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LONG TERM FLIGHT ELECTRODES

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FOREWORD

This investigation was conducted under NASA Research Contract ~~NAS 92762~~ NAS9-2762 with the Institute of Research and Instrumentation, Houston, Texas. The prinicpal investigator is grateful for the cooperation and many helpful suggestions of Mr. J. L. Day, who was instrumental in generating many of the ideas utilized in the research approach.

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INTRODUCTION

Since the advent of the first crude electrocardiograph, various means have been devised to intercept the minute electrical voltages which appear at the body surface as a result of heart activity within. As a group designation the device is generally referred to as the physiologic electrode; that is, an electrical terminal for the bioelectrical source. Classically the electrode is a piece of conductive metal held in contact with the skin by means of an attached elastic strap. Also, classically, the ECG is accomplished on an entirely static body. As a combination, the plate electrode attached to a static body appears to be a marginally satisfactory system. However, as the advantages of stress cardiogram on a dynamic body become apparent, the inadequacies of the classical electrode also becomes evident. Perusal of the commercially available devices disclosed the fact that no electrode did exist which uniquely satisfied the requirements for a stress cardiogram, and the electrode was subject to further limiting restrictions imposed by flight gear, comfort, etc.

The scope of the present work has been limited to matters concerning the reproducibility, stability, and methods of preparation for the various types and forms of biomedical electrodes, in an attempt to resolve or settle some of the contradictions and conflicting opinions concerning these important types of electrodes.

A further aim of this investigation is to perform a useful service which existing electrocehmical publications do not offer, i.e., it is intended to meet a demand for a critical and selective compilation of information on biological and/or physiological electrodes.

SILVER-SILVER HALIDE ELECTRODES

The silver-silver halide electrodes may be grouped into five types according to the methods of preparations: (1) Electrolytic, the electrolytic deposition of both silver and silver halide, (2) Thermal, the decomposition in a furnace of paste of silver oxide, silver chlorate (or bromate, iodate), and water to form the silver-silver halide, (3) Thermal-electrolytic, the electrolytic formation of the silver halide on thermally produced silver oxide paste, and (4) pressed pellet electrode, such as silver powder in combination with powdered silver chloride, and (5) miscellaneous, such as the use of precipitated silver halide in silver. The status of the silver-silver halide electrode will be considered in detail with particular emphasis on the electrolytic and pressed pellet types. The data on the standard electrode potentials and on the use of these electrodes as reference standards in non-aqueous, and mixed solvents are also covered in this report.

REPRODUCIBILITY AND STABILITY OF THE SILVER-SILVER CHLORIDE ELECTRODE

An examination of the literature reveals conflicting data and opinions concerning the reproducibility and constancy of the silver-silver chloride electrode. It has been suggested that electrolytically deposited silver could not be used with reliance unless the strains in it were removed in some manner. The coating of thermally deposited silver is considered nearly strain-free, since it is annealed during the process of deposition. Work has also been reported that the potentials of electrodes having electrolytic silver on platinum were 1.7 mv. less than those of granular silver electrodes prepared by reduction of silver nitrate with ferrous sulfate. This may indicate that the energy content of the electrolytic electrode was higher, possibly owing to a state of strain of the surface. Very little information on this point has been reported. The large bias potentials observed by some investigators on intercomparison of the electrolytic type of electrodes may probably be attributed in part to strain in the electrode surface (due to the nature of the platinum base) or to the methods of silver deposition and chloridizing.

A further point which has been the subject of conflicting views concerns the sensitivity of the silver chloride electrodes to light. The electrodes have been used in darkness or subdued light by a large number of investigators and some indicate that light does cause an appreciable change in potential of the silver-silver chloride electrode. On the other hand, there have been a number of reports to the effect that these electrodes were not appreciably sensitive to sunlight and could be used without the inconvenience of working with restricted illumination. In the latter instances the electrodes were a plum shade in color, and on direct exposure to light did not appreciably change in potential or color. The electrodes that were reported by some to be sensitive to light were white in color. On exposure to light these changed in potential and darkened to a brown color. Work performed in this laboratory indicated that the shade or color of the silver chloride electrode has no effect on its potential.

