, -OCO-, -OH, and -O-, are generally reluctant to form a polymer, ..."[43] Alcohols also are good quenchers, and thereby serve a dual purpose. However, ethanol as an additive is shown to produce a very rapid gain loss when Stablohm* is used for the anode wire [1,4,5] (see further discussion in II.C.4.). A fraction of a percent to a few percent of alcohol is usually considered optimal; a higher concentration will affect the drift velocity of electrons. The other useful and convenient "additive" is water vapor: a very small quantity can be used to help stop or reduce aging phenomena or even restore to useful operation chambers which have been damaged by aging; ~few hundred ppm to ~few thousand ppm of water vapor is generally used (some results are also listed in Table III). Water is effective in preventing the occurrence of large dark currents associated with Malter-type breakdown, but it is also very effective in restoring wire chamber operation after these problems have occurred [24-29]. The mechanism for the recuperative effects of water is not understood, but it may be that some electrical conductivity of the water aids in discharging electrical charges that have built up on thin insulating films on the cathode. In addition, the water can help in the quenching process since it is effective in absorbing x-rays.

It is noted that of the 21 entries listed in Table II, nine experienced no symptoms of aging, and these either had no PVC and no silicones present, or used alcohol or methylal to suppress aging, or both. Of the 12 experiments which had serious aging problems, ten reported some of the materials used in the gas system, and seven of these had materials believed to cause aging (PVC, RTV, vacuum grease, cable insulation), while one used G10, which may have had mold release agent on its surface. In one case [44], soft urethane adhesive was directly implicated in aging, since the problems disappeared when the urethane was simply covered over with a layer of "five-minute" epoxy (which gives some endorsement for the safety of this type of epoxy).

Another point to be observed in Table II is that in experiments which incurred problems, a reduction or elimination of their problems would nearly always result from adding a very small amount of alcohol, water or methylal. Table II might be summarized by saying that collected charge levels as high as 0.3-0.4 C/cm were reached with several gas mixtures, providing that certain materials were avoided (PVC, RTV, etc.) and that some additive known to reduce effects of aging was present.

C.3. Rejuvenation of Damaged Chambers

As we have discussed in section C.2., certain additives to the gas can be very effective in extending the lifetime of a radiation damaged wire chamber. Attempts have also been partially or completely successful, at times, in repairing the coated wires in chambers by mechanical or chemical means. Methods used have been actually wiping or scrubbing the wires, or using a very good solvent (e.g. acetone). Unfortunately, most polymeric deposits are highly branched and cross-linked, rendering them mechanically quite robust, with excellent adhesion to the substrate (wire)[37] (see also Yasuda, bibliography). This same structure causes them to be

* Stablohm is a resistive, non-gold-plated wire: see Glossary.

generally insoluble and resistant to chemical attack. These properties make the deposits difficult to remove even from chambers with relatively few wires, and all but impossible from larger chambers. For this reason, the emphasis here is the prevention rather than the cure of aging problems. However, there are at least two other methods of rejuvenation worth mentioning: removal of deposits by (a) heating, or (b) ablation. An example of the former method is the heating of small diameter carbon fiber anode filaments by electric current, driving off a liquid deposit that had formed by polymerization involving TMAE [45] (see section E.5). It is not known whether this technique works in the case of solid deposits. The concept of ablation refers to removal of deposits either through sputtering by heavy ions (e.g. Ar^+) in the plasma or by etching, i.e. chemical reaction with plasma species. If the coated wire is made electrically negative and a discharge is initiated, ions will be attracted to the wire and the physical bombardment by energetic ions can wear away the deposit by sputtering ("erosion" by momentum transfer processes), particularly at high points on the wire ("whiskers") where the electric field is more intense. There is no known case of this method having been tried on a large wire chamber. However, the etching technique has been successful in laboratory tests [46]. By creating a discharge, it was possible to grow filaments (whiskers) from a cathode wire with gas mixtures of Ar/C_2H_6 or Ar/CH_4, but when Ar/CO_2 was substituted, the whiskers were etched away, presumably by the chemical action of oxygen released from the CO_2 in the plasma discharge at the tip of the whiskers (see Section C.4. for a discussion of etching by CF_4 gas component).

Some of these techniques could be important for helping to maintain operation, but little is known about the practical aspects of how to keep operational a large wire chamber system based upon any of these ideas. Therefore, as we stated above, the emphasis here will be always on <u>prevention</u> of wire aging.

C.4. Results from Laboratory Tests

In Table III are collected results from many accelerated aging tests done on small test chambers or proportional tubes. It is not feasible to publish all known test results, and so certain tests are chosen which appear to be representative of classes of gas mixtures and other operating conditions. The selection of test results for Table III places emphasis on more recent results. These tests are intended to determine the aging robustness of a well-defined set of operating parameters using some source of radiation much more intense than would be encountered in beam-line experiment in order to shorten the time interval over which aging will occur. Usually the source of radiation is a radioactive isotope (e.g. Fe^{55}, Sr^{90}, or Ru^{106}) or an x-ray generator. The anode wire current is usually monitored over the time period of the test, and the assumption is usually made that the gain is proportional to the current. Thus, a current decrease is interpreted as a corresponding decrease in gain. Another commonly used method of monitoring gain is the measurement of the peak in a pulse height spectrum using, e.g., a Fe^{55} source. Tests are done in a period ranging from a few days to a few weeks, and the implicit assumption is that the observed aging effects depend only on the total amount of radiation, and not upon the rate at which the dose is administered. The degree to which this assumption is true has not been well tested, and there are some results indicating that a given radiation dose delivered over longer time periods causes more severe aging [47]. Nevertheless, with this caveat in mind, we will still find it useful and relevant to study accelerated aging tests as a help in designing detectors for an experiment. It must be realized that these tests are done under much more ideal conditions of purity than would normally exist in an experiment, but there is the hope and expectation that similar conditions of purity can be attained in the experiment by identifying and suppressing contaminants that do affect aging. We now explain the meaning of quantities tabulated in the columns of Table III. As was done in Table II, gas mixtures are listed in groups of the same or similar mixtures, starting with argon-based gases and proceeding to increasingly smaller argon content, to argon-free mixtures. The tests are aimed primarily towards achieving resistance to gain loss, and so the parameterization chosen is:

$$R = -\frac{1}{G}\frac{dG}{dQ} \text{ (\% per Coulomb/cm)}, \qquad (3)$$

where G is the gas gain, dG is the loss of gas gain over the period of testing, and dQ is the corresponding charge collected per unit length. Values of **R** listed in Table III range from very small values (<10%/C/cm) to very large values (**R** $>10^6$%/C/cm). By this author's classification, the various levels of aging are described as : **R** < 10 "negligible"; **R** = 10-100, "moderate"; **R** = 100-500, "large; **R** > 500, "extremely rapid".

Here the implicit assumption is that for a given set of operating conditions, the fractional gain loss is linearly related to the charge collected per unit length of wire, which in turn is proportional to the radiation dose per unit length. This assumption appears to be at least approximately true for a small enough gain decrease. The third column lists the amount of collected charge per cm of anode wire, and measures the product of gas gain and the integrated radiation dose on the wire. The initial gas gain is given in the fourth column; this is, in principle, the number of electrons collected by the anode for a single electron-ion pair produced in the gas (outside the avalanche region). This usually is a very approximate value, and although the parameter **R** has been found to depend upon gain, decreasing as gain increases, it is not so strong a dependence that the gain must be very accurately known. If the aging includes effects other than just loss of gain (e.g. electrical discharge) these will also be listed in this column. Dark current or Malter-type phenomena are not normally seen in these tests since conditions have been chosen to avoid these phenomena. The intensity of radiation multiplied by gain determines the current per cm given in the next column. Finally, the anode surface material can have an important influence on the wire aging : any gold-plated wire is chemically inert (if, as is not always true, the plating completely covers the surface), but this may not be true of other wire surfaces, and some show rapid aging in the same environment where a gold plated wire shows no ill effects [1,4,5]. Not given is the flow rate, for the same reasons as for Table II: 1) It has a significant but not large effect on aging, and 2) it is not possible with the information available to parameterize the gas flow in a way to make a valid scale for all the tests. The effect of gas flow rate will be discussed below and some examples given in Table IV.

It will be immediately apparent from Table III that the tests are taken to much higher radiation dosage, as measured by charge, than is the case for the entries in Table II, and frequently without large aging effects. This can probably be ascribed to the more carefully controlled purity of the environment, though, as discussed above, the dose rate may be factor. Gain loss is seen to be quite small, $\lesssim$30%/C/cm, for a large number of tests, including many using gases without any additives: Ar/C_2H_6, Ar/CH_4, $Ar/CO_2/CH_4$, CF_4/iC_4H_{10} and dimethyl ether. It is noteworthy that there are also some other results listed giving poorer values for **R** with these same gas mixtures. These differences are not random or statistical in nature, but are due to differences in the conditions, most likely the presence or absence of certain trace constituents (contaminants) in the gas during testing. Fig. 3 exhibits results from several wire aging tests using different gases and wires.

Frequently, it is seen (also in Table II) that, when gold plated wire is used, the addition of small (~1%) concentrations of alcohols (ethanol, isopropanol) to a gas that is associated with aging will eliminate or substantially reduce the rate of gain loss (see also Section C.2.). Water vapor (100-1000 ppm) seems also to be effective in this regard, although not so much as alcohols, but it is quite effective in suppressing electrical discharges, as was discussed earlier (section II C.2).

Table III. Results From Laboratory Tests

Gas	Approx. Gain Loss or Other Changes[1] - (1/G)dG/dQ (%/C/cm)	Approx. Collected Charge (C/cm)	Approx. Gain	Approx Anode Current Density (μA/cm)	Anode Wire Surface Material[2]	Reference
$Ar/CH_4/CO_2$ (93/4/3)	~25	1.9	10^7	~2	Au	III-1
Ar/CO_2CH_4 (89/10/1)	~170	0.3	10^7	~2	Au	-1
$Ar/CO_2/CH_4$ (89/10/1) (w/ and w/o) 0.7% H_2O	80-200	0.3	$2x10^5$	~1	Au	-2
$Ar/CO_2/CH_4$ (89/10/1 high purity Ar)	~15	0.5	20,000	0.6	Au	-3
Ar/CH_4 (80/20)	~40	0.2	20,000	0.6	Au	-3
Ar/CH_4 (80/20) (Matheson grade Ar)	<10	0.2	20,000	0.6	Au	-3
$Ar/iC_4H_{10}/CF_3Br$ (74.5/25/0.5) +~4% Methylal ("Magic Gas")	N.C.	0.3	10^7	(?)	Au	-4
Ar/C_2H_6 (60/40)	N.C.	0.1	10^6	(?)	Au	-4
Ar/C_2H_6 (50/50)	~60	0.3	50,000	~1	Au	-2
Ar/C_2H_6 (50/50) +0.5% C_2H_5OH	NC	1.5	50,000	0.44	Au	-5
Ar/C_2H_6 (50/50) (w/and w/o 0.7% H_2O)	<12	0.3	$2x10^5$	~1	Au	-2
Ar/C_2H_6 (50/50) +1.4% C_2H_5OH	<10	0.5	20,000	0.6	Au	-3
Ar/C_2H_6 (50/50) +1.4% C_2H_5OH	~1000	0.04	20,000	0.6	Stablohm	-3

Gas	Approx. Gain Loss or Other Changes[1] - (1/G)dG/dQ (%/C/cm)	Approx. Collected Charge (C/cm)	Approx. Gain	Approx Anode Current Density (μA/cm)	Anode Wire Surface Material[2]	Reference
CO_2/iC_4H_{10} (92/8)	S.C.	0.15-0.4	$2x10^5$	0.26	Au	III-6
DME (high purity)	<20	0.5	$\sim 10^5$	0.6	Au	-3
DME	(small)	4.0	(?)	~5	Au	-7
DME	(small)	1.0	(?)	~3	Au	-8
DME	<5	2.0	10^8	~2	Au	-9
(New results, since January 1986, follow)						
DME(pure)[3]	10,000	0.01	10^3	1.0	Nicotin	-10
DME(pure)[3]	N.C.	0.4	10^3	1.0	Stainless steel	-10
DME(pure)[3]	N.C.	0.9	10^3	1.0	Au	-10
DME (pure, filtered)[3]	500	0.04	10^3	1.0	Stablohm	-10
DME (pure, filtered)[3]	N.C.	0.8	10^3	1.0	Stainless steel	-10
DME (pure, filtered)[3]	N.C.	1.0	10^3	1.0	Au	-10
DME	N.C.[4]	1.0	$4x10^5$	0.4	Au	-11
DME (pure), stainless steel tubing	~80	0.3	$5x10^4$	0.6	Au	-12
	~170	0.1	$5x10^4$	0.6	Stablohm	-12
DME, Semiconductor Grade[5], all inert metal plumbing, epoxy seals	11	0.6	$5x10^4$	0.4	Stablohm	-12
	4	0.6	$5x10^4$	0.4	Nicotin	-12
$Ar/CO_2/CH_4$ (89/10/1)	~2	0.3	20,000	0.6	Au	-12
$Ar/CO_2/CH_4$ (89/10/1)	~100	0.5	20,000	0.6	Stablohm	-12

Gas	Approx. Gain Loss or Other Changes[1] - (1/G)dG/dQ (%/C/cm)	Approx. Collected Charge (C/cm)	Approx. Gain	Approx Anode Current Density (μA/cm)	Anode Wire Surface Material[2]	Reference
$Ar/C_2/H_6$ (50/50) Matheson grade[6] (Nylon plumbing)	<5	0.3	20,000	0.6	Au	III-13
$Ar/C_2/H_6$ (polyethylene plumbing)	~12	0.3	20,000	0.6	Au	-13
$Ar/C_2/H_6$ (PVC plumbing)	~5	0.3	20,000	S.C. on Subsequent Tests	Au	-13
Ar/C_2H_6 (50/50) +0.25% iC_3H_7OH	4	1.0	$\sim 2x10^4$	0.7	Stablohm	-14
Ar/C_2H_6 (50/50) +0.7% iC_3H_7OH Matheson and PREP Grades Ar[6]	<10	0.4	$2x10^4$	0.6	Stablohm	-13
Ar/C_2H_6 (50/50) (HP grade Ar)	<5	2.0	20,000	0.6	Au	-12
Ar/C_2H_6 (50/50) (Matheson Grade Ar, "slow" aging test)	12	0.5	20,000	0.13	Au	-15
Ar/CO_2 (80/20)	~0 ~0	1.0 0.06	$1.4x10^5$ 6500	0.6 0.03	Au Au	-16 -16
Ar/CO_2 (60/40)	4	1.0	$2x10^5$	0.85	Au	-16
$Ar/C_2/H_6$ (50/50) +0.2% H_2O +0.4% H_2O (at 3 Atm. pressure)	S.C. S.C. S.C.	0.07 >1.0 >0.8	$\sim 6x10^4$	0.3	Au	-17

Gas	Approx. Gain Loss or Other Changes[1] - (1/G)dG/dQ (%/C/cm)	Approx. Collected Charge (C/cm)	Approx. Gain	Approx Anode Current Density (μA/cm)	Anode Wire Surface Material[2]	Reference
$Ar/C_2/H_6$ (50/50)	D.C.	6.0	10^6	1.4	Au	III-18
	D.C.	7.2	$3x10^5$	1.4	Au	-18
(G10 Chambers)	0±1	1.5	$3x10^5$	0.4	Au	-18
	4-7	6.5	$5x10^4$	1.4	Au	-18
	10	2-3	$5x10^4$	0.3	Au	-18
$Ar/C_2H_6/CF_4$ (48/48/4)	D.C.	4	$5x10^4$	0.25	Au	-18
	<5	1.7	$5x10^4$	0.17	Au	-18
CF_4/iC_4H_{10} (80/20)	0 ± .2	4.2	$7x10^5$	1.4	Au	-18
	<5	8.0	$5x10^4$	1.2	Au	-18
	<2	1.2	$2x10^4$	0.3	Au	-18
CF_4/iC_4H_{10} (80/20) 4mm Diam.	10	0.2	$5x10^4$	0.6	Au	-12
CF_4/DME (90/10) Straw Tube	3	0.7	$5x10^4$	0.6	Au	-12
C_3H_8 + 0.2% H_2O or OXISORB filter	100	0.2	10^4	0.02	Au	-19
Ar/C_2H_6 (50/50) HP Grade Ar[6] +						
Silicone Oil	50	0.15				
Mineral Oil	2	0.15	$2x10^4$	0.6	Au	-12
Mech. Pump Oil (bubbled into test chamber)	1	0.18				
Silicone Oil (Dow 704)	43	0.4	$2x10^4$	1.2	Au	-12
RTV (GE,108)	~100	0.1	$4x10^4$	1.5	Au	-12

Gas	Approx. Gain Loss or Other Changes[1] - (1/G)dG/dQ (%/C/cm)	Approx. Collected Charge (C/cm)	Approx. Gain	Approx Anode Current Density (μA/cm)	Anode Wire Surface Material[2]	Reference
Ar/C_2H_6 (50/50) + 530 ppm CH_3Cl	7 (periodic break-down)	0.4	$2x10^4$	0.6	Au	III-12
Ar/C_2H_6						
+ 1000 ppm O_2	14	0.3	$2x10^4$	0.6	Au	-12
+ 3000 ppm	2	0.2	$2x10^4$	0.6	Au	-12
Ar/C_2H_6 (50/50) +1000 ppm H_2O (4mm diam. straw tube)	~30	0.4	$5x10^4$	0.6	Au	-12
Ar/C_2H_6 (60/40) + ~1 ppb TMPD[7]	180	0.3	10^5	0.05	Ni/Cr	-20
CO_2/C_2H_6(95/5)	46	0.1	$5x10^4$	0.3	Stainless Steel	-12
"	36	0.4	$5x10^4$	0.3	Nicotin	-12
+0.5% iC_3H_7OH	97	0.08	$5x10^4$	0.3	Stainless Steel	-12
"	102	0.3	$5x10^4$	0.3	Nicotin	-12
CO_2/iC_3H_7OH (98/2)	120	0.12	10^5	0.04	Au	-21
CO_2/iC_4H_{10} (92/8)	S.C.	0.035				
$CO_2/iC_4H_{10}/iC_3H_7OH$ (90/8/2)	5	0.9				
$CO_2/iC_4H_{10}/H_2O$ (92/8/0.66)	6	0.5				
CO_2/C_2H_6 (92/8)	150	0.03 (D.C.)	$\sim 10^5$	~1.0	Au	-21
+ 1% C_3H_7OH	8	0.4				
+ 0.66% H_2O	77	0.7				
$Ar/CF_4/O_2$ (50/40/10)	130,000	$0.5x10^{-3}$	$2x10^4$	0.6	Au	-12

Gas	Approx. Gain Loss or Other Changes[1] - (1/G)dG/dQ (%/C/cm)	Approx. Collected Charge (C/cm)	Approx. Gain	Approx Anode Current Density (μA/cm)	Anode Wire Surface Material[2]	Reference
$Ar/C_2H_6/NH_3$ (49.5/49.5/1)	6670	0.03	$2x10^4$	0.6	Au	III-12
CH_4 + ~0.1% TMAE[8]	$1.3x10^6$	$0.1x10^{-3}$	$2x10^5$	0.4	carbon (7μm diam.)	-22
CH_4	NC	1.0	(?)	(?)	(?)	-23

1 G.L. = Gain Loss; D.C. = Dark Current (excessive); S.C. = Self Sustained Current (Malter Discharge), N.C. = No Change in Gain.
2 The composition of Stablohm and Nicotin are given in the Glossary. Au stands for gold-plated wire (usually gold-plated tungsten).
3 For description of purity levels and method of filtering, see reference III-13.
4 A substantial wire diameter increase was observed even though there was no gain loss.
5 A very pure grade, obtained from Matheson Gas Produces, Newark, California. The plumbing system in this test consisted only of electropolished stainless steel and a few cm of copper (no plastics).
6 Gases obtained from Matheson Gas Products. There are several grades of argon available. Grades used here are (highest to lowest purity): Matheson grade, Ultra High Purity (UHP), Prepurified (PREP), and High Purity (HP).
7 TMPD: [Tetra-Methyl-Phenylene-Diamine].
8 TMAE: Tetrakis - (Dimethylamino) - Ethylene, a compound with a low photoionization potential, 5.4 eV.

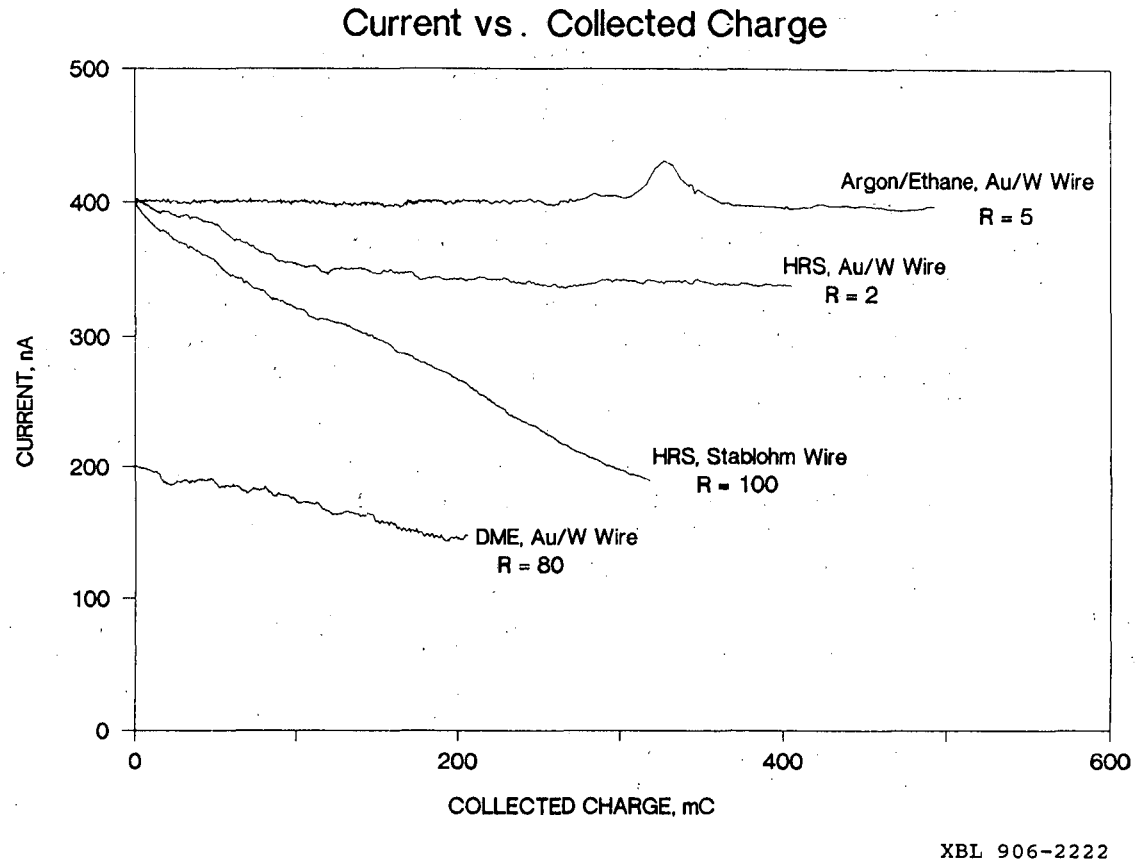

Fig. 3. Plots of current vs. collected charge for argon/ethane (50/50), HRS gas (89% Ar + 10% CO_2 + 1% CH_4), and dimethyl ether. Two types of anode wire were used with the HRS gas. Plastic tubing was used for gas plumbing in the DME test. Values of the aging rate, R = -(1/G)(dG/dQ)%/C/cm are marked on the corresponding plots. Charge was collected on about 6 mm of wire [66].

However, ethanol and water as additives in an argon/ethane mixture using a resistive wire, Stablohm, results in very rapid gain loss. Subsequent investigations indicate that this also happens when methanol or water is used, but not when isopropanol is used [4,5]. This curious behavior may be explained by oxidation of certain active elements in the Stablohm (e.g. aluminum) due to free oxygen bonds in fragments of ethanol molecules produced in the avalanche; isopropanol is thought to break up differently than ethanol in such a way that free oxygen bonds are not produced (see section II.F.)[4,5]. In support of this interpretation is the fact that gases having oxygen as part of a primary constituent, such as Ar/CO_2 and $Ar/CO_2/CH_4$, have relatively poorer aging properties when used with Stablohm wire [4].

In certain cases there is a demonstrated positive correlation between levels of gas purity and stability of gain[4]. Measurements of Freon levels in dimethyl ether were well correlated with the value of **R**, and it required only concentration levels of parts per million to give significant effects [4, 41, 48]. It is important to be aware that effects resulting in gain loss due to the extraordinarily large electronegativity of certain contaminants (e.g. Freon 11), can easily be taken for aging, as some recent tests have indicated [49]. In particular, the current decrease observed during a wire chamber test can also be caused by increasing concentrations of electronegative gas contaminants, such as Freon 11, in the DME gas stream. This may be the natural consequence of "fractional distillation" from the gas cylinder where both the DME and contaminant (e.g. Freon 11) are liquids (under pressure), but the contaminant has a higher

boiling point. Several tests using dimethyl ether (DME) exhibit low aging rates; other tests have identified several wire chamber and plumbing materials incompatible with dimethyl ether: see Tables I, X, Appendix A, and references 41 and 48 for more detailed information. It will be seen that there are some conflicting results with respect to aging rates of the resistive wires Nicotin and Stablohm in DME, but stainless steel wire seems to be resistant to aging in DME as well as in other gases containing oxygen.

The use of gases having CF_4 as a component appears to result in little or no aging at the level of relatively large collected charge densities and without taking special precautions to guard against contaminations. It has also been shown [50, 51] that the electron drift velocities for gases containing CF_4 are very high (>10 cm/μsec), and the diffusion constant is low [52]: these properties makes this an attractive candidate for a drift chamber gas in future experiments at high luminosity colliding beam machines (e.g. the SSC). Tests seem to show that these latter two properties still are present with a relatively small fraction of CF_4 (e.g. 10% CF_4+90% CH_4) [51], but the radiation resistance of these more dilute mixtures has yet to be determined conclusively. A recent result concerning CF_4 gas mixtures comes from the group at TRIUMF [53]. Wires which had aged in an argon/ethane gas mixture, and which were found to be coated, using an electron microscope (SEM), were subsequently etched nearly clean when irradiated in a CF_4/isobutane gas mixture. The gain returned to normal, and only extremely thin residual coating could be observed under reduced SEM voltage (5kV). A confirmation of this result was obtained by the present author [III-15]: a wire previously aged by bubbling argon/ethane through silicone oil (see table III) was subsequently restored to full gain by using CF_4/isobutane (80/20) during a subsequent irradiation. The result of this test is shown in Fig. 4, where the wire current is plotted vs. collected charge. The current is seen to rise erratically as the deposits are etched away until a condition of full gain is achieved as indicated by the constant current value at the end of the test.

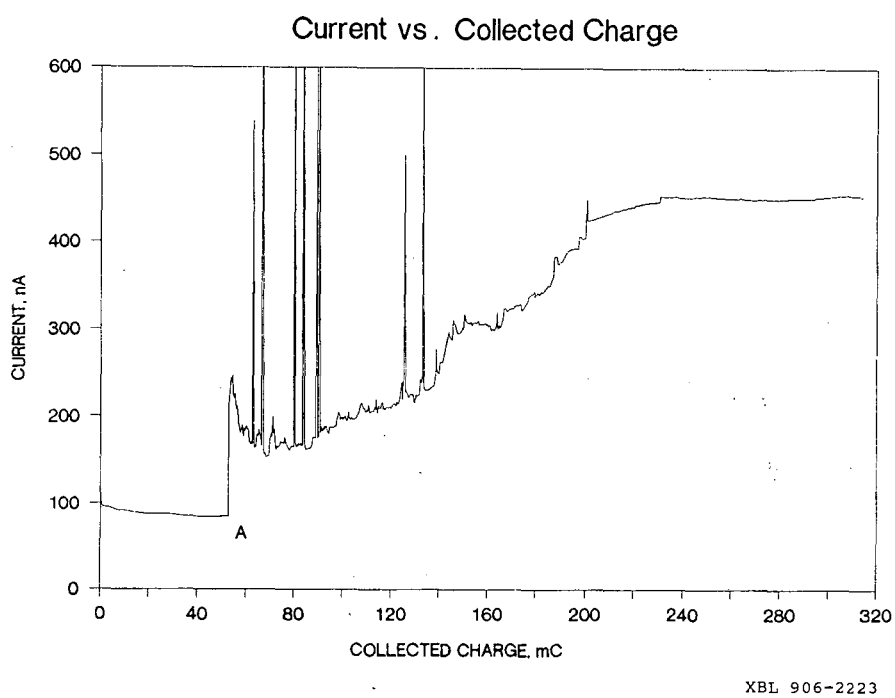

Fig. 4. Aging plot (current vs. charge) using CF_4/iC_4H_{10} (80/20) gas with an anode wire previously aged by bubbling argon/ethane gas through silicone oil during irradiation [Table III, III-12]. The gain is seen to increase until the full initial gain is achieved and discharges cease. The voltage was increased at A, to achieve higher current; then it was held constant [III-15].

D. Dependence of Wire Aging on Certain Physical Parameters

D.1. Gain

The rate of gain loss per Coulomb/cm, **R**, has been found to depend upon several parameters including the avalanche gain: as the gain and therefore current density is increased, the value of **R** decreases, other conditions being held constant. Several examples of this behavior can be found [4,25]. The effect, though not very large, is quite significant. In one set of test using Ar/C_2H_6, the value of **R** was halved when going from avalanche mode ($G \sim 2\text{-}6 \times 10^4$) to streamer mode ($G > 10^6$) [25]. One possible explanation is that the density of ions and radicals is decreased in the avalanche plasma for larger gains. This could be due to space charges causing local weakening of the field, thereby causing the avalanche to spread over a larger region. Since the polymerization rate should increase with the density of radicals, we would observe a decrease in the aging rate at higher gains when normalized to the charge transferred. Another possible mechanism however, is merely the local temperature rise in the avalanche, due to the electrical energy dissipated, resulting in suppression of condensation on the wire (i.e. coating) of non-volatile polymers, especially when operating at higher gains. A similar effect is seen in studies of plasma chemistry at low pressure, and is illustrated in Fig. 5 [54]. Here it can be seen that the deposition rate saturates with respect to power input. The interpretation in this case is an insufficient supply of monomers to produce deposits in the saturation region (see D.2.and D.3. below).

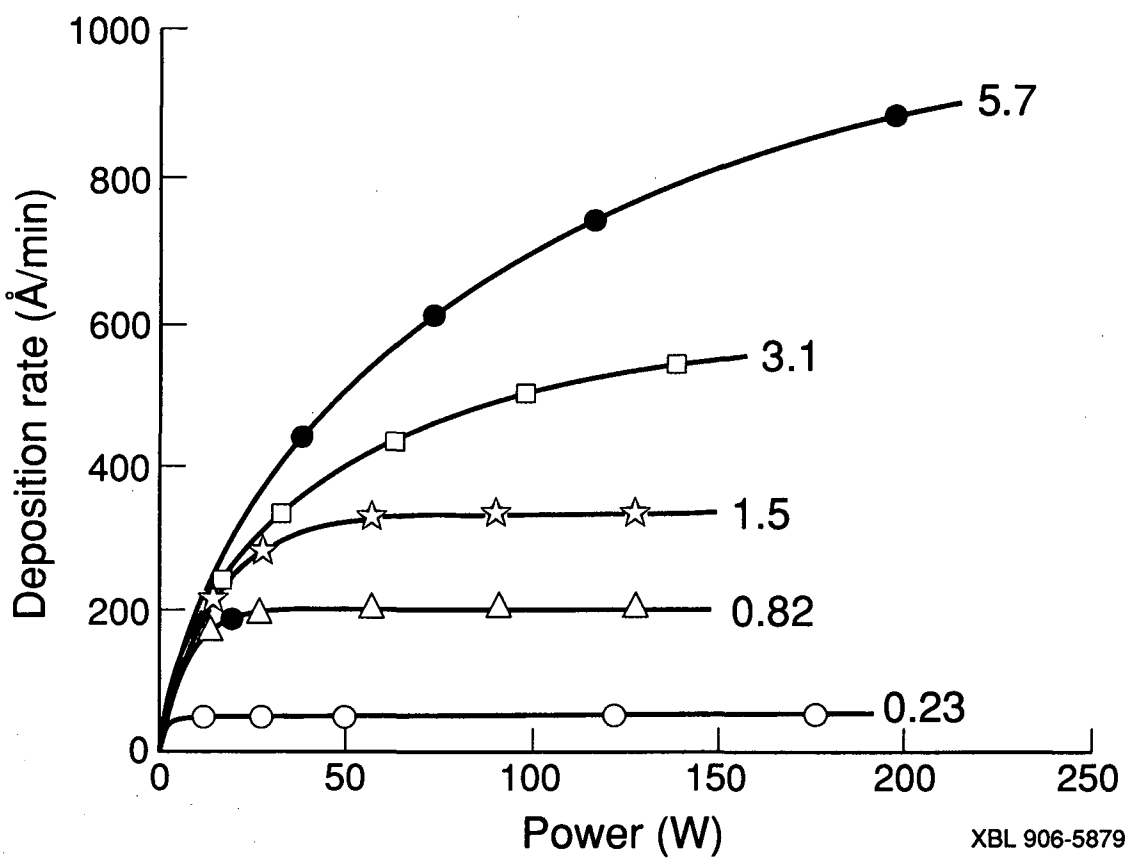

Fig. 5. Dependence of deposition rate of the plasma polymer of tetramethyldisiloxane on discharge wattage at the monomer flow rates as indicated on the plots (cubic centimeters per minute). These curves show that for a given flow rate, the deposition rate increases less rapidly than linearly with respect to power [54].

D.2. Gas Flow Rate

Conventional wisdom would say that aging would be lessened by increasing the gas flow, since this tends to sweep away the harmful radicals and ions that can result in wire coatings. However, this reasoning is not always correct, since it is also possible that the polymerization process is "fed" by some ingredient in the input flow stream (a monomer in the reaction, an impurity, etc.) which is the limiting factor in the plasma reaction. By increasing the flow, more of this ingredient is available to speed up the coating rate (see section II.B). Fig. 6 shows this behavior as observed at low pressure, in plasma chemistry studies, where the polymerization rate can either increase or decrease with gas flow rate [55]. In our regime of interest, wire chambers, there are some results which suggest that we are usually on the decreasing side of the curve: the aging rate decreases with increasing gas flow. This trend is not a large one [4,56, 57] except in the case of zero gas flow [56] as is seen in Table IV. In the limit of zero flow (sealed counters or chambers), there is a large increase in the rate of gain loss and examples of this are common in the early literature [16].

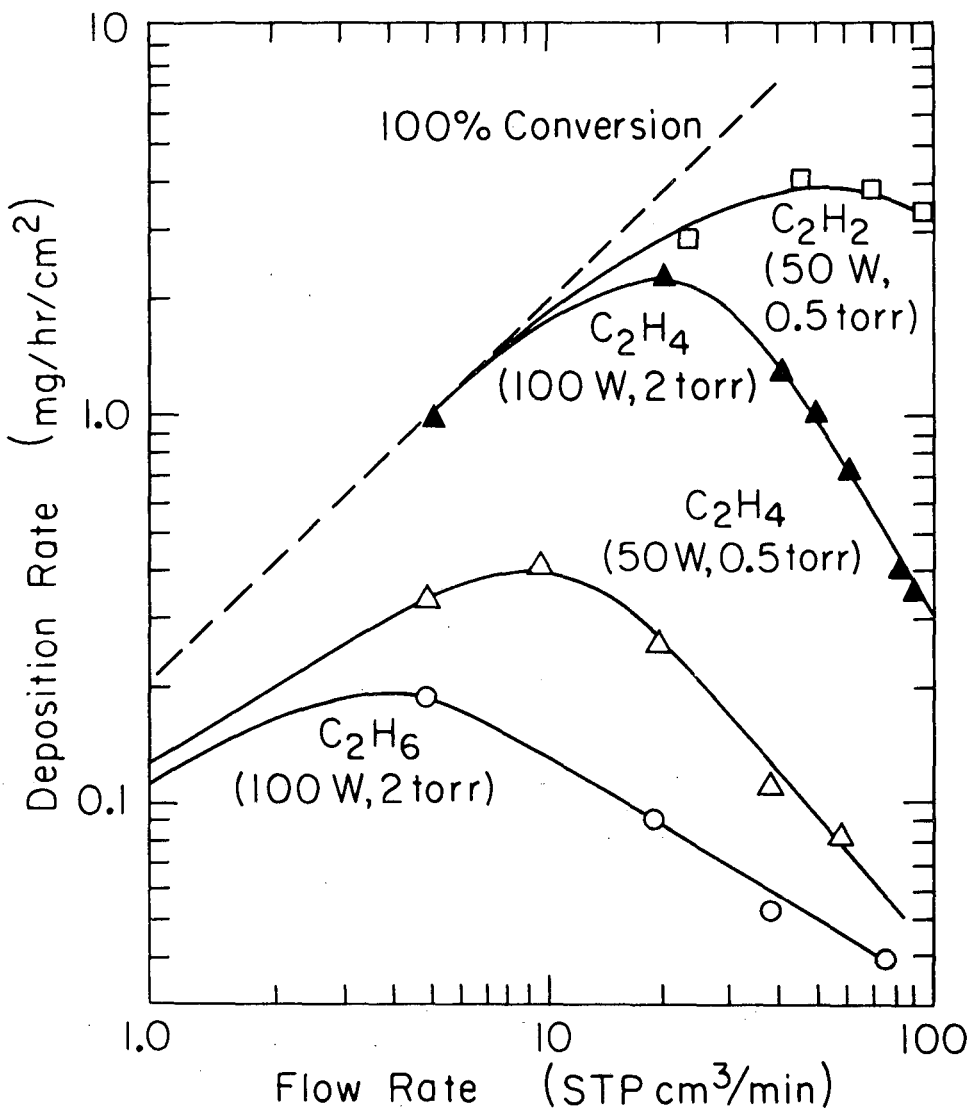

Fig. 6. Double logarithmic plot of rates of polymer deposition of ethane, acetylene and ethylene as a function of monomer flow rate [55].