In addition, a drift in the potential of silver-silver chloride electrodes has been attributed to the effect of air dissolved in the solution. The cause for this poor behavior in acid solutions was probably a slow primary oxidation reaction:

$$2\ Ag + 2\ HCl + 1/2O_2 \rightarrow 2\ AgCl + H_2O$$

When the oxygen was removed from the solutions by purging with nitrogen, the potential of the electrode was observed to be steady and reproducible.

ELECTRODE CONFIGURATION

The improved electrode developed is shown in Figures 1&2. This device differs from the classical electrodes in many respects. The direct metal-to-skin contact is eliminated and an ionic-conductive path is substituted. The current passes through a compatible electrolytic gel which provides the conductive electrical bridge with a peripheral area that incorporates an integral layer of contact adhesive (Stomaseal) for attachment to the body.

Electrical contact was made through a copper wire (Calmont Wire and Cable Company) to the back of the silver disc. In this electrode, the danger of mechanical disturbance of the sensitive silver-silver chloride layer was minimized by the rigid structure of the lucite housing. Electrical noise was also minimized by sealing the silver disc to the lucite housing with a non-conductive Epoxy cement (Scotchcast Resin #8).

The skin area where the electrode is to make contact is first cleansed with alcohol to remove surface oils and easily removed foreign matter. The area is then washed with a detergent solution. The adhesive layer applied to the lucite housing is now uncovered by removal of the protective film which is provided for preservation of the contact adhesive until ready for use. The electrode is then pressed into place on the skin.

The major source of error in making measurements, according to the technique described, is unsuspected leaks to the ground. The insulation of the lead to the silver electrode should be of the highest order and have optimum electrical and physical properties. Scotchcast #8 is desirable, however, other materials such as acrylics are quite adequate substitutes.

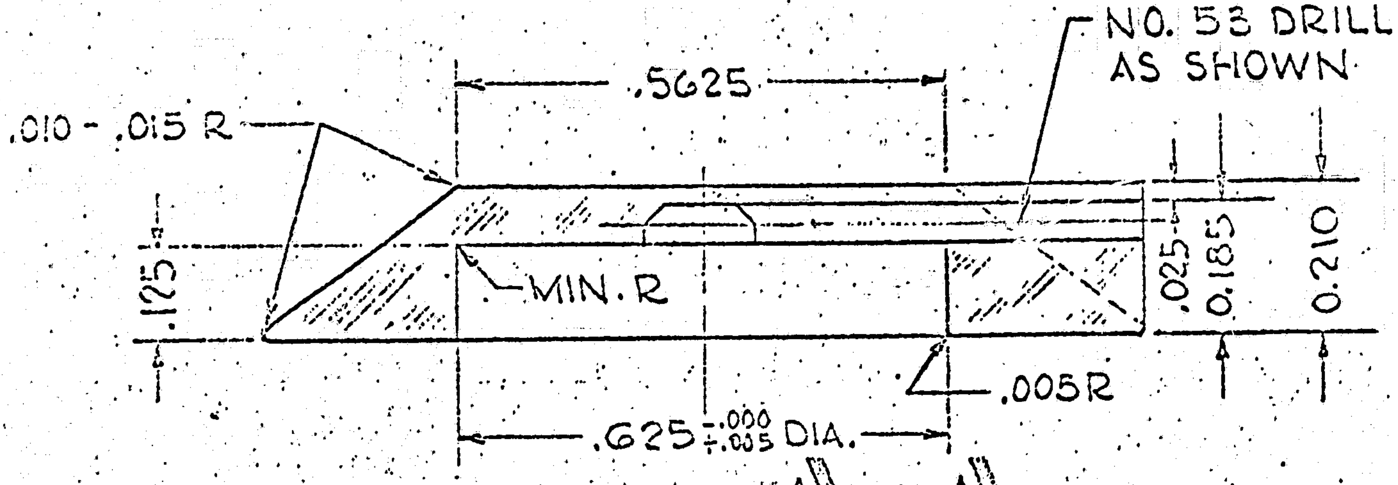
As an aid to systematic evaluation of the device, electrical, physical, and other criteria are considered next. Each criterion will be explained and a brief discussion of the appropriate IRI characteristics will follow.