Table IV. Gas Flow Rate Dependence of Wire Aging.[4,56,57] Values are for gain loss rate: $R = \frac{1}{G}\frac{dG}{dQ}$ (%/C/cm), where G is avalanche gain and $Q(\frac{\text{Coulombs}}{\text{cm}})$ is accumulated charge/cm. Flow velocity is the average gas velocity parallel to wire direction.

Gas Mixture	Wire	Flow Velocity (cm/sec)	R(%/C/cm)	Current Density (nA/cm)
$Ar/C_2H_6(50/50)$	Au/W	1.6	33	1130
	"	0.8	69	920
	Stablohm	2.1	90	1250
	"	0.4	237	1130
$Ar/C_2H_6/H_2(49.5/49.5/1)$	Stablohm	2.1	96	1350
		0.3	70	1280
$Ar/CH_4/CO_2(93/4/3)$	Au/W	1.0	22	670
		0.2	54	500
$Ar/C_2H_6(50/50)$	Au/W	0.5	4	250
		0.05	64	250
$Ar/C_2H_6(50/50)$ (3 Atmosphere Pressure)	Au/W	0.00	0.027 C/cm (SC breakdown)	300
no H_2O	Au/W	0.84	0.07	
	Au/W	0.00	0.026 C/cm	300
0.2% H_2O	Au/W	0.84	>1.0	

D.3. Gas Density

Although few wire chambers operate below 1 Atm. pressure, several have operated at higher pressures and some have experienced aging effects, [26,37] while other have not [28,58,59]. There appears to be no obvious correlation between pressure and aging effects. In the conventional view of the avalanche, the higher pressure implies a smaller energy of electrons (~E/p) due to reduced mean free path, but a larger concentration of molecules, from which radicals are produced. These two effects operate in opposite directions on reaction rates, and there are many other effects, so one cannot make any straightforward predictions. For the few cases studied, there is no clear pressure (density) behavior. There is some evidence for temperature effects, insofar as these may be independent of density effects. There are some tests which indicate that the aging rate is lower at higher temperatures [60]. This result is consistent with a model explaining the reduction in aging at high gains as an effect due to increased heating of the avalanche plasma at the higher gains. In section D.1. above, an example from plasma chemistry was given which could be interpreted as this same heating mechanism. A more direct example of temperature dependence is shown in Fig. 7, where the polymerization rate of C_2F_4 can be seen to drop abruptly as the temperature increases [61].

D.4. Radiation Intensity

There is some evidence, as yet unconfirmed, that R is a function of radiation intensity (dose rate) other factors being keep fixed, and that R is larger for smaller radiation intensities. This is a point that needs investigation, both qualitatively and quantitatively, since it is the implicit assumption in the parameterization, R, that aging rates in experiments can be predicted using the measured value of R from laboratory tests conducted at much higher radiation intensities than in actual experiments. It is not an especially difficult investigation to make, but requires some patience to accumulate enough charge on the low intensity tests, and some care in

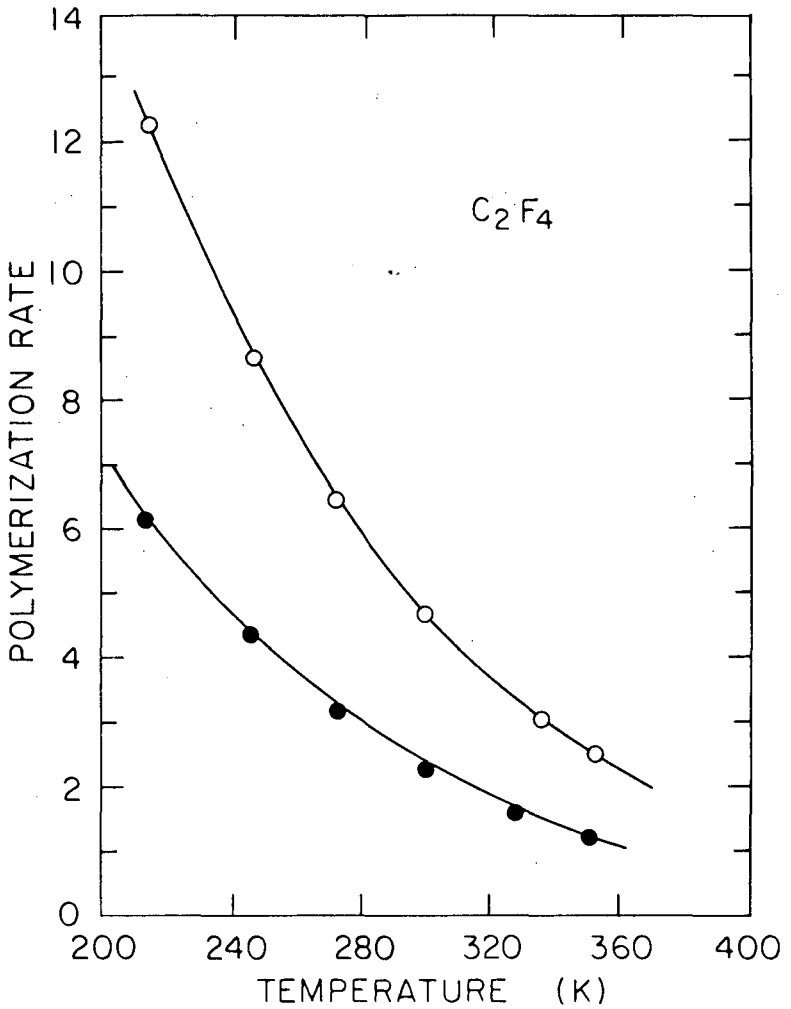

Fig. 7. Temperature dependence of polymerization rate for tetrafluoroethylene monomer, C_2F_4. Power levels of 9.8 and 4.9 watts are denoted by data points o and ●, respectively [61].

preventing variations in other factors from affecting the extended test run. There is not much reason to believe that such a dependence should exist, if at low and high intensities there is time for the plasma and gas to fully "recover", (i.e., come into equilibrium) between ionizing events. If this is not true, e.g., if space charge, gas heating or other plasma effects do not relax completely between events, then such a radiation intensity dependence may exist.

E. Observations and Analysis of Wire Deposits

The effects of certain materials on wire aging was discussed briefly in connection with Table II, where PVC, RTV, silicones, and chlorinated solvents were mentioned as agents thought to accelerate aging. The mechanisms or reactions that result in these substances as being the most harmful are not known. Several important facts have emerged, however, with regard to anode coatings: (1) Silicon has a phenomenal ability to end up in anode wire deposits, and is also found occasionally on the cathode; (2) phthalates, used as plasticizers in plastics, are also found on anode and sometimes on cathode wires; (3) sulfur and halogens are found on both anode and cathode wires, but the sulfur tends to concentrate on the anode, halogens on the cathode.

E.1. Methods of Analysis

There are many methods of surface analysis to determine elemental composition, or compounds in wire coatings, and we will briefly mention a few that have been widely used.

Scanning Electron Microscope/X-ray Emission Spectroscopy (SEM/XES)

Electron microscopy is used to examine the surface structure, while characteristic x-radiation induced by the electron beam can identify individual elements for $Z \gtrsim 11$. The depth probed is about 1 μm. The electrical conductivity of the structure at any point can also be probed, and this technique has shown many wire coatings to be insulators (see Section III.B.).

Auger Electron Spectroscopy/Ion Etching (AES)

Electron beams are used to excite Auger electron emission to depths of a few μm and give elemental composition. The spot diameter may be of the order of 10 μm. Used together with Ar ion sputtering, a depth profile of atomic composition may be obtained. Identification of elements of $Z \gtrsim 6$ is possible, and some information on molecular bonds is obtained.

Mass Spectrometry (MS)

Analysis is done in this case by heating a sample of wire to drive off vaporizable (non-crosslinked) components from the coating material (also called "pyrolysis"). This is done in a vacuum coupled to a mass spectrometer, and the temperature is increased in a programmed manner. The gases evolving from the wire coating are analyzed by the mass spectrometer to identify whole molecules and molecular fragments, a technique which complements the elemental analysis in Auger work.

A variety of other surface analysis techniques have also been used [62], and some of these are summarized in Table V.

Table V. Surface Analysis Techniques [63]
All techniques listed can detect chemical composition, but none can detect morphology

Technique	Detect Hydrogen	Detect Bonding	Analysis Depth	Etch Capability	Spot Diameter
MS	Y	Y	-	-	-
SIMS	Y	Y	10 Å	Y	50 μm-1 mm
AES	N	Y	50 Å	Y	50 μm
XRF	N	?	?	N	0.1-1 cm
XPS	N	Y	50 Å	N	0.1-1 cm
FTIR	Y	Y	-	N	-
LAMMA	Y	Y	5 μm	N	1 μm

E.2. Silicon Deposits

We began the discussion of wire coating with examples of hydrocarbon polymerization, because this mechanism is relatively well understood in the field of plasma chemistry. However, gases with very small (~1%) amounts of hydrocarbon gas [4,25,64], or none at all [39, 65] also have wire coatings. Indeed nearly everyone who has used analytic techniques to examine aged anode wires has found silicon in some form. One semi-quantitative study [39] of multiwire chamber deposits on anode wires has placed a lower limit on the number of silicon atoms deposited per avalanche electron collected (not per electron initiating the avalanche), and the result was $\gtrsim 0.008$: At least one silicon atom is deposited for ~100 electrons! This is an enormously high rate especially considering that the content of silicon in the gas was not more than 100 ppm, and more likely it was less than 10 ppm. This chamber did have potential sources of silicon: G10 frames (which might have had silicone mold-release on their surface), silicone rubber (RTV) seals, and a silicone oil bubbler. Recent laboratory test results [66], given in Table III, indicate that moderate aging is induced by bubbling an argon/ethane

chamber gas mixture through silicone oil directly upstream of the test chamber. However, the aging observed was due to a diffusion pump oil, having a stated vapor pressure of 1.4×10^{-8} Torr [40]; the corresponding concentration in the gas was only 18×10^{-12}!. The single-part RTV tested in a similar fashion resulted in aging at about twice the rate of silicone oil. Due to the high molecular weights of silicone polymers as compared to hydrocarbon polymers, the former are expected to be much less volatile, and therefore deposit more readily on wires. Clearly, silicone oils, greases and RTV's (single-part, at least) should be scrupulously excluded from contact with the chamber gas. (See also Section II.C.4. for a discussion of the ability of CF_4 gas mixtures to etch away silicone deposits).

E.3. Phthalates

Using mass spectrometry it has been possible to show that phthalates are found at least in one instance [37] on the anode, and to a lesser degree, on the cathode. As mentioned before, they are commonly added to plastics to render them pliable, and are very common in flexible gas tubing, such as PVC (Tygon) and electrical cable insulation. Dioctyl and dibutyl phthalates, in particular, have been detected in wire coatings, indicating that their vapor pressures are high enough for them to be important agents in the plasma reactions [37]. They appeared unreacted in the deposits, suggesting that they may not be involved in the reactions.

E.4. Sulfur and Halogens

Sulfur has often been found on anodes [38, 60, 65, 67, 68]. As in the case of silicon, the origin of sulfur is not very clear. One suggestion [69] is that the source of the sulfur observed in deposits is in mold-release agents which contain sulfur, and are used in fabrication of many plastic components. Halogens can be present in the gas source, or can be introduced by outgassing of residues from cleaning with chlorinated solvents quite commonly used (trichlorethylene, trichlorotrifluroethane, and others). If these solvents are properly purged, there should be no problem. However, it is known from plasma chemistry that chlorine in a plasma can accelerate polymerization processes enormously. Fig. 8[70] shows the effects of Freon 12 (CF_2Cl_2), Freon 14 (CF_4) and methyl chloride (CH_3Cl) on the deposition rate in methane in a low pressure plasma chemistry experiment. As shown in Fig. 8, CF_4 has a much smaller effect than chlorinated halocarbons; it appears that fluorine is so strongly bound that free radicals of fluorine are not easily made in the plasma (C-F bond: 5.4 eV). On the other hand, the chlorine bond can be more easily broken (C-Cl bond: 3.5 eV); but is still strong enough to make chlorine radicals very reactive. They can even act as gas phase catalysts [70], enhancing the concentration of free radicals by abstraction of hydrogen from hydrocarbon species; for example:

$$e^- + CFCl_3 \rightarrow Cl\cdot + CFCl_2\cdot + e^- \quad \text{(Freon 11)} \qquad (3.5\ \text{eV}) \qquad (4)$$

$$Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot \qquad (-1.0\ \text{eV, exothermic}) \qquad (5)$$

$$CH_3\cdot + CH_4 \rightarrow C_2H_5\cdot + H_2 \qquad (\text{exothermic}) \qquad (6)$$

$$C_2H_5\cdot + CH_4 \rightarrow C_3H_7\cdot + H_2\text{, etc.} \qquad (\text{exothermic}) \qquad (7)$$

$$e^- + HCl \rightarrow H\cdot + Cl\cdot + e^-\text{, etc.} \qquad (4.5\ \text{eV}) \qquad (8)$$

The $Cl\cdot$ (atomic chlorine) acts as a hydrogen abstractor (see Glossary) to produce hydrocarbon radicals which can polymerize. It is not depleted since it reappears in reaction (8) when the HCl is dissociated. Furthermore, chlorine is very electronegative and the Cl^- ion can be readily drawn to the anode wire where polymerization at the surface can occur.

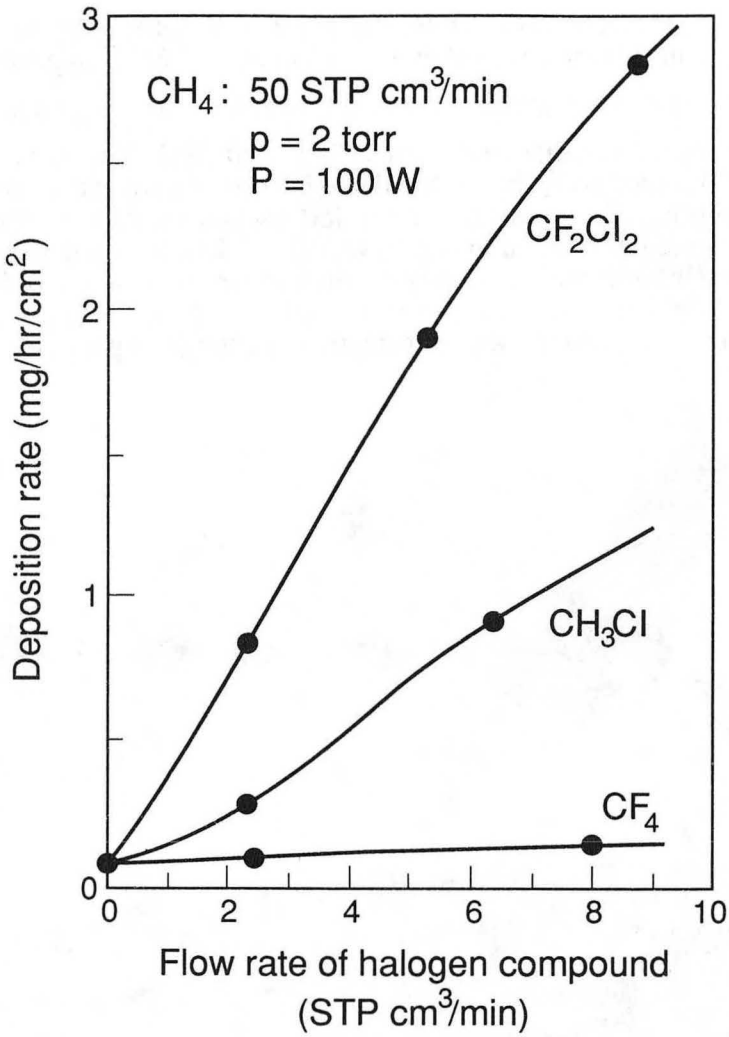

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Fig. 8. The effects of addition of CF_2Cl_2, CH_3Cl, and CF_4 on the polymer deposition rate of methane [70].

These effects may also be important in our regime. However, it has been shown recently [49] that a few ppm of Freon 11 ($CFCl_3$) does not appear to cause serious aging in dimethyl ether but rather causes severe signal loss due to the extremely large electronegativity of Freon 11 [66]. (See also Section II.C.4). The apparent aging observed in several tests listed in Table III can perhaps be explained by the increasing concentration of Freon 11 in the DME supply bottle as the DME is used up. Since both the DME and Freon 11 are in a liquified state in the bottle (at 60 psig pressure) and because the Freon is less volatile, this will result in a gradually increasing concentration of the Freon 11 in the gas, causing a gradual current decrease, which would appear to be aging.

E.5. TMAE

TMAE is a convenient abbreviation for tetrakis (dimethylamino) ethylene, a photoionizing vapor having a very low ionization potential (5.4 eV), which is added in very small quantities ($\lesssim$0.1%) to the chamber gas to be sensitive to photons. It is used especially in Cerenkov ring

imaging detectors (RICH or CRID counters) as a way of converting the UV photons to electrons, which can then be detected by wire chambers. TMAE appears to hold the record for most rapid aging of a wire chamber gas, with R ~ 1,300,000%/$\frac{C}{cm}$ initially; when mixed with methane, and using a 7 μm diameter carbon fiber anode[45]. The aging rate can be slowed by factors of 3 or 10 respectively, by using ethane instead of methane, or by using a 33 μm diameter carbon fiber. The wire deposit is colorless, and oxidizes on contact with air to form liquid droplets, which are shown in Fig. 9[45,71]. A definitive analysis of deposits is very difficult, since their composition quickly changes in air. In this extraordinary case, the approach to this problem is to "clean" the wire periodically by heating it (with an electric current), or possibly to keep the wire constantly hot enough to prevent coatings from occurring [45].

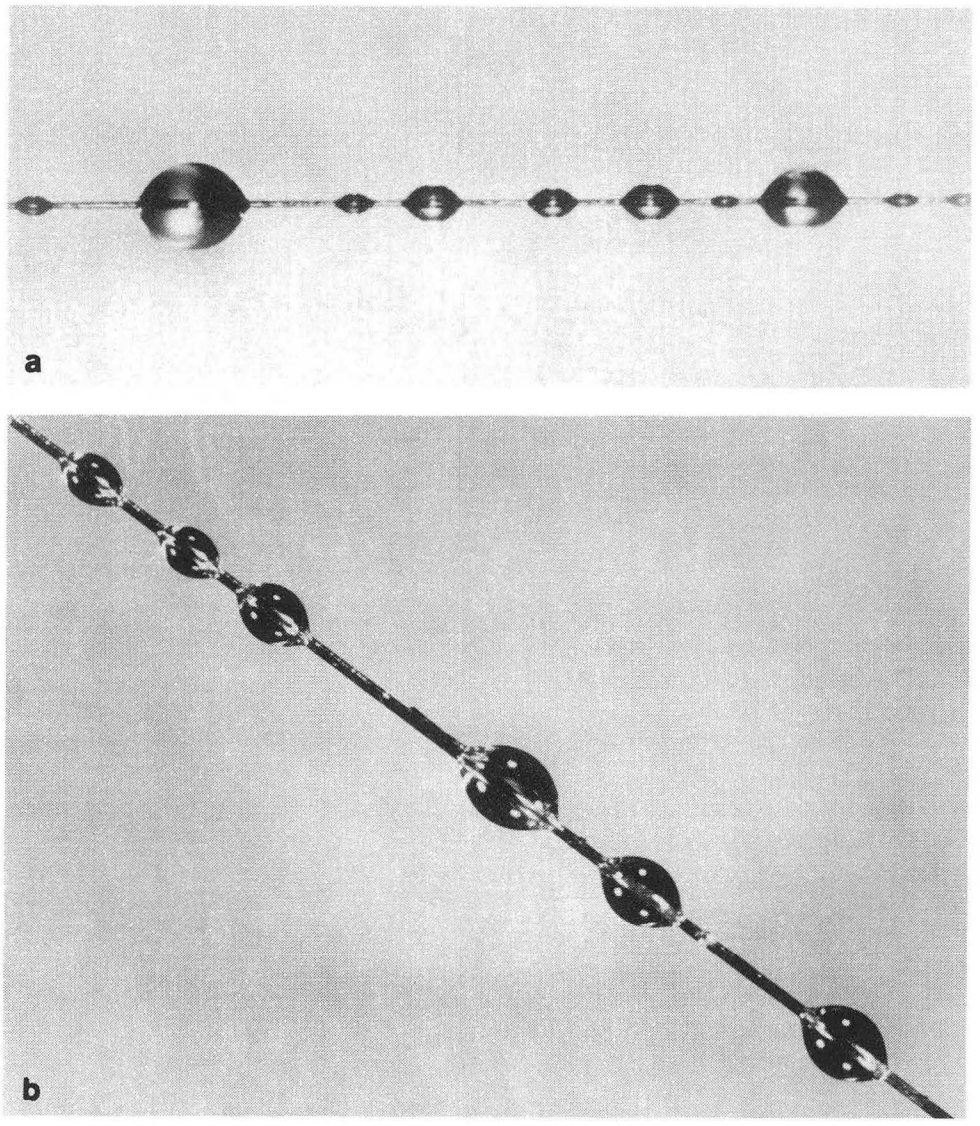

Fig. 9. a) Liquid deposits in CH_4 + TMAE (27° C) on 7 μm diameter carbon wire after several hours in air. The deposits obtained after a total charge dose of about 6 x 10^{-3} C/cm at one atmosphere pressure[45]; b) CH_4 + TMAE (20° C) at one atmosphere pressure, after about 7x10^{-3} C/cm [71].

E.6. Other Examples

There are two gas mixtures which were found to have exceptionally fast aging (on gold plated wires) [72]. One of these was $Ar/C_2H_6/NH_3$ (49.5/49.5/1), with a measured value of R ~6670%/C/cm (with 30 mC/cm charge collected); the anode wire had a snowy white appearance in the irradiated area. The other example is $Ar/CF_4/0_2$ (50/40/10), which resulted in a nearly complete gain loss in a few minutes (~ 0.5 $\frac{mC}{cm}$) and a measured R ~ 130,000%/ $\frac{C}{cm}$. No wire deposit could be seen under an optical microscope in this case. The curves of current vs. charge for these runs, as well as one for Ar/C_2H_6 (50/50) are shown in Fig. 10. These gases were discovered in an attempt to understand effects of certain gas constituents, and it is not known as yet what plasma chemistry leads to such a rapid aging.

F. Effects of Wire Material

In most cases the wires of a wire chamber can be gold plated. This is very desirable, since gold is quite inert, and therefore is not attacked chemically by reactions with species in the gas or plasma. There may, however, be situations where gold plating is not acceptable, the most notable of which is the use of resistive anode wire in the charge division technique. The avalanche charge divides inversely as the resistance to the ends of the wire, where it is

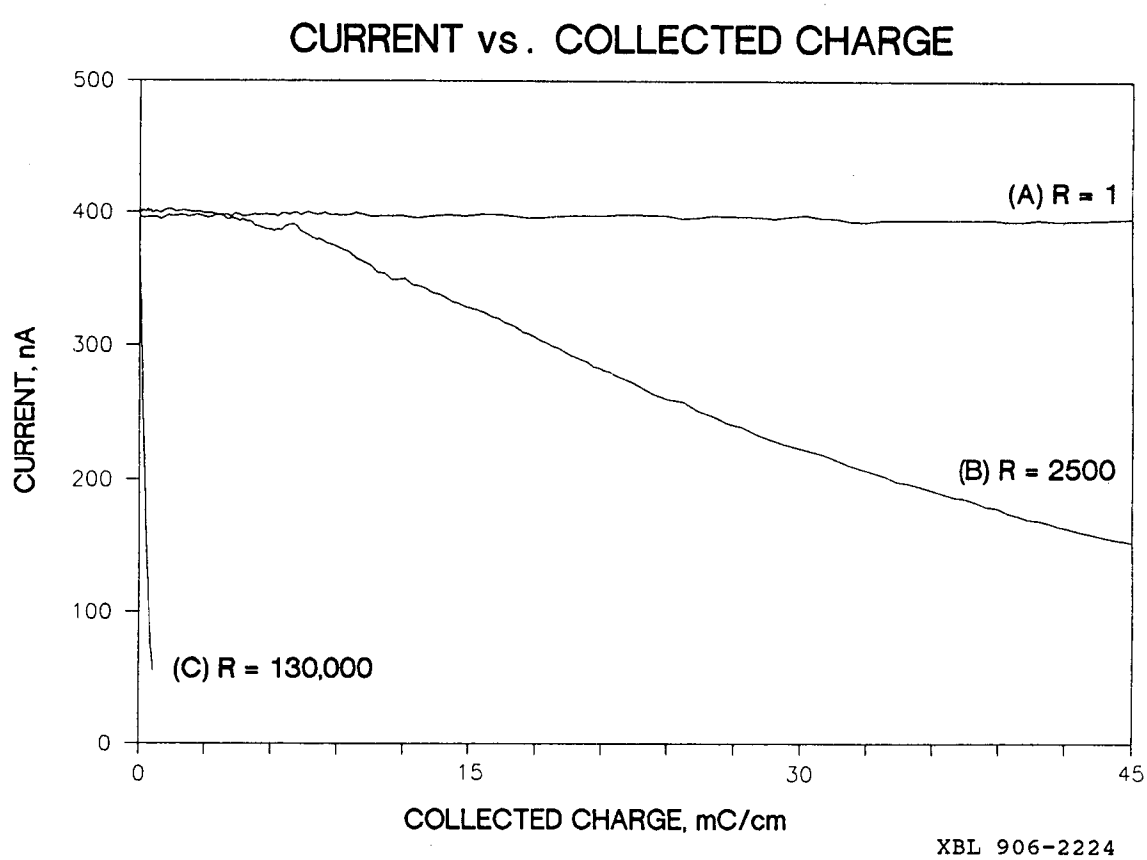

Fig. 10. Aging tests with three different gases showing large variations in the magnitude of aging rates for otherwise similar conditions. Gold-plated wire was used for the anode in all cases. (a) 50% argon + 50% ethane. (b) 49.5% argon + 49.5% ethane + 1% ammonia, (c) 50% argon + 40% CF_4 + 10% oxygen. The argon/ethane test extended to about 2.0 coulombs [72].

detected, so that the location of the avalanche along the wire may be determined from the ratio of the detected charges. A position resolution of about 1% of the wire length is typically obtained, but this resolution cannot be achieved using gold plated wire, since it is far too conductive. It had been known for some time that ethanol vapor (~1.4%) as an additive in an argon/ethane (50/50) gas mixture was very effective in suppressing aging, and it came as a surprise that the same gas caused greatly accelerated aging [4,5] when used with a popular resistive wire, Stablohm 800. The mechanism of degradation is not precisely known but is thought to be oxidation of certain active elements in the wire material, which includes aluminum and copper in this case.

The discovery that non-gold-plated wires can be seriously attacked by ethanol as an additive led Atac to a systematic study of different alcohols on a variety of wire materials [5]. Tests were done in a small wire chamber with anode wires made of aluminum, nickel, copper, chromium, stainless steel, and platinum. The gas mixtures used were argon/ethane (50/50) with ethanol, methanol and isopropanol as additives. The results showed that with aluminum wire, rapid aging occurred with both ethanol and methanol. Nickel wire also aged (with methanol vapor), but not as rapidly as aluminum wire. Neither of these types of wire showed any obvious visible deposit or diameter increase, and the loss in gain and resolution was ascribed to thin insulating layers of oxide causing charge accumulation that weakens the field near the wire. None of the remaining wires exhibited appreciable aging, though it is not quite clear why this is so for copper, which oxidizes easily, except perhaps that copper oxide is a relatively good conductor (a semiconductor) [5].

Little or no aging was observed using these same wire materials with isopropanol as an additive [4,5]. One explanation for this different behavior [5] is that while ethanol and methanol dissociate in a way so that a radical containing a free oxygen bond is available to oxidize the anode material, e.g. $C_2H_5O\cdot$, the isopropanol dissociates differently without exposing such a bond, e.g. $(CH_3)_2CHOH \rightarrow (CH_3)_2CO$ (acetone) + H_2. It was also verified that using isopropanol rather than ethanol in argon/ethane gas causes only very modest aging with Stablohm 800 wire [4,5].

III. Interpretation and Models: Plasma Chemistry

A. Simple Examples of Plasma Reactions

In the thin tube of plasma surrounding the anode wire, many complex physical and chemical phenomena are occurring simultaneously. The electrons drawn toward the wire gain energy from the intense electric field (several hundred kV/cm), but lose it again in collisions with atoms and molecules, which in turn results in excitation, ionization, and fragmentation processes. The electrons therefore have a broad distribution of energies, with an average of a few electron volts. Fig. 11 shows a typical electron energy distribution [73]. This energy is sufficient to break chemical bonds, thereby fragmenting molecules and forming radicals, but it is somewhat less than that required for ionization: ionization results from the few electrons on the upper end of the energy spectrum above the ionization threshold. Table VI and Table VII give bond strengths and ionization potentials for a variety of chemical species that are of interest. These tables refer to dissociation energies which are characteristic of specific bonds as indicated. Each bond energy given in Table VI is a characteristic value for that particular bond averaged over a number of different molecules in which it appears. (In most listings, dissociation energies are given in kilocalories/mole: 1 eV = 23.06 kcal/mole). The implicit assumption here is that the bond energy depends only on the two atoms connected by the specific bond and not on the possible effect due to the rest of the molecule. This concept is approximately correct, and justifies the use of bond energies for many purposes. In Table VII, however, dissociation energies are given for bonds as measured in certain specific molecules that may be of interest. The values are taken from references as indicated, with the exception of the O-O bond in Table VI, which has been estimated by the present author from several

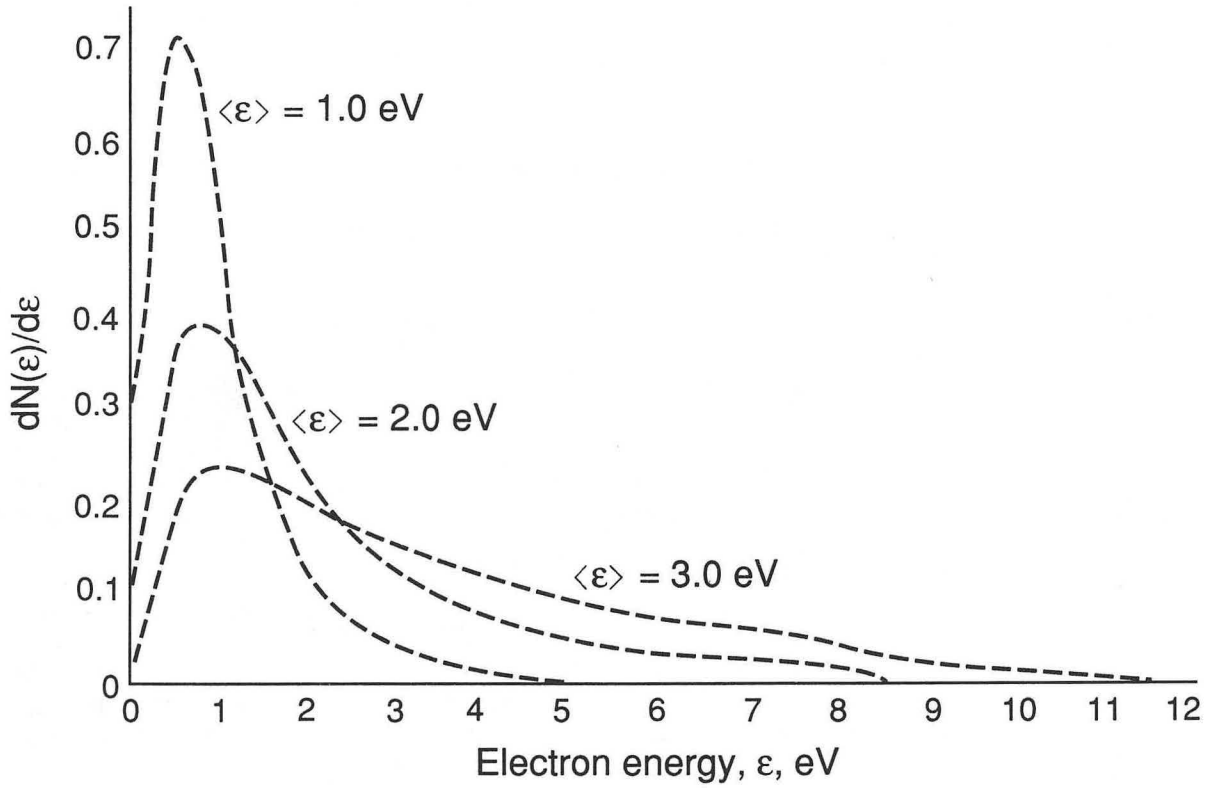

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Fig. 11. Typical electron energy distribution in a plasma . Rms electron energies are as indicated [73].

tabulated bond dissociation energies. The tail of the electron energy distribution extends into the energy region where ionization occurs, but the preponderance of electron energy transfers results in excitation of atoms and breaking of bonds to form radicals. The de-excitation of single atoms or simple molecules can result in photon emission; complex molecules (triatomic and larger) can fragment instead. The result is a large excess of free radicals over ionized states, and the chemistry in the plasma is dominated by these radicals. Here is an example of just a few of the reactions which may occur in ethane, with the corresponding electron energies required [74]:

<u>Initiation Reactions</u>

$e^- + C_2H_6$	$\rightarrow C_2H_4 + H_2 + e^-$	1.4 eV	(9)
$e^- + C_2H_4$	$\rightarrow C_2H_2 + H_2 + e^-$	1.8 eV	(10)
	$\rightarrow C_2H_2 + 2H\cdot + e^-$	6.3 eV	(11)
	$\rightarrow 2\ CH_2: + e^-$	7.3 eV	(12)
	$\rightarrow C_2H_4^+ + 2e^-$	10.5 eV	(13)
	$\rightarrow C_2H_2^+ + H_2 + 2e^-$	13.1 eV	(14)
	$\rightarrow C_2H_3^+ + H\cdot + 2e^-$	13.3 eV	(15)

Some of the subsequent reactions which can occur leading to 2nd and 3rd generation active species are:

Propagation Reactions

Radical Reactions		Ion Reactions	
$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot$	(16)	$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+\cdot + CH_3^+\cdot$	(19)
$H\cdot + C_2H_5\cdot \rightarrow 2CH_3\cdot$	(17)	$C_3H_5^+ + C_2H_4 \rightarrow C_5H_9^+$	(20)
$H\cdot + C_2H_2 \rightarrow C_2H_3\cdot$	(18)		

Table VI. Average Bond Energies [75]

bond	Dissociation energy (eV)
C—C	3.6
C=C	6.4
C≡C	8.7
C—H	4.3
C—N	3.2
C=N	9.3
C—O	3.7
C=O	7.8
C—F	5.4
C—Cl	3.5
N—H	4.0
O—H	4.8
O—O	1.7

Table VII. Dissociation Energy and Ionization Energy for Some Gases [76]

Compound	Dissociation energy (eV)	Ionization energy (eV)
H	-	13.6
Ar	-	15.8
Xe	-	12.1
H_2	4.5	15.4
N_2	9.8	15.6
O_2	5.2	12.1
Cl_2	2.6	11.5
F_2	1.6	15.7
Br_2	2.0	10.5
HF	5.9	15.8
HCl	4.5	12.7
HBr	3.8	11.6
CO	11.2	14.0
NO	6.5	9.2
$H\text{-}CH_3$	4.6	12.6
$H\text{-}CH_2$	4.8	9.8
H-CH	4.4	10.4
H-C	3.5	11.1
$H\text{-}C_2H_5$	4.3	11.5
$H\text{-}iC_3H_7$	4.2	11.1
$H\text{-}tC_4H_9$	4.0	10.6
$H\text{-}C_6H_5$	4.8	9.2
H-CN	5.4	13.8
H-OH	5.2	12.6
$H\text{-}NH_2$	4.7	10.2
H-CHO	3.8	10.9
$H\text{-}CHCH_2$	4.6	10.5
$H\text{-}CH_2OH$ (methanol)	4.1	10.8
$CH_3\text{-}CH_3$	3.9	11.5
$CH_2{=}CH_2$	7.5	10.5
$CH{\equiv}CH$	10.0	11.4
NC-CN	5.6	13.6
O=CO	5.5	13.8
$O\text{-}N_2$	1.7	12.9
O-NO	3.2	9.8
$H\text{-}CH(CH_3)OH$ (ethanol)	4.0	10.5
$H\text{-}CH_2OCH_3$ (DME)	4.0	10.0
$CH_3OCH_2OCH_3$ (methylal)	-	10.0
$CH_3O\text{-}OCH_3$	1.6	-
$HO\text{-}iC_3H_7$ (isopropanol)	4.0	10.2
$F\text{-}CH_3$	4.7	12.8
$Cl\text{-}CH_3$	3.6	11.3
$Br\text{-}CH_3$	3.0	10.5
$Cl\text{-}CF_3$ (Freon 13)	3.7	12.9
$Cl\text{-}CF_2Cl$ (Freon 12)	3.3	12.3
$Cl\text{-}CCl_2F$ (Freon 11)	3.2	11.8

These radicals (R_n) and ions (I_n) can now react further to produce species of increasing molecular weight : (n = number of monomers in the molecule)

$$I_n + \begin{pmatrix} C_2H_4 \\ C_2H_2 \end{pmatrix} \rightarrow I_{n+1}, \quad R_n + \begin{pmatrix} C_2H_4 \\ C_2H_2 \end{pmatrix} \rightarrow R_{n+1} \tag{21}$$

It is in this stage of development that polymers begin to form. The polymer can begin to grow in the gas, then diffuse to the wire and become attached where it continues to grow, or essentially the entire growth process may occur on the wire. If the polymer fragment is ionized (to become either a positive <u>or</u> negative ion), it may be attracted to a wire (cathode or anode) by the electric field. Finally, the polymer growth stops when two radicals happen to combine to form a polymer chain with completed (but not necessarily saturated) bonds.