The primary source of interference when the subject moves is displacement of the electrodes and temporary changes in the resistance between the electrode and the skin. Inasmuch as there are constant electromotive forces - galvanic and those produced by polarization between the skin and the electrode, changes in the resistance induce current fluctuations which sometimes exceed the amplitude of the useful signal. The electrode construction suggested, and the manner of attachment, serve to reduce these sources of interference to the minimum in that they ensure reliable mechanical and electrical contact ie, the visco-elastic gel; minimization of the galvanic e.m.f. and the polarization e.m.f. by use of the gelatin coating.

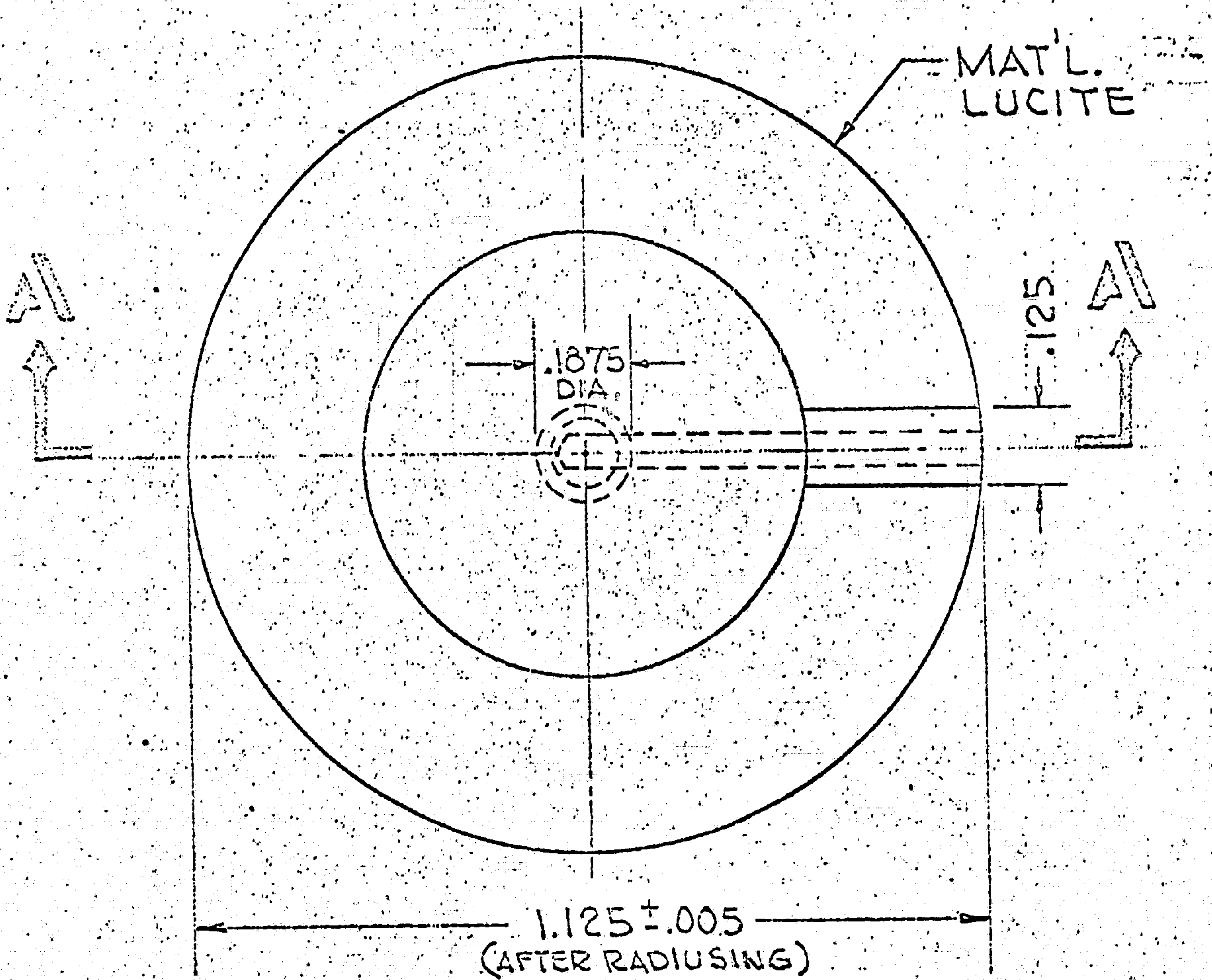
Trials of these gelatin electrodes have shown that they have a low sensitivity to mechanical effects: tapping on the electrode or pulling on the lead did not cause any material interference during the recording on an Offner Recording potentiometer with these electrodes, whereas, with ordinary electrodes, silver-silver chloride electrodes there were gross distortions under these conditions.