<u>Termination Reactions</u>

$$R_n + R_m \rightarrow P_{n+m}, \quad I_n^+ + e^- \rightarrow P_n \tag{22}$$

Photons emitted during recombination processes also contribute to excitation of monomers into free radicals and ions.

As indicated above, the polymer growth occurs mainly by means of reactions of free radicals. For simple hydrocarbon chains, the reaction rates for C_2H_4 and C_2H_2 are far higher than for C_2H_6 or CH_4 as the initial monomers; this is illustrated in Fig. 6. It is convenient, and perhaps even precise, to imagine that C_2H_4 and C_2H_2 are produced from the initial monomers by reactions that are illustrated above, and that the chain growth is dominated by the following reactions:

$$CH_3\cdot + C_2H_4 \rightarrow C_3H_7\cdot, \quad C_3H_7\cdot + C_2H_4 \rightarrow C_5H_{11}\cdot, \text{ etc.} \tag{23}$$

$$\begin{array}{ccccccccccc} H & & H & H & & H & H & H & & H & H & H & H & H \\ HC\cdot & + & C= & C & \rightarrow & HC & -C & -C\cdot, & HC & -C & -C\cdot & + & C & =C & \rightarrow & HC & -C & -C & -C & -C\cdot, \text{ etc.} \\ H & & H & H & & H & H & H & H & H & H & & H & H & & H & H & H & H & H \end{array}$$

A similar growth pattern can be written starting with C_2H_2. Finally, the chain growth is terminated when the chain radical meets another radical and the bonds are satisfied for both. However, the same polymer could later begin to grow again as a result of bombardment by an electron, or ion, or by a UV photon opening up an unsaturated carbon-carbon bond. Considerable cross-linking of bonds occurs due to this subsequent bombardment, which accounts for the mechanical robustness and insolubility in good organic solvents of many wire deposits.

Polymers other than hydrocarbons can form, which may resemble those made commercially from pure monomers: e.g. polytetrafluoroethylene (Teflon), polymethylmethacrylate (Plexiglas, Lucite), polyamides (Nylon), polyvinyl chloride (Tygon), etc. It is however, an oversimplification to think that the wire deposits, which are neither made from pure monomers nor by a process similar to the commercial one, have any close identification with the aforementioned products.

However, there are situations when one naively might expect polymer formation, but it does not occur. We have seen in Table III that the gas mixture of CF_4/iC_4H_{10} (80/20) has very good aging [48,III-18] properties in spite of the rather poor performance of iC_4H_{10} in many mixtures with Ar, and the fact that CF_4, by analogy with the examples above (replacing H by F) might be expected to produce polytetrafluoroethylene (PTFE or "Teflon"). Indeed, it is known from plasma chemistry studies that at higher power densities, hence at high electron energies, CF_4 does not polymerize into PTFE, because fluorine must be split off the CF_4 to form the $(CF_2)_n$ polymer chain[73]. However, the F-F bond is weak (1.6 eV), and is easily broken in the discharge. The resulting radical, F·, is very reactive and drives the plasma

reaction in the direction of ablation, diminishing the PTFE chain, rather than resulting in polymerization. The balance between these processes is called by Yasuda "competitive ablation and polymerization" (CAP) and is illustrated in Fig. 12[77]. F· can also react with silicon frequently found on anode wires to form SiF_4 which is volatile (see Section II.C.4.). If hydrogen is added, however, the CF_2: polymerizes rapidly, forming deposits. This is because the H-F bond is very strong (5.9 eV), so that the F· radicals are "scavenged" or used

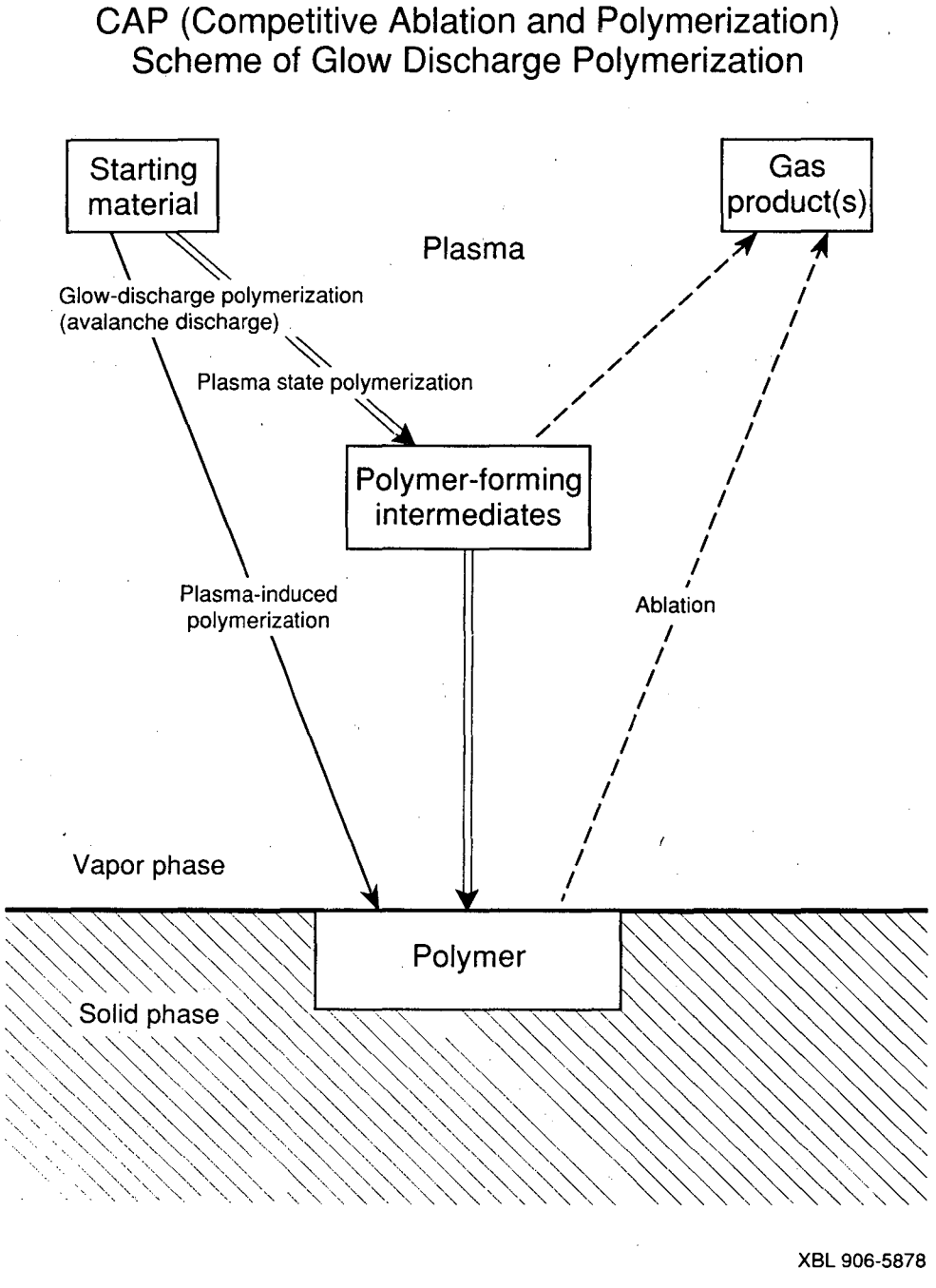

Fig. 12. Overall mechanism of glow discharge polymerization mechanism, exhibiting competitive ablation and polymerization [77].

up by the hydrogen allowing the polymerization to proceed. Perhaps a similar case exists for the CF_4/iC_4H_{10} gas mixture, there being too little hydrogen produced from iC_4H_{10} to cause polymerization of $(CF_2)_n$. However, CF_4 also appears to reduce deposits in argon/ethane (50/50) gas mixtures when added at only a 4% concentration [57, III-18]. Here one expects a much higher hydrogen/CF_4 ratio in the plasma, yet no polymerization seems to occur. In another instance, the addition of a small amount of hydrogen (~0.1%) in a sealed proportional counter containing methane or isobutane is said to extend the counter lifetime significantly, and in the case of methane, by a factor of fifty [30]. However, this method does not seem to be effective when using ethane [24] or isopentane [65]; and in plasma chemistry experiments, polymerization occurs even in the presence of hydrogen [8]. This is only one mysterious aspect of plasma chemistry, which perhaps will be explained soon by more detailed investigation of the relevant plasma processes.

B. Reaction Kinetics and Controlling Parameters

There can be many processes leading to deposition of polymers inside gaseous discharges, which are called, generically, plasma polymerization. A great deal of information is available in the literature (see Bibliography section on plasma chemistry) in just one sector of this field: r.f. polymerization at low pressure (~ 1 Torr). Some of this knowledge is expected to be relevant to the qualitative understanding of our sector of interest: polymerization by d.c. discharges at $\gtrsim$ 1 Atm. pressure. Deposition rates vary according to pressure, flow rate, power density, and many other factors, and different rates are affected differently, in general. Since the polymerization processes represent competition between different reactions, and the rates are generally not known at high pressures, there is not yet even a complete qualitative understanding in this sector.

In Table VIII are given some relevant physical parameters for a plasma under typical wire chamber conditions: We have chosen a pressure of 1 Atm, and a typical gas mixture. The corresponding parameters under typical low pressure plasma conditions are also given for comparison. The values given are order-of-magnitude indications only, since electric field and pressure vary over wide ranges in either regime. It will be noticed that there are large differences in pressure and electric field. However, the electron energies are not so very different. This suggests that the chemical reactions occurring may be similar. However, the power density, electron density and mean free path are quite different between the two regimes. Examples of the effects of these parameters in plasma chemistry experiments are given in Figures 3 and 4. Many effects of electric field and pressure, such as the electron energy distribution, are expected to scale by their ratio (E/p), i.e. according to gas density. The important effect here is the increase in electron kinetic energy between inelastic collisions, hence the (E/p) dependence, since the time between collisions scales as (1/p). Plasma reactions have threshold values, if endothermic, and as the average electron energy rises, new reactions begin to occur. These thresholds are typically associated with bond strengths and dissociation energies, and excitations and ionization levels (see Tables V, VI and VII). Which reactions are energetically allowed, and the balance between these reactions as determined by the reaction rates and concentrations of reacting species, will determine the final result, e.g. the polymerization rate. This in turn is controlled by

Table VIII. Physical Parameters of a Plasma [78]

Parameter	Low Pressure/r.f. Discharge (In Plasma Chemistry Experiments)	High Pressure/d.c. Discharge (In Experimental Detector)
Gas Pressure	0.1 - 5 Torr	~760 - 3000 Torr
E/p	10 - 50 V/(cm · Torr)	100 - 400 V/(cm · Torr)
Electron Energy	1 - 10 eV	~5 - 10 eV
Collision Mean Free Path	~ 1 mm (inelastic)	~1-3 μm (ionizing)
Electron Density	10^8 - 10^{11} e^-/cm^3	10^{14} - 10^{17} e^-/cm^3/avalanche
Power Density	0.01 - 100 watts/cm^3	10^8 - 10^{12} watts/cm^3/avalanche
Gas Flow	0.1 - 1.0 Gas Volume/min	0.01 - 0.001 Gas Volume/min

the concentration of electrons above the various reaction thresholds, i.e. the avalanche electron energy distribution. A typical electron energy distribution might be as shown in Fig. 11[73]. Power density is a measure of the electron energy, and is related to the gain of a wire chamber.

The photographs of wire deposits shown in Fig. 13[79] exhibit how the morphology of the deposits depends upon pressure, and therefore average electron energy, as well as upon flow rate. The wire samples pictured here have been exposed to a variety of different operating conditions, and quite different structures are evident in the photographs. The deposits can be either powder, oil film, or rigid film ("whiskers"), as described in Fig. 14[80]. Fig. 9 gives examples of a liquid coating observed in a gas containing ~0.1% of TMAE[45,71].

Illustrations of some of the factors affecting deposition rates can be found in the publications of low pressure results (see for example chapters 8, 9 of Yasuda); no corresponding systematic studies have yet been made at atmospheric pressure although some results were shown in Table IV. In Fig. 7 we saw the effect of gas flow upon deposit rate at different pressures and power densities. There is a maximum because the rate is dominated at low flow by the limited availability of monomer (it is "used up"), and at high flow by the insufficient residence time of the free radicals for all of them to react before being swept out by the gas flow. A more dramatic demonstration of this is given in Fig. 15[81], for a cylindrical tube reaction vessel, not too different from a proportional tube geometry. Shown here is the deposition rate vs. the distance along the electrode in the gas flow direction, for two different flow rates: below and above the maximum described above. At low flows, we see the drop in deposit rate in the direction of gas flow as the monomer is significantly depleted as it flows through the tube. The opposite is true at higher flows, presumably due to increasing concentration of radicals as the flow proceeds.

In Fig. 6 we saw the relative polymerization rates for ethane, ethylene and acetylene: they are roughly in the ratio 1:100:1000. One way of explaining the difference in reactivity is by the simple model given in III.A, in which C_2H_4 and C_2H_2 play dominant roles because of their unsaturated bonds; ethane must first be converted to one of these unsaturated hydrocarbons before polymerization can occur at a high rate, and hence ethane is relatively less reactive. A similar remark can be made for other linear chain unsaturated hydrocarbons, and this tendency is supplemented by an effect of the molecular weight: the heavier the gas molecule, hence the less volatile the faster the deposition rate.

Another example of factors controlling the plasma reactions is that of oxygen-containing compounds. It is quite well established that alcohols, methylal, water, and some other oxygen-containing molecules are effective in reducing aging when used in the form of minor constituents ("additives"). Indeed pure dimethyl ether has an extremely low aging rate, and also contains oxygen. Two possible mechanisms come to mind: (a) radicals containing the oxygen atom may be relatively inactive, and thus when they are added to the chain they effectively "block" the further growth of that chain, or (b) the oxygen readily forms volatile products with radicals (e.g. H_2O, CO, CO_2), thereby decreasing the concentration of radicals

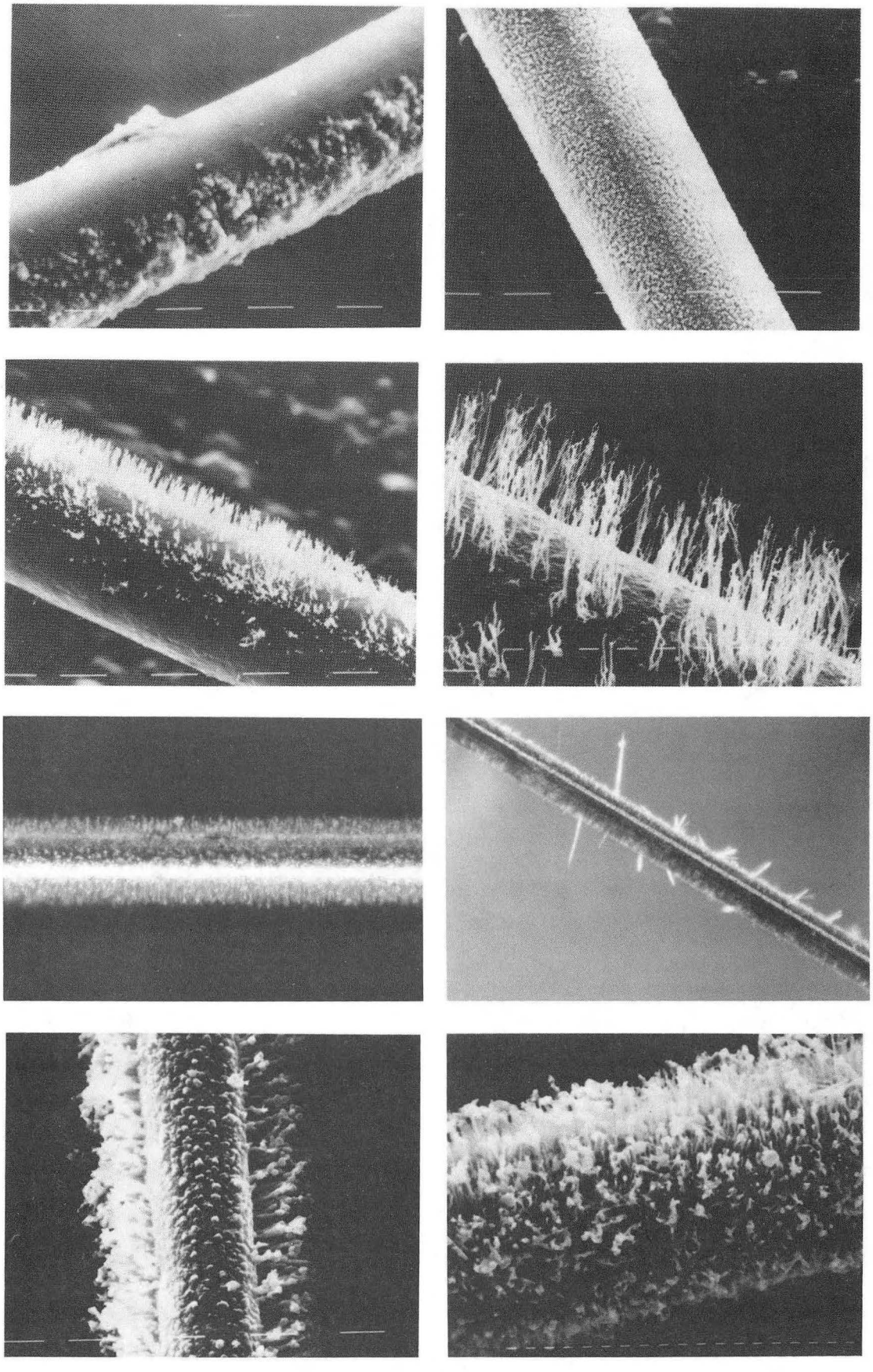

Fig. 13. Examples of deposits on anode wires [79].

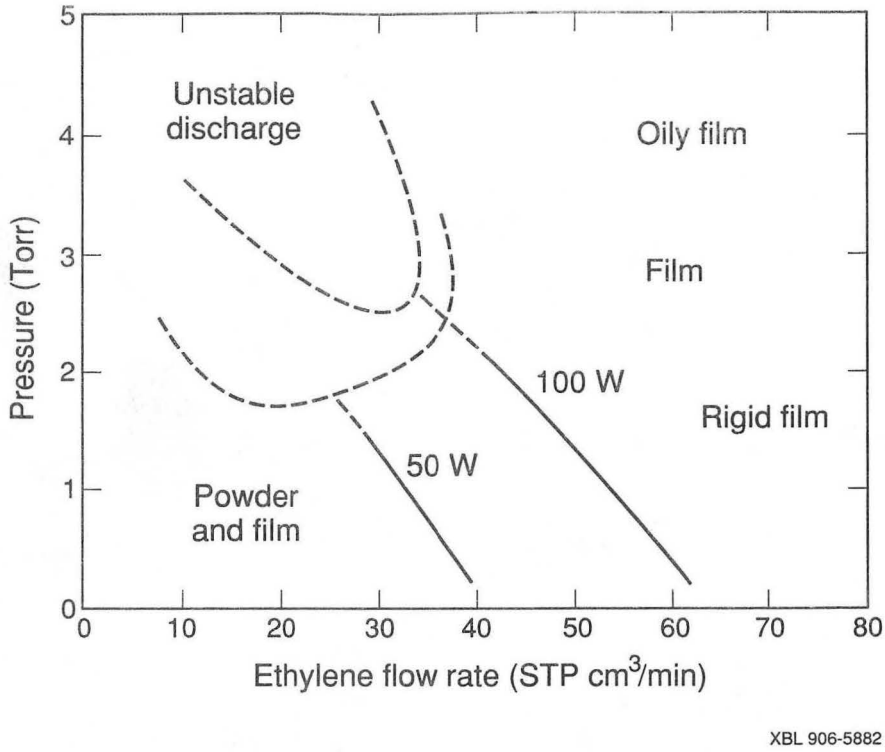

Fig. 14. Dependence of the type of polymer formed on power, pressure, and flow rate [80].

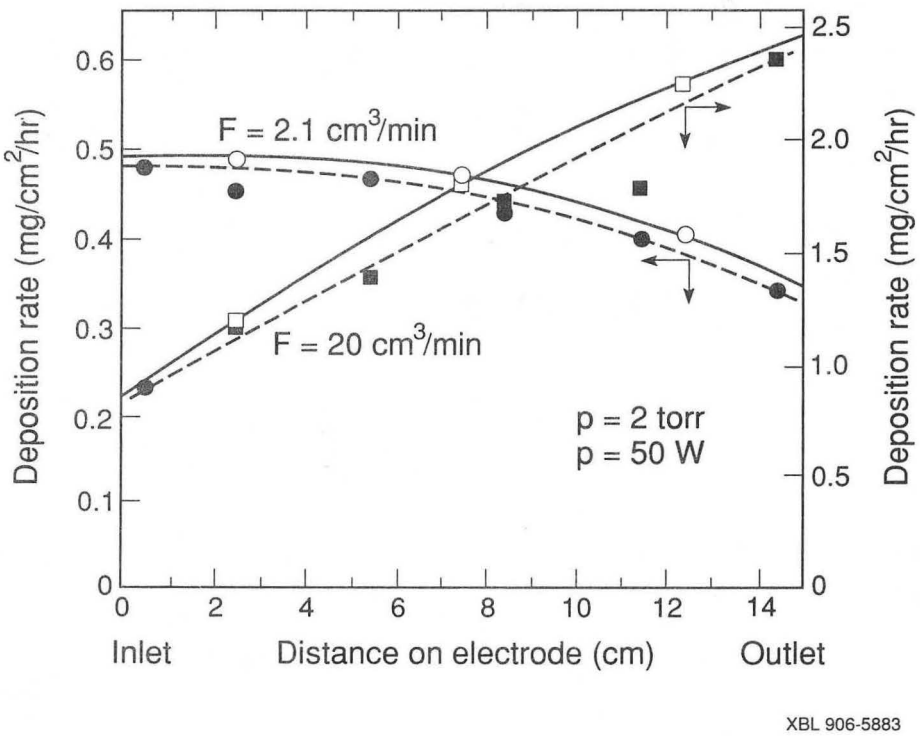

Fig. 15. Effect of monomer flow rate on the deposition rate distribution along the electrode length (pressure 2 Torr, power 50 W). The solid and dashed curves correspond to two different techniques used for determining the amount of polymer deposited [81].

available for polymerization. There is confirmation of this general picture from plasma chemistry studies [82].

Other properties of plasma species which may be important in polymerization and deposition processes are electronegativity and electric dipole moment. Electronegativity measures the affinity of an atom or molecule for attachment of an electron. Negative ions thus formed are then carried by an electric field toward the anode. The dipole moment could, in principle, also be an important factor in transport processes since a non-uniform electric field will exert a force on a dipole element, drawing it towards regions of higher fields. Many free radicals may be expected to have permanent or induced dipole moments. In plasma chemistry experiments, electrodes are usually planar or tend to be of large radii, so that fields are nearly uniform, but in wire chambers, fields are very non-uniform in the vicinity of the wires. Therefore, we may expect that not only electrons, but species having a dipole moment and negative ions formed from electronegative species can be attracted toward the anode wire, and will tend to concentrate there. Similarly, positive ions and species with dipole moments can be attracted to the cathode wire. Table IX gives the electron affinities and permanent dipole moments for some atoms and molecules. In the wire chamber case, both of these properties could contribute to the transport of reactive species to the wires. However, a simple estimate shows that even near the anode wire, where the field gradient is strongest, the force on a typical permanent dipole is about six orders of magnitude less than the electric force on a negative ion. Since ion drift velocities near the anode wire are ~10^5 cm/sec, this would mean that drift velocities of neutral species, such as free radicals, might be about 1 mm/sec, and a characteristic concentration time at the wire would be ~0.01 seconds (assuming ~25μm diameter wire). Lifetimes of some free radical species can be of this order or longer, so it is conceivable that such a dipole attraction mechanism plays a significant role in polymerization, especially since the rates of some reactions may increase quadratically with radical concentration.

Table IX. Electron Affinity and Permanent Dipole Moment: Some Examples [83]

Atoms: Ions Formed	Electron Affinity (eV)	Molecules and Radicals: Ions Formed	Electron Affinity (eV)
Cl^-	3.61	NO_2^-	3.91
F^-	3.45	SiF_3^-	3.35
Br^-	3.36	CN^-	3.17
I^-	3.06	SH^-	2.19
S^-	2.07	CF_3^-	1.85
O^-	1.47	OH^-	1.83
C^-	1.12	CCl_3^-	1.22
H^-	0.80	NH_2^-	1.12
		CH_3^-	1.08
		$C_2H_5^-$	0.89
		O_2^-	0.45
		CH_3O^-	0.38

Table IX. Permanent Dipole Moments [83] (continued)
(In Debye units: D=3.34 x 10^{-30} Coulomb-meter)

Water	1.85D
Methanol	1.70D
Ethanol	1.69D
Isopropanol	1.66D
Dimethyl Ether	1.30D
Carbon Dioxide	0
Methane	0
Ethane	0

The electronegative species, by contrast, are expected to be drawn to the wires very quickly and be concentrated there, even though their concentration may be far less than that of the radicals. However, when it is noted that halogens, particularly chlorine, cause dramatic increases in deposit rates (discussed in section III.C)., and it is seen that the halogens are among the highest in electronegativity, then it is suggestive that this property could be of importance. Indeed the strong effect of halogens on reaction rates may be largely due to electronegativity [66]. Likewise, a concentration of species which suppress wire coatings, such as those of oxygen-containing additives (water, alcohols, etc.) may occur due to electronegativity (for example, oxygen is quite electronegative) or possibly also due to dipole moments. It is of interest to note in this regard that elements O, F, and Cl are among those having the most powerful retardant (O, F) and promoting (Cl) effects upon polymerization, and are also among the most electronegative. Sulfur, which is commonly found in deposits on anode wires, is also quite electronegative.

With this transport mechanism in mind, we may construct a model of processes occurring inside a wire chamber leading to wire deposits. Parts of the following model are purely hypothetical. An avalanche begins forming several ionization mean free paths (λ_i) from the anode wire, there being a new electron created for every ionizing collision, or a doubling of avalanche electron concentration each λ_i. For typical avalanche gains (~50,000), the avalanche would begin at about 16 λ_i (if λ_i were a constant), or perhaps ~50 μm from the wire surface. The length along the wire is also of this order of size. Molecular species (gas molecules, free radicals and ions) collide near the anode wire at a rate of about 10^9-10^{10}Hz, leading to reactions in the plasma. These reactions lead, in general, to both volatile species, which are carried away in the effluent gas (if the chamber is not sealed), and to non-volatile species, which can deposit on the wire and other surfaces. The positive ions which are produced in the avalanche will drift relatively slowly (10^3-10^4 $\frac{cm}{sec}$) to the cathode, and may charge-exchange on the way if neutral species with lower ionization potentials are encountered . The positive ion, perhaps not the initial one from the avalanche, is neutralized at the cathode and thereby left in an excited state. The de-excitation of this neutralized ion may occur (1) by photon emission (typical of noble gases), (2) by extraction from the cathode of an electron that can drift back to the anode and cause a secondary avalanche (undesirable), or (3) by fragmentation with neither photon nor secondary electron emission, a process typical of organic molecules (the desired result of a "quenching" gas)[13]. In the case of the quenching gas, fragmentation results in free radicals, which can polymerize to form a cathode wire deposit. If this deposit is a good electrical insulator, the Malter effect can ensue. Before the insulating deposit reaches the extent required for the classical self-sustained Malter discharge, however, the cathode may become "sensitized" by having some smaller amount of deposit and correspondingly smaller electric fields from the dipole layer. This has been discussed earlier (in Section II.A.4). The work function of the cathode surface is effectively reduced. Such a phenomenon has been frequently

observed, and is usually an indication of a more serious problem in the offing (self-sustained Malter discharge). The sensitive regions are prone to higher dark currents, because lower energy photons, ions, etc. can more easily cause the release of secondary electrons. These excessive dark currents then cause more deposits to form at the same spot on the cathode since the ions of the second generation proceed directly back along the same electric field lines that the secondary electrons followed. Due to this regenerative process, a localized deposition soon accumulates to the extent sufficient to establish a self-sustained discharge. The Malter layer buildup may also be accelerated by avalanche formation at the cathode wire if the field there is large enough. In this case, the cathode avalanche is initiated by electrons drawn from the cathode wire by field emission due to the Malter layer, or perhaps by positive ion de-excitation , or by both processes. The concentration of free radicals can be greatly enhanced in this way, and can therefore result in a greatly accelerated polymer deposition. It is commonly understood that it is essential to design wire chambers such that the field at cathode wire surfaces does not exceed a certain strength, usually taken to be about 10-20 kV/cm. This field is somewhat smaller than values usually calculated for onset of avalanche processes, but not by large factors. Since wire imperfections will increase fields locally, and any incipient Malter layer formation will reduce the work function at the cathode surface, there is a need to keep the ambient field here at least as low as 20kV/cm. This argument is supported by values obtained for the Townsend coefficient, which show that significant gain will occur in argon for fields much in excess of this value.(see, for example: F. Sauli, Bibliography, and reference 64).

C. Catalytic Behavior

Halogens greatly enhance polymerization rates in the low pressure experiments, and there are some aging results from wire chamber tests that directly implicate chlorine in rapid aging. Reports from plasma chemistry studies also show that chlorides polymerize more rapidly than flourides, and that a larger number of chlorine atoms per hydrocarbon induces more rapid polymerization (see Fig. 8). It has been reported that the aging rate in dimethyl ether is very sensitive to the concentration of $CFCl_3$ (Freon 11), while there is a much lower sensitivity to CF_2Cl_2 (Freon 12), $C_2F_3Cl_3$ (Freon 113), and $CHClF_2$ (Freon 22)[48]. The bond strength C-F (5.35 eV) is considerably stronger than that of C-Cl(3.52 eV). Since the average electron energy is a few eV, and only electrons in the upper tail of the energy distribution are effective in breaking bonds, weaker bonds are broken much more frequently. Therefore, free Cl can be more readily produced than free F. The bond energies for H-F, H-Cl, and H-C are 5.9 eV, 4.5 eV, and 3.5 eV, respectively. Thus H can be easily removed (abstracted) from hydrocarbons by either F or Cl, to make HF or HCl. However, Cl is much more readily detached from a halocarbon impurity than is F, and therefore might be expected to play a more prominent role than F. A suggestion of the type of reaction that might occur was given in Section II.E.4, reactions (4)-(8). The reactions indicated are exothermic with the exception of the two produced by the incident electron, (4) and (8), where the energy required is indicated. We see that the $Cl\cdot$ radical is restored again by reaction (8), and behaves, in a general sense, as a "catalyst": it is not itself directly consumed. Similar processes could be exhibited for ethane or other heavier hydrocarbons. Chlorine was taken as an example, but bromine (Br) also acts as a hydrogen abstractor. The H-Br bond energy is 3.8 eV, more than that of H-C, but less than that of H-Cl (iodine is endothermic with a bond energy of 3.10 eV). There are hydrogen abstractors other than halogens that can drive polymerization reactions, but perhaps none as well investigated. There are recent measurements of electronegativity of various Freons which support this model, since Freon 11 is found to be far more electronegative than the other Freons tested [66]. However, as discussed earlier (sections II.C.4. and II.E.4.), additional tests seem to show little or no aging effects of Freon 11 in DME, in spite of large signal loss due to the electronegativity [49]

D. Plasma Chemistry Studies at Atmospheric Pressure

An important question, yet to be answered, is whether there is a close connection between results in the low-pressure regime (~ 1 Torr) of the plasma chemistry investigations that are already extensively described in the literature, and the relatively high-pressure (~760 Torr) regime that applies to wire chambers. This question can be addressed to both qualitative and quantitative aspects. We have seen that reaction rates depend, sometimes sensitively, upon a variety of parameters, including pressure, power density, gas flow, electric field, and the mode of discharge: r.f. or d.c. With such a difference in these controlling parameters between the regimes of classical plasma chemistry and wire chambers, there seems to be little reason to expect much of a connection, though this remains to be examined (certain scaling laws, besides (E/p), may apply). Qualitatively, there do seem to be suggestions that similarities exist such as the effects of chlorine, oxygen, and silicon, and the dependence upon gas flow and (E/p), but there are other factors, such as effects of quenching and the chemical attack of surface material which are not encountered, or are relatively unimportant, in the classical plasma experiments.

An example of a study of ac (60 Hz) discharge in nitrogen at atmosphere pressure was cited by Hess [84] to demonstrate that there is, in this instance, strong supporting evidence for the similarity between the high pressure/low frequency (i.e. wire chambers), and the low pressure/high frequency plasma reactions. Using gas chromatography/mass spectrometry, a study was made of reactions between the N_2 carrier gas, 560 ppm of CH_4, and varying amounts (35-1100 ppm) of O_2[85]. The electrode geometry in this case was cylindrical with inner and outer electrodes of about 3 mm and 9 mm diameter, and the voltage source was a 16 kV 60 Hz transformer. A 1-2 mA current was drawn over the ~ 25 cm electrode length, giving a current density at the inner electrode of about 40-80 $\mu A/cm^2$, a value similar to that on the anode wires during wire chamber aging tests (equivalent to about 400-800 nA/cm on a 30 μm diameter wire). The electric fields on the electrodes are also not so very different in two regimes, being 2-3 times lower on the inner electrode, and 2-3 times higher on the outer electrode than those in typical wire chamber operation on the anode and cathode, respectively. The principal results are shown in Table IX. The product molecule concentration showed that the methane is partly dissociated (~ 200 ppm or about 36%), the amount being independent of the added O_2, and presumably being determined only by the current. When the input O_2 level exceeds the dissociated CH_4 level, it appears as excess in the effluent. At low levels of O_2, we see that the dissociation products of CH_4, which are expected to be mostly $CH_3\cdot$ radicals, react to form H_2, HCN, NCCN, CH_3CN, and C_2H_6, and some CO and CO_2. As the input O_2 level is increased, the $CH_3\cdot$ radicals are oxidized to form CO, CO_2 and H_2O (not measured), thereby causing the observed reduction in the amounts of all the other products. It is reasonably clear which reactions are occurring, and in fact the authors conclude that "the similarity of the product distribution to that of the low-pressure reaction of methane with discharged nitrogen indicates that these systems share a similar chemistry." Some of the features of the observed reactions were directly explainable in terms of reaction rates measured at low pressure, but other important reaction rates were not measured. There is, however, nothing to indicate that these observations could not, in principal, be deduced from low pressure results, a conclusion that could be of considerable importance to later work.