Another advantage of this method for the derivation of electrode potentials is that it avoids the use of bands or straps around the chest which restricts movements; the subject is practically unaware of the electrodes and they function for several hours uninterruptedly.

It is suggested that this type of electrode be used for the recording of other potentials (ECG, EMG, EEG) in man or animals during movement or in a quiescent stage.



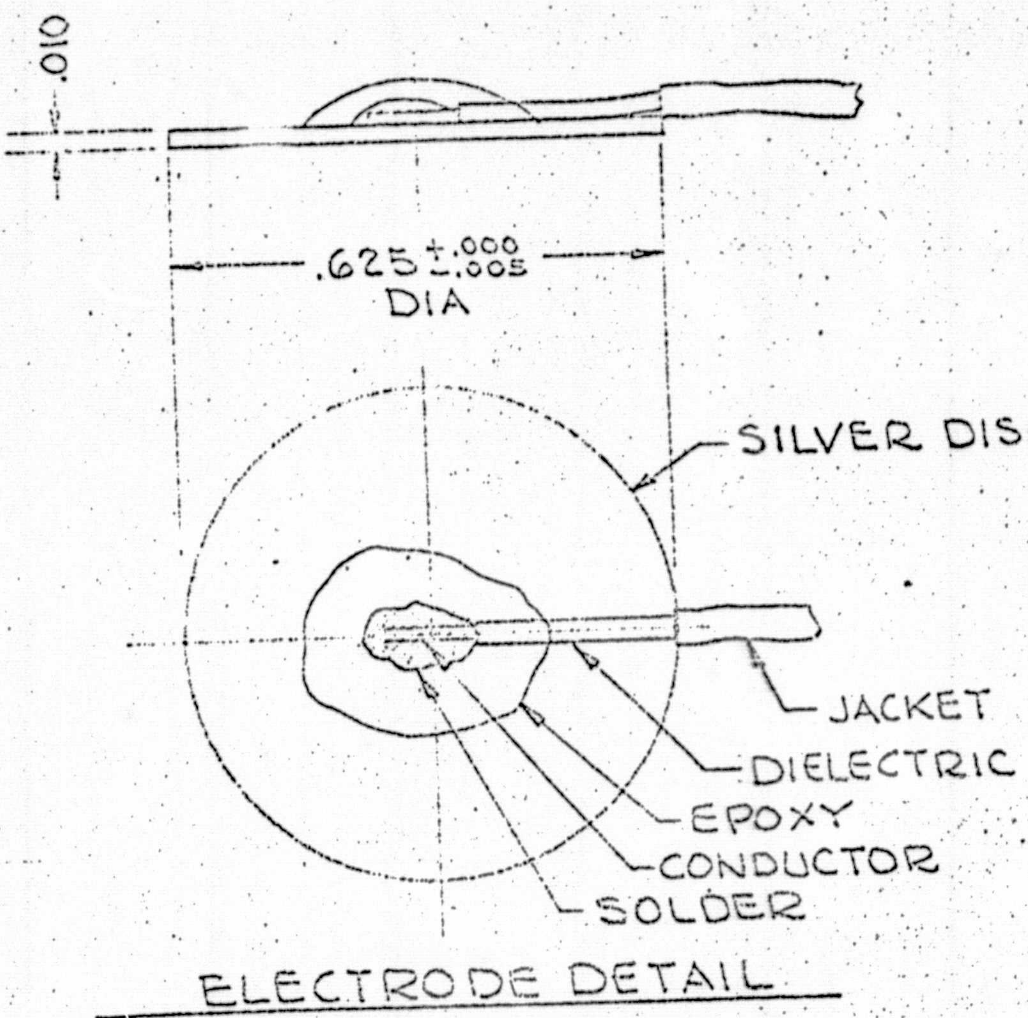
SECTION A-A



TOP VIEW

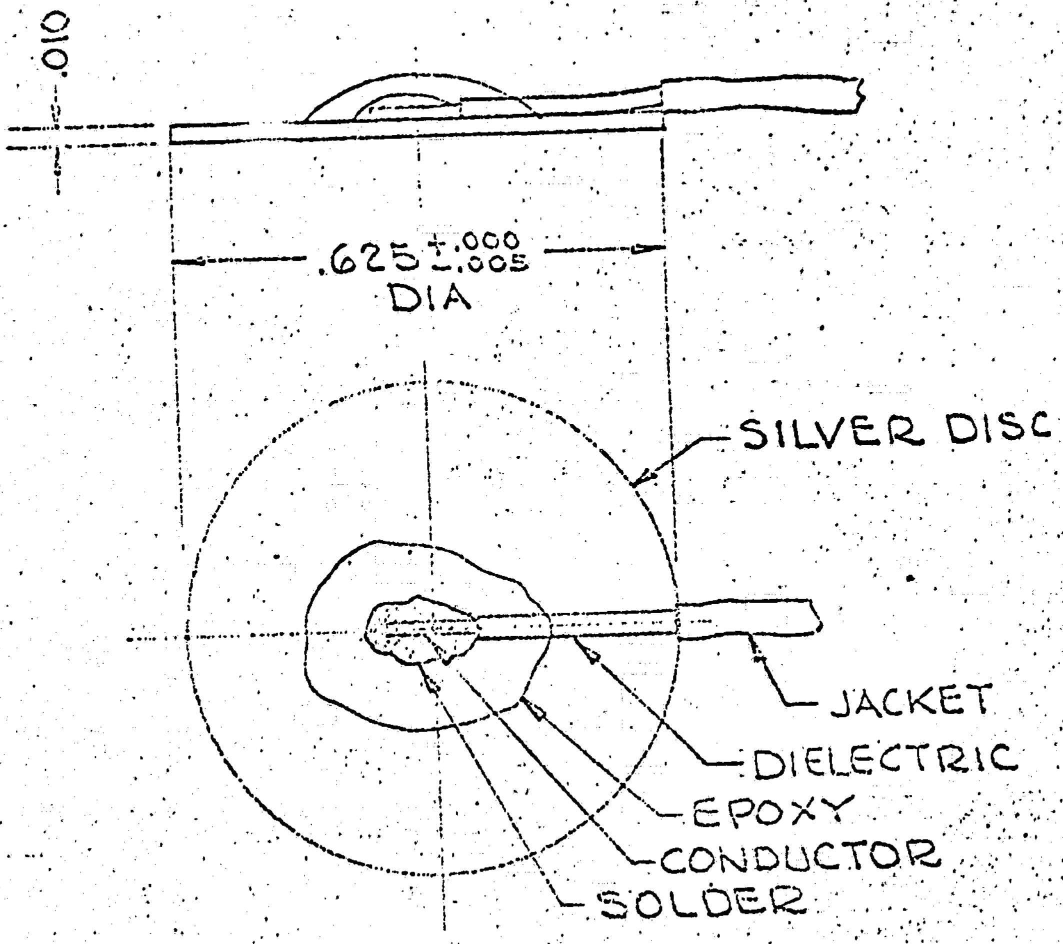
ELECTRODE HOUSING

FIG. 1



ELECTRODE DETAIL

FIG. 2



ELECTRODE DETAIL

FIG. 2

ELECTRODE CHARACTERISTICS

A careful study of the silver-silver chloride electrode to evaluate the effect of light, dissolved air, and the change in potential of this electrode with time has also been made.

The electrodes were tested in the presence and absence of air, using a solution of 1.0 M potassium chloride as the supporting electrolyte. The reproducibility among individual electrodes when silver-silver chloride electrodes are prepared at the same time was found to be 0.02 mv.