Table X. Effect of Oxygen Additions on Effluent Yield for AC Discharges in N_2/CH_4[85]

Conditions:

N_2 Carrier Gas, flow rate = 350cm^3/min
CH_4 Input = 560 ppm
1 atmosphere pressure
Current ~ 1mA, 60 Hz

Effluent	Input O_2 Concentration (ppm)		
Species	35	500	1100
O_2	25	75	800
CH_4	345	360	360
C_2H_6	0.7	<0.2	<0.2
H_2	370	110	90
HCN	100	10	7.3
NCCN	1.2	<0.2	<0.2
CH_3CN	0.6	<0.4	<0.4
CO	4.8	45	60
CO_2	4.0	135	125
Carbon Recovery (%)	52	95	96

IV. Further Investigations

A. Current Activities

A great deal has been learned about the pragmatic approach toward minimizing or avoiding wire aging problems. This tends to divide into three general areas of important factors: (a) the selection of the primary gas mixture and wire surface material; (b) the careful control or avoidance of certain gas contaminants or materials which accelerate aging through their outgassing or their reaction with the gas; (c) the choice of specific additives to the gas that help to suppress wire aging. Of course, some benefits can be derived by intelligent choice of other operating parameters, such as gain, gas flow rate, etc. However these usually do not exert the powerful influence over aging rates that are manifested by the choices made in (a) through (c). In many cases, the specific use intended for the chamber will restrict the choices available in (a)-(c). For example, a wire chamber vertex detector would select a gas with low diffusion ("cool"), small multiple scattering of particles, a relatively slow drift velocity, that could be run at high gain (1-3 x 10^5) to achieve good spatial resolution, and that could withstand the high radiation dose near the beam with acceptable aging. Dimethyl ether would be an appropriate choice of gas or perhaps a mixture using CF_4, such as CF_4/isobutane. If it is further desired to use charge division to obtain the longitudinal coordinate of the recorded signal, then a resistive wire must be used, a gold-plated wire being too conductive. Certain resistive wires may be attacked by gases or their additives (e.g. ethanol or water attacks Stablohm severely). Stainless steel wire appears to be inert to water and ethanol, but not to CF_4 mixtures(see Table III). Other applications will mandate different choices: a central tracking chamber might use pulse height information to obtain ionization measurements for particle identification, and hence would be required to operate at a lower gain ($\lesssim$ 5 x 10^4) than a vertex detector to avoid too much signal saturation. A wire chamber sampling calorimeter would require still different choices. In all of these cases, however, there would be certain purity requirements, and possibly certain additives used. At present there is still much to be learned about the factors in (a)-(c), and a good deal of activity is in progress. We discuss these categories in turn.

In the selection of the primary gas mixture, one should be looking for these qualities: (1) good quenching, (2) the component having the lowest ionization potential does not lead to polymerization in a discharge (plasma); (3) the products of plasma chemistry reactions are volatile. The search for new gases satisfying these criteria has revealed some promising candidates. One of these which is attractive for some purposes is CF_4/iC_4H_{10} (80/20), which appears to have very good aging properties (see Table III and Section II.C.4.), has a high drift velocity, high ionization density and yet has low diffusion [48,73]. This could be the choice for a detector in a high rate, high radiation environment, such as for SSC experiments [86]. Unfortunately, CF_4 is somewhat expensive. However, the remarkable stability of operation suggests that the presence of CF_4 even in much lower concentrations may be effective in reducing aging, and this idea is being studied [57]. Recent measurements of drift velocity show that high drift velocities are obtained with as little as 10% CF_4 (+ 90% CH_4)[51]. It is of interest to note that the use of CF_4 had been suggested earlier by Hess based on observations of plasma chemistry [84]. Another gas, not so new, that has been mentioned several times above but has so far only been used in laboratory tests to the knowledge of this author is dimethyl ether (DME). This gas has very low diffusion, ages very well when pure, but seems frequently to contain certain Freons, especially Freon 11 , which cause either aging [48] or progressive signal loss as a consequence of the electronegativity of the contaminant [49]. DME is also a somewhat expensive gas. Other relatively new gas mixes that appear to age very well are given in Table III, and include several CO_2-based gases: CO_2/iC_4H_{10}, CO_2/C_2H_6, and Ar/CO_2. In certain of these cases, an additive such as an alcohol (usually iC_3H_7OH) or water is needed to maintain stability, especially in the case of CO_2/iC_4H_{10}. A special requirement that may be placed on gases used at proton colliders (e.g. at FNAL, SSC), particularly for calorimeter applications, is that no hydrogen exist in the gas in free or combined form. This is because collisions of the copiously produced slow neutrons with hydrogen in the chamber gas cause large random energy deposits resulting in severe noise problems. These are some of the gases that are currently of interest, but this does not by any means preclude others not yet "discovered" that might be as good or better.

As for purity and material requirements, we have mentioned many materials proven to cause or suspected of inducing rapid aging, and these will be emphasized again in the discussion (Section V) below. Suffice it to say that there are a good number of "mysteries" as to what causes problems, and the lists given of "good" and "bad" materials are by no means complete or definitive. Moreover, even if we now had such complete lists, the job would not be done, because the problem of controlling or eliminating the "bad" materials is not a trivial task in a fully-mounted experiment. In some cases, it will be advisable to try to eliminate harmful impurities by installing appropriate filters or traps in the gas system, rather than by ordering very high purity gas and making a scrupulous choice of plumbing and chamber materials.

Finally, the judicious use of additives can eliminate or reduce aging problems even in the presence of otherwise harmful impurities. The explanations given for mechanisms resulting in the beneficial effects of alcohols, methylal and water are plausible, but not firmly established. These additives may react adversely with chemically active elements in the wire surface as is experienced with some resistive wires. The prescriptions for which additive to use, and how much, are now defined only by previous experiences of others, and it seems likely that additional beneficial additives may be found.

Therefore, it is appropriate to summarize the current activity as being productive toward finding new ways of solving wire aging problems, but that there is still much more to be learned through the present pragmatic approach.

B. For the Future

We have given in section III.D an example [84,85] of a direct measurement of the plasma chemistry occurring in an electric discharge at atmospheric pressure. Some of the same phenomena observed in low-pressure plasma experiments were also observed in this example,

such as the oxidation of certain hydrocarbon and cyanogen compounds by low levels of oxygen, the products being volatile and flowing out of the chamber. It was also seen in this experiment that polymeric residues formed on the electrodes in the absence of oxygen, showing that oxygen was effective in eliminating these deposits. This experiment was capable, in principle, of measuring reaction rates and determining reaction constants for the important reactions. One can imagine that a similar exploration can be made for wire chambers, the only differences being that the discharge is by d.c. rather than by a.c. current, and the fields at the electrodes are somewhat different resulting in different electron energies in the plasma. Again, in principle, the dominant reactions could be identified and measured under actual wire chamber operating conditions, and the effects of changes in these conditions measured as well (e.g. changes in gain, pressure, flow rate, etc.). Direct answers could be obtained on effects of impurities and additives. This would help toward establishing a model for the relevant plasma processes, and would allow some greater degree of predictability. Of course, this is too large an effort to accomplish on a short time scale; a lesson in that regard is the recognition of the immense amount of research invested in low-pressure plasma research to gain a semi-quantitative understanding.

However, there are parts of this approach which are appealing: (1) Many of the important reactions have already been identified, and some have been measured, in the low-pressure regime; as discussed earlier, there are strong indications that the same qualitative understanding is valid in our area of interest at atmospheric pressure. (2) Some of the same techniques that have been developed can be applied in our regime. (3) It is probably not necessary to examine more than a limited number of the most important reactions to reach an adequate understanding. One of the first goals of doing such atmospheric-pressure experiments should be to see whether there is a connection with the low-pressure measurements so that many of these latter results can be taken over and used. This would avoid a comprehensive, and therefore burdensome, set of measurements at atmospheric pressure. It is hoped that by such an approach a rather explicit model (or models) can be established to help identify conditions and gases that will permit good aging performance in wire chambers.

An example of recent investigations along these lines is shown in Fig. 16[42]. Chromatograms are shown that are the result of analyzing the effluent gas from a proportional counter under test. Argon/Ethane (50/50) is used as the supply gas, flowing at about 20 cm^3/min. In Fig. 16a is shown the result without any avalanche current, while in Fig. 16b an Fe^{55} source is used to induce a substantial current, about 4μA. The effluent gas is cryotrapped in both cases at a temperature just above the ethane boiling point, and the resulting condesate is analyzed using a gas chromatograph/mass spectrometer system. As is evident from a comparison of these graphs, a variety of species produced in the avalanche are detected, as manifested by the many strong peaks observed. Analysis of these peaks using the mass spectrometer shows them to be largely unsaturated hydrocarbons, just as expected from our simple models of the polymerization process. Somewhat unexpected is the occurrence of oxygen in many of the species. Oxygen was not available as a principal gas component but is known to occur as a contaminant in the supply gas at about 10 ppm concentration. Apparently, this oxygen is strongly involved in the plasma processes. As we discussed earlier, oxygen can inhibit further polymer chain growth, and there appears to be evidence in this example of that effect: when an oxygen filter is used upstream of the proportional counter, the resulting chromatogram shifts towards higher masses. Similar result have been obtained using other wire chamber gases, and further studies are in progress aimed at a more complete understanding of the process in the avalanche leading to polymer formation.

Although better understanding of the basic processes of wire aging should prove to be important, this line of investigation should not preclude the more direct approaches now utilized: (1) careful documentation of wire chamber aging in actual experiments, and (2) accelerated aging tests under controlled and monitored conditions in the laboratory. With regard to (1), it may prove useful to sample the gas as it exits from the wire chamber with the intent of measuring the trace components in the gas. By deliberately introducing these detected components in the gas of a laboratory test one may be able to identify the harmful and benign

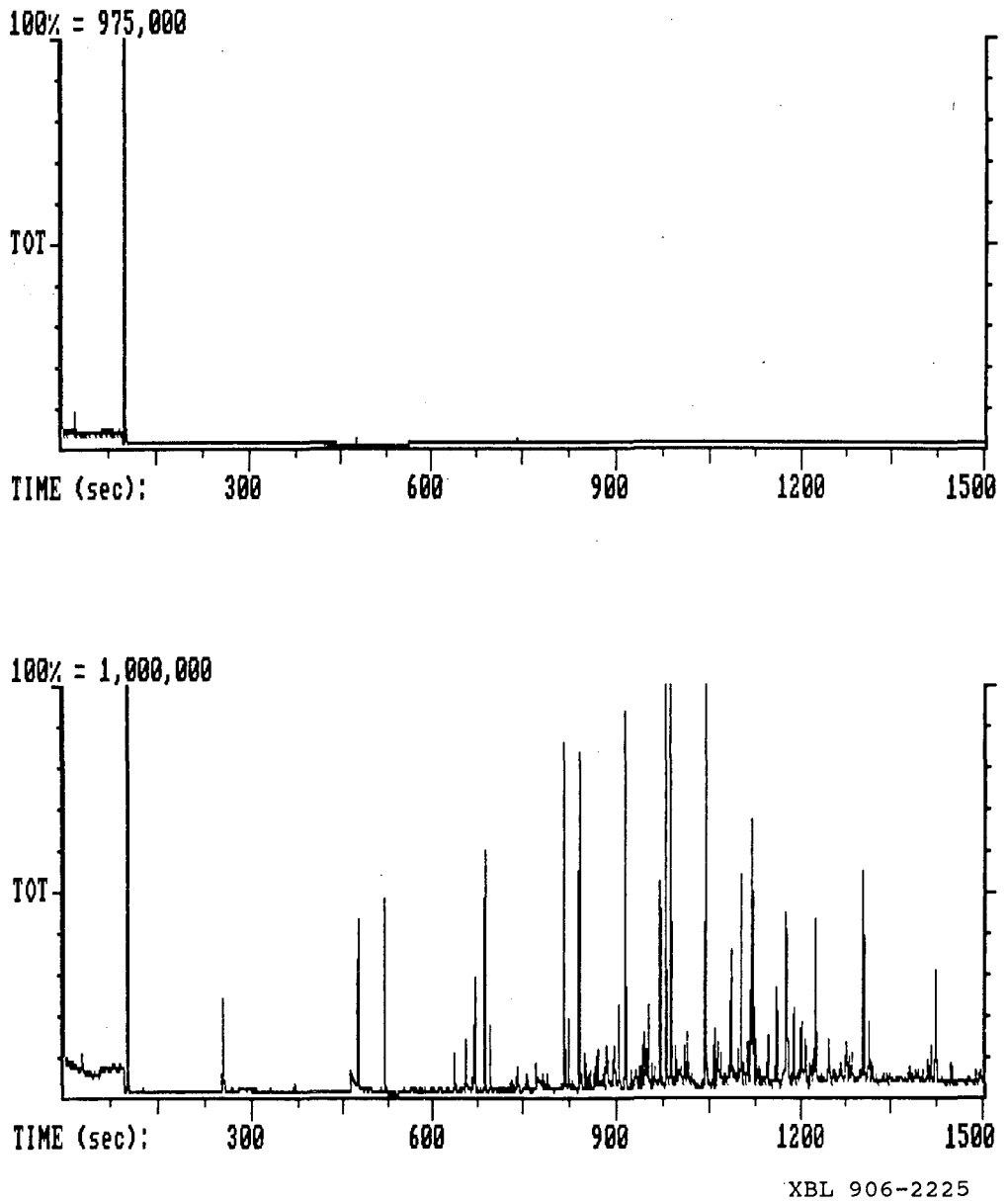

Fig. 16. Chromatograms of analyses of plasma chemistry reaction products. Pictured are: (a) result with no irradiation, (b) result when plasma-chemical reactions are induced by irradiation with an Fe^{55} source. The current density in (b) was 4.2 microamperes/6 cm, and cryotrapping was used to concentrate the sample over a 12 min period. The vertical is the total ion response of the mass spectrometer

contaminants, and to measure their effects. Appropriate measures can then be taken to avoid the harmful agents (e.g., using filters or traps, judicious selection of plumbing and chamber materials, etc.). With regard to (2), accelerated laboratory tests may be somewhat misleading if the wire aging does not scale simply with the total dose. Some tests should be done with the same total dose, but with different radiation intensities to establish the scaling, or measure departure from scaling. Perhaps there are other long-term aging effects unconnected with radiation effects (such as chemical attack of the wire surface).

The identification of suitable gases, wire materials, and other parameters can be most easily accomplished with laboratory tests. The extension of favorable tests to successful use in an experiment will be faced with additional problems, principally of maintaining the required purity. There needs to be a variety of such "solutions" for the variety of applications that will exist for wire chambers.

V. Principles and Guidelines

In this section we will try to give helpful guidelines in building and operating wire chambers in order to reduce aging problems. These guidelines are based upon reported experiments with detectors in experiments and upon laboratory tests. Four lists are shown in Table XI: (A) "Bad" materials or procedures, which are reasonably well established as causing serious aging problems; (B) "Good" materials or procedures, which are fairly well established to be either beneficial or at least not harmful; (C) Materials which have questionable reputations, or for other reasons may not be generally endorsed; (D) Other procedures which are probably acceptable, but have not had extensive testing. Some of these classifications are arbitrary, and based partly on this author's own experiences and prejudices.

It should be noted that a great many of the guidelines have to do with gas purity. This is because there exist quite a number of reports which indicate that clean gas systems together with a supply of very pure gas can reduce aging to small or negligible levels, while gas of the same or lesser purity flowing in a contaminated system will result in unacceptable aging. In a large-scale experiment, where the conditions are often difficult to control, the required level of gas purity many not be attainable by just eliminating all the known bad materials. Another approach, which has not yet been widely used but probably has much merit, is to place appropriate traps and filters just upstream of the chamber. There is the expectation that contaminants <u>downstream</u> of the chamber cannot diffuse into the chamber to cause significant aging, providing a reasonable gas flow is maintained, and the contaminating sources are not very close to the chamber. There is evidence to support this claim, but no firm "proof". Under these conditions, only the materials of the chamber itself can cause aging problems, and these can be more easily controlled. Bubblers then may be used well downstream so that vapors do not enter the chamber. Recent tests with an argon/ethane mixture indicate that the vapors of silicone oil and one-part RTV cause wire aging, and therefore mineral oil or deionized water rather than silicone oil should be used. If the gas is not recirculated, a long exhaust line might be used instead of a bubbler. To eliminate the gas contaminants, installation of a cold trap or a filter to "isolate" the chamber should be effective. For contaminants such as the lighter Freons, a molecular sieve of the appropriate type may be the answer. Certain sieves will stop halogens and let the desired chamber gases through, but care must be taken in the choice of sieve to be sure that the principal gas components do not react with the sieve.

Finally, it would seem prudent to take samples of the gas just at the entrance and exit of the chamber, and have them analyzed for trace components. Perhaps this would only be done at the beginning of an experiment, and occasionally thereafter, but it requires some knowledge of technique to extract a satisfactory sample. However, a proper gas analysis, coupled with previously measured effects of observed contaminants, should allow prediction of the aging rate with some confidence, assuming the radiation level during the experiment can be estimated.

Table XI. Recommendations: Materials and Procedures

A. "Bad" Materials or Procedures

- Halogen impurities, especially chlorinated compounds
- Silicon Oils or greases
- Single-part RTV adhesive
- Polyurethane adhesive (soft)
- PVC (Tygon) tubing
- Teflon tubing (unbaked)
- Neoprene rubber gaskets, O-rings
- Some Cu tubing (drawn using oil lubricant)
- Acid flux for solder
- Mold-release agent (plastic pieces, G10 sheets)
- Certain plastic cable insulation (with plasticizers)

- Unbaked Teflon, Macor, Mylar, (and probably other plastics) Viton, glass-bonded mica, in contact with dimethyl ether[1]
- Ethyl bromide in contact with Al

- Any gas containing CO_2 with wire having a chemically active surface

- Aluminum oxide layer on cathode with high cathode field ($\lesssim$10 kV/cm)
- Stablohm wire with ethanol or methanol

- Chlorinated solvents used in cleaning gas plumbing components

B. "Good" Materials or Procedures

- Glass, Lucite, Mylar
- Stainless Steel, Al (except as cathode)
- Gold plated wires (all electrodes)
- Electropolished stainless steel tubing
- Hydrogen-fired Cu gas tubing
- Nylon (best), Poly-flo (good) tubing
- Most other clean metals
- Hard epoxies
- High-purity chamber gas in general

- Highest purity Ar (other than Research Grade)
- CP grade ethane
- Coleman grade CO_2

- Delrin, Nylon, Kalrez, in chambers with dimethyl ether[1]

- Clean suspected plumbing connections, valves, etc. in high purity grade of isopropanol

- Gas filters and traps, close to (and upstream of) chambers: consider using molecular sieves
- Additives to gas when needed: ethanol and/or water with gold plated wire; isopropanol with all wire

Table XI. Recommendations: Materials and Procedures (continued)

- Electrical discharges: can dissociate chamber materials, creating harmful deposits, vapors
- Even a single exposure of gas system to contaminated gas (this can leave behind outgassing residues)
- Trace analysis of gas entering and leaving chamber
- Low field ($\lesssim$20 kV/cm) on cathode and other "negative" electrodes
- Do laboratory tests on wire chamber prototype

C. Questionable Materials

- Contact cements (acrylic): low viscosity cements can "bloom"
- Five minute epoxies (somewhat hygroscopic, otherwise, OK)
- Vinyl tapes
- G10: Probably OK by itself, but may have silicone mold-release agent on surface, which would be "bad"
- Nicotin and Stablohm wires: may age rapidly with any oxygenated compounds in gas. Stablohm is acceptable when isopropanol additive is used with Ar/C_2H_6. Recent laboratory tests indicate that both wires be used with DME. See results in Table III with ethanol, dimethyl ether).
- Stainless steel wires: do not age in most applications, but do age rapidly in CF_4/isobutane (80/20).

D. Other Recommended Procedures

- Very pure gas mixtures are satisfactory without additives, but gas system must be kept very clean (difficult).
- Mineral oil or deionized water in bubblers, or direct exhaust of gas with no bubbler, through long exhaust line

[1] A much more complete list can be found in Appendix A of various materials exposed to dimethyl ether, and the observed effects (list is courtesy of M. Jibaly and S. Majewski, University of Florida, now at University of Northern Iowa and CEBAF, respectively).

VI. Conclusions and Summary

We have examined the progress which has been made in understanding the processes leading to aging effects in wire chambers. These effects are largely due to wire coatings resulting from a variety of possible polymerization processes. Although these processes are not yet specifically identified in wire chambers, there exist sufficiently close analogies with similar processes observed and studied in the more mature field of plasma chemistry that it is reasonable to assume that these same reactions apply to wire chambers as well. Data relevant to observed wire aging is collected both from experiences with wire chambers in various experiments, especially those in high energy physics, and from laboratory tests on wire aging, where the conditions are relatively well controlled and monitored. A reasonably coherent picture emerges, which, when correlated with results from plasma chemistry, seems to offer some qualitative explanations for aging processes.

Still, the present state of knowledge does not allow one to formulate a complete set of procedures to follow in order to avoid wire aging. It is necessary to generalize from the reported results to obtain what may be considered guidelines for prudent design and operation of a wire chamber system, with regard to minimizing wire aging.

Summarized in tables are the reported aging results from experiments and laboratory tests, and guidelines for use of safe materials to use in construction and operation of chambers. Some additional advice is given on achieving a low rate of aging in an experiment by filtering and monitoring gas composition. Finally, it may not be so difficult to gain a much better understanding than we now have of the plasma chemistry which is predominant in the wire aging processes. To illustrate this point, there is some discussion of results from the field of plasma chemistry with examples showing the relevance to wire chamber aging phenomena. Systematic investigations in this area may prove to be quite fruitful in reaching the ultimate goal of selecting suitable wire chamber gases, wires, and operating conditions that will suppress the aging rate to a predictable and acceptable level.

Acknowledgments

A review paper necessarily draws upon information and ideas from a large number of collaborators, and in this area, particularly, progress depends crucially upon collection and dissemination of results. First and foremost, the contributors of the information included herein are gratefully acknowledged. My collaborators on this project include Professors Dennis Hess and Michael Williams of the Department of Chemical Engineering of the University of California and Jonathan Wise in the graduate school of Chemical Engineering, who have been extremely helpful in providing the guidance in the fields of plasma and polymer chemistry, and have also contributed very much in many ways to the preparation of this paper. My thanks also go to Bob Kenney, who has read the manuscript several times, pointing out potential improvements. Finally, I give my thanks to Aletha Lundblad, whose patience in the initial preparation of the paper was indispensable, and to Martin Jara and Jeanne Miller, who helped to put it into final form.

Glossary

Blooming: A term used here to describe the deposition of a light coating of solid material in the vicinity of an evaporating solvent. In the case encountered here, the evaporation of some low viscosity acrylic cements can leave insulating films of plastic on the cathode, resulting in high dark current or Malter discharge.

DME: Dimethyl Ether, $\begin{array}{c} H\ \ H \\ HC\text{-}O\text{-}CH \\ H\ \ H \end{array}$, a low diffusion ("cool") gas with very good radiation hardness and quenching properties. It also has a relatively high ionization density for charged particle tracks and quite a low diffusion constant, and is therefore a good candidate for high resolution ("vertex") wire chambers.

Free Radicals (Sometimes simply called "radicals".): Any species, charged or neutral, with one or more unpaired electrons (unsatisfied valence bonds).

Examples of neutral radicals are: $\begin{array}{c} H \\ HC\cdot \\ H \end{array}$ or $\cdot\begin{array}{c} H\ \ H \\ C\text{-}C \\ H\ \ H \end{array}\cdot$ which are written as $CH_3\cdot$ and $\cdot C_2H_4\cdot$ (or C_2H_4:). Free radicals are chemically very reactive, and are an important ingredient in polymer formation. Neutral radicals are thought to play a much more prominent role than charged radicals (or ions) in the plasma chemistry of interest here.

Freons: A trade-name (DuPont) for halogenated hydrocarbons used for refrigerants, aerosol propellants, etc. The nomenclature is now changing to CFC, standing for "chlorofluorocarbons". Freons are generally volatile, non-toxic, and non-flammable. Examples: Freon 11, $CFCl_3$; Freon 12, CF_2Cl_2; Freon 13, CF_3Cl; Freon 14, CF_4; Freon 113, $C_2F_3Cl_3$; Freon 22, CHF_2Cl; Freon 13B1, CF_3Br (Used in CERN "Magic Gas"). (see CRC* handbook under "refrigerants" for a more complete listing). Certain Freons, e.g. $CFCl_3$, cause ozone-depleting reactions in the upper atmosphere, and are being replaced by more benign compounds. The Freon naming scheme (by Dupont) is such that if 90 is added to Freon number, the digits in the resulting sum give the number of carbon, hydrogen, and fluorine atoms in the compound, the remaining atoms needed to saturate the molecule being chlorine (if not designated otherwise, e.g. 13 B1). In Freon 22, for example, 90 + 22 = 112, indicating one carbon, one hydrogen, and two fluorine atoms per molecule.

G10: Tradename for a fiberglass-epoxy flexible bonded material, frequently used for wire chamber walls in sheet form.

Hydrogen Abstraction: The process of removal of a hydrogen atom from a molecule by a radical, thereby causing the remaining molecule to become a free radical. An example would be the Cl· radical, which can abstract a hydrogen from methane to form a $CH_3\cdot$ radical: $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$

Iso-butane, -propanol, etc.: "Iso" denotes a specific type of branched chain structure of a molecule having the same atomic composition, but different molecular structure than a linear chain. For example,

$\begin{array}{c} H\,H\,H\,H \\ HC\text{-}C\text{-}C\text{-}CH \\ H\,H\,H\,H \end{array}$ represents butane and $\begin{array}{c} H\ \ H\,H \\ HC\text{-}C\text{-}CH \\ H\ \ |\ H \\ HCH \\ H \end{array}$ represents isobutane.

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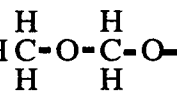
* Handbook of Chemistry and Physics, CRC Press.

We abbreviate iso- as "i", so that isobutane is written iC_4H_{10}.

Magic Gas: A mixture or Ar/iC_4H_{10}/Freon 13 B1 (75/24.5/0.5) developed at CERN and used to obtain large pulse-height signals (self-quenching streamer pulses) from multi-wire proportional chambers [21].

Malter Effect, Malter Layer, Malter Dipole: The deposit of a thin insulating layer, called a Malter layer, on a cathode (or wire negative with respect to anode) can collect positive ions that are drawn from the avalanche at the anode. Since the layer is insulating these ions continue to collect until a very large electric dipole, called a Malter dipole is established across the layer. This layer consists of the positive ions on the side toward the anode, and the induced negative image charge on the conducting cathode surface. The resulting electric dipole field can be large enough to overcome the work function of the cathode material (~4-5 eV for non-alkali metals) and extract electrons, a process known as field emission. Many of these electrons are not neutralized at the ion layer, but continue into the gas, drift to the anode, and initiate secondary avalanche discharges, resulting in still more positive ions, which then drift to the cathode and reinforce the Malter layer. This regenerative process results in a "self-sustained" current that causes more deposits to build up continually and to spread to other uncoated regions, resulting eventually in a breakdown of chamber operation.

Methylal:



. It is liquid at room temperature (B.P.=45°C). Added to "Magic Gas" by the CERN group, the lower ionization potential (10.0 eV) for methylal than that of argon (15.8 eV) results in charge exchange, the methyal ion being neutralized at the cathode and then de-exciting by fragmentation, instead of by photon emission as does argon.

Monomer: The monomer is the initial molecule which enters into the polymerization processes. The monomer reacts with itself in the polymerization process to form a high molecular weight compound, or polymer.

Nicotin Wire: A resistive wire, used as anode wires for the charge-division readout technique. Manufactured by Microfil (Switzerland). Nicotin consists of: cobalt (38.9%), chromium (19.3%), nickel (15.6%), iron (13.3%) and molybdenum (11.4%) (see Stablohm wire also).

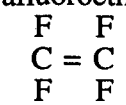
Plasma: A region containing electrically positive, negative and neutral species, usually resulting from an electrically-induced discharge (direct or alternating current). The net charge of the region is approximately zero. The charged species can be positive or negative ions, or electrons, while the neutral species may be excited or ground state atoms or molecules, or free radicals.

Plasma Chemistry: Chemical reactions between various species in a gas plasma. Until the present, most plasma chemistry investigations have been done at low pressures (~0.1-1.0 Torr), using r.f. (radio frequency) discharges to produce the plasma.

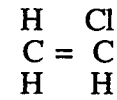
Plateau Region: A relatively flat portion of the curve describing counting rate (or counting efficiency) vs. voltage applied to a counter. Below the plateau, not all particles are detected due to insufficient gain, and at the upper end of the plateau spurious counts are detected due to "noise" and feedback effects.

Polymer: A molecule, frequently very large, formed by linking together one or more types of monomers in the polymerization process. Polymers formed in plasma processes are generally solid, and highly branched and cross-linked, such that the resulting polymeric material has excellent adhesion to the substrate (e.g. the wire), has strong resistance to most chemicals, and is insoluble in most good solvents (i.e. it is very difficult to remove).

PTFE (or TFE Teflon): Polytetrafluoroethylene; a fluorocarbon polymer: Teflon (tradename of Dupont). The monomer is:



PVC: Polyvinyl chloride. The Vinyl chloride monomer is:



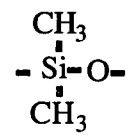
A polymer frequently used in plastic tubing (e.g. Tygon brand PVC tubing), and usually with plasticizers (e.g. dioctyl phthalate) added to render the tubing flexible. (Phthalates are found in wire deposits).

Quenching: The ability of a constituent of a gas mixture to absorb energetic photons (or otherwise absorb energy, e.g. by charge exchange) and de-excite without photon or electron emission from the molecule of the constituent, usually by fragmentation of the quenching molecule. Hydrocarbon gases (e.g. CH_4, C_2H_6, iC_4H_{10}) are commonly used as quenching gases.

RTV: Room temperature vulcanizant. A commonly used silicone-based sealant. It can be used as a one-part "gel" (which may smell like acetic acid), or prepared as a mixture of two liquids. The former type of RTV is known to be associated with aging [4], while little is known of the aging effects of the latter.

Self-sustained Current: See Malter Effect.

Silicone(s): A generic name for silicone polymers, whose backbone chain consists of alternating silicon and oxygen atoms, with hydrocarbon groups appended to the silicon atoms. Monomer:



Species: In a plasma, any constituent atom or molecule (including ions and free radicals) which may pla reactions.

Stablohm Wire: A resistive wire, used as anode wires for the charge-division readout technique. Manufactured by California Fine Wire (U.S.). Stablohm 800, which is simply called Stablohm in this article, consists of: nickel (75%), chromium (20%) and (aluminum + copper) (5%). (See also Nicotin wire).

(First) Townsend Coefficient, α: The mean number of ion pairs produced per unit length of drift along the electric field direction by an electron in an avalanche. The reciprocal is the mean free drift path for ionization. The reduced value, α/p, depends only on the reduced field, E/p, where p is the gas pressure.

Vertex Detector: A specialized high spatial resolution wire chamber used to reconstruct tracks from charged particles originating at a common production point, or vertex.

"Whiskers": Jargon used to describe bristle-like deposits often seen on anode or cathode wires and resulting from wire aging processes. Whiskers are thought to be forms of organic polymers usually, but could be similar to carbon filaments in some cases.

Wire Chamber: A gas-filled radiation detector that senses formation of ion pairs in the gas due to passage of charge particles or interaction of photons. The electronic signal obtained depends upon an avalanche process occurring in the intense field very near the anode or "sense" wire. The drifting primary electrons are multiplied by a large factor in the avalanche, which can be as high as $\sim 10^6$. This factor is called the gas gain, or simply "gain". Wire chamber sense wires have a small diameter, typically ~10-50 μm, while cathode wires usually have a much larger diameter, perhaps 100-200 μm. The cathode may also be a continuous electrode, such as a conducting sheet or tube wall. In the latter case the chamber has been traditionally called a "proportional counter". This name refers to

the fact that the response at lower gains is proportional to the initial ionization. Wire chambers may also be operated in modes other than the avalanche mode, e.g. Geiger and self-quenching streamer modes, resulting in much larger responses (not proportional); these latter types of chambers are not emphasized in the present paper.

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APPENDIX A*

EFFECTS OF EXPOSURE OF VARIOUS MATERIALS TO DME

Material	Structure/Form	Type of Exposure	Observed Effects	References
Adiprene[a]C	Not specified	Lab immersion testing[k]	11% linear swell	7
Brass	Gas connectors	Many months exposed to gas	No problem in chamber operation	6
Buna N	Not specified	Lab immersion testing[k]	20-25% linear swell	7
Butyl Rubber	Not specified	Lab immersion testing[k]	8-12% linear swell	7
Carbon-fibre compos.	Not specified	1 month exposed to gas	OK except weight increase[c]	2
Celanese X[j]	Sample	1 month immersed in gas	0.5% weight increase	4
Delrin[a]	Feedthrough	1 month in pressurized gas	Swelling	1,3
	Feedthrough	1 month in pressurized gas	Swelling, 1% weight increase	4
	Sample	1 month in pressurized gas	1.2% weight increase	4
	Endcap	Many weeks exposed to gas	No problem in chamber operation	6
Epoxy[d]	Not specified	1 month exposed to gas	OK except weight increase[c]	2
Fluorosilicone	Not specified	Lab immersion testing[k]	3% linear swell	7
Glass-bonded mica	Endcaps	Several days exposed to gas	Produced flakes on wires	6
Kalrez[a]	O-ring	Normal exposure to gas	No change in current or gain	2
	O-ring	Many weeks exposed to gas	No problem in chamber operation	6
	Not specified	Lab immersion testing[k]	3% linear swell	7
Kapton[a]	Foil	1 month in pressurized gas	1% weight increase	4
	Sample	1 month immersed in gas	3.5% weight increase	4
Macor[a]	Endcap plugs	Many days exposed to gas	Caused quick wire damage (deposits)	6
Monel (Ni alloy)	Gas tubing	Many weeks exposed to gas	No problem in chamber operation	5,6

APPENDIX A*
continued

Mylar[a]	Foil	1 month exposed to gas	OK except weight increase[c]	2
	Small pieces w/SnO_2 coat	Many weeks exposed to gas	No problem in chamber operation	6
	Aluminized Straw	1 month in pressurized gas	1% weight increase, 0.1% length increase,	1,3
	Aluminized straw	1 month in pressurized gas	2.5% weight increase, 0.35% length increase, tends to curl along length	4
	Aluminized Straw	1 month immersed in gas	1.4% weight increase	4
Neoprene W	Not specified	Lab immersion testing[k]	11-13% linear swell	7
Nordel[a] (EPDM)	Not specified	Lab immersion testing[k]	9% linear swell	7
Nylon 11 (Rilsan®)	Gas tubing	Many months exposed to gas	No problem in chamber operation	5,6
Plexiglas (acrylic)	Not specified	1 month exposed to gas	Weight increase,[c] signs of surface damage[g]	2
Polyethylene	Sleeve gasket	Not specified	Performs very well[l]	8
Polypropylene	Laminated gasket	Not specified	Performs very well[l]	8
Polyurethane	Not specified	Lab immersion testing[k]	20-40% linear swell	7
PVC	HV wire insulation	1 month exposed to gas	OK except weight increase[c]	2
Scintillator NE 110	Not specified	1 month exposed to gas	Weight increase,[c] milky appearance, scaled surface	2
Silicone	Not specified	Lab immersion testing[k]	15-17% linear swell	7
Silicone oil	Outlet gas bubbler	Several weeks exposed to gas	Produces Si contamination on wires	5
Stainless steel	Cathode surface wires, etc.	Many months exposed to gas	No problem in chamber operation	6
Stesalit[h] glass epoxy	Not specified	1 month exposed to gas	Weight increase,[c] signs of surface damage[g]	2
	Sample	1 month immersed in gas	0.1% weight increase	4
T-100[b]	Not specified	Lab immersion testing[k]	2% linear swell	7

APPENDIX A*
continued

Teflon[a]	Not specified	1 month exposed to gas	OK except weight increase	2
Teflon (FEP type)	Gas tubing	Several hours/days of exposure to gas	Poisoning gas with electronegative outgassing	5
Thiokol FA	Not specified	Lab immersion testing[k]	7% linear swell	7
Torr-Seal[f] epoxy	Around windows and holes	Many weeks exposed to gas	No problem in chamber operation	6
U-105[b]	Not specified	Lab immersion testing[k]	9% linear swell	7
Vetronite (G-10)[f]	Not specified	1 month exposed to gas	OK except weight increase[c]	2
	Sample	1 month immersed in gas	0.4% weight increase	4
Viton[a]	O-ring	Normal exposure to gas	Attacked by ethers,[e] produces F on wires	2
Viton[a]A	Not specified	Lab immersion testing[k]	33-59% linear swell	7

*This table has been kindly contributed by Mohammed Jibaly and Stan Majewski of the University of Florida, Department of Physics (now at University of Northern Iowa and CEBAF, respectively).

[a] ®E.J. Du Pont de Nemours & Co. (Inc), Wilmington, DE.
[b] ®American Gasket and Rubber Company.
[c] The authors do not give the percentages of weight increase.
[d] The authors do not specify what kind of epoxy.
[e] The nature of the "attack" is not explained by the authors.
[f] ®Varian Associates Lexington, MA.
[g] The surface damage is observed as a change in surface appearance under the electron microscope, which the authors attribute to a dissolution of the bonding agent between fibers.
[h] ®Stesalit AG, Zullwil, SO., Switzerland. Stesalit is a non-woven fiberglass matting embedded in epoxy resin.
[i] G-10 is a NEMA standard for a non-brominated woven fiberglass-epoxy laminate.
[j] Made by Celanese Corp., New York, NY.
[k] The sample is left in a sealed pressurized tube for the full span of its lifetime (≈3-4 years), and the expansion is measured at the end of this period (private communication from Ester Nudel, du Pont, Delaware).
[l] The reference did not provide specific details about the testing procedure or the observed performance.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720