The aging effect, i.e., change in potential with age of the silver-silver chloride electrode was also studied. It was observed that older electrodes were slightly electropositive to newer electrodes and that the effect was always in the same direction and of the same order of magnitude, within 0.05 mg. Since similar electrodes were always opposed to one another, this effect was partially compensated for, so that error from this source was minimized. The possibility of the occurrence of an aging effect may not have been recognized in some of our earlier work. This may have lead us to discard the totally electrolytic type of electrodes in favor of the gelatin coated electrode. This would account for large differences in the standard electrode potential of silver-silver chloride electrode and the

mv?

gelatin coated silver-silver chloride electrode.

Having eliminated the factors above with reference to the aging effect, the effect of concentration-polarization within the silver chloride layer was studied as a possibility of causing this effect. Thus, when silver electrodes are chloridized electrolytically, the solution in the pores of the silver chloride becomes more dilute than the surrounding solutions. Freshly prepared electrodes should then act as cathodes towards electrodes previously aged in the solution, since the latter have had the electrolyte within their pores replenished. Agreement of the electrodes within a set prepared at a given time is no criteron that their potential has come to equilibrium, since the aging effect is different from the fluctuating bias potential by a few hundredths of a millivolt. The latter would be present in both equilibrium and non-equilibrium electrodes. The role of concentration-polarization was clearly shown by oppositely polarizing a set of two electrolytic electrodes that had been at equilibrium. A small current for a short period of time produced mutually opposite concentration-polarization in the electrodes. The electrode which has been the anode during the passage of the current behaved as the cathode, and the other as the anode, to aged electrodes. A period of approximately 24 hours was required, with nitrogen stirring, for these electrodes to regain equilibrium. In dilute hydrochloric acid, an oxidation occurs in the presence of dissolved air, which causes a slight decrease in the concentration of the acid within the interstices of the silver chloride layer. This decrease in concentration causes an oxygen-saturated solution to act as a cathode to an oxygen-free electrode. From the changes in potential (0.21 mv.) it is estimated the change in effective concentration-polarization and have been exposed to aging environments (light, air, electrolyte) for periods as long as 30 days without appreciable changes in electrode potential.

The random drift frequently observed in the potential of an electrode pair, and the aging effect observed with these types of electrodes, which are dry and completely free from electrolyte before immersion in the solution, may indicate that other factors in addition to concentration-polarization are operative in causing this drift of potential with time. A change in the nature of the sensitive silver chloride surface of the electrode, e.g., solution of the smaller silver crystals or uncovering of "hot spots" on the silver crystal, may well contribute to this effect.

With certain impurities, such as proteins (e.g. gelatin), iodide and sulfide, the effect on the electrode potential may be explained through the formation of a salt of lower solubility than silver chloride on the surface of the electrode. An accurate computation of the molality of gelatin necessary to form solid silver-gelatinate on the surface of a silver-silver chloride electrode may not readily be made with the aid of the standard electrode potentials. A general expression of the relationship in terms of the standard Nernst potential is given below:

$$E° \text{ Ag Gel} = E° \text{ Ag} \frac{RT}{F} \ln Ksp \text{ (Ag Gel)}$$

Where Ksp is the solubility product constant of the respective silver gelatinate salt. Thus, for the silver electrode in equilibrium with a solution saturated with both silver chloride and silver gelatinate, this expression becomes $E° \text{ AgGel} - E° \text{ AgCl} = .0591 \log M_{cl}/M \text{ Gel}$, since fcl and fgel are assumed to be nearly equal.

Traces of bromide have been observed to have abnormally large effect on the potential of the conventional silver-silver chloride electrode. Whereas, bromide as well as other halides, sulfides, and oxides have little, if any, effect on the standard potential or the gelatin coated electrode. The cause of this is probably due to the protective action (membrane effect) of this hydrophyllic colloid.

PREPARATION OF GELATIN COATED ELECTRODE

The silver-silver chloride electrode made by slow plating of silver chloride from KCl solution onto silver can be a convenient and most satisfactory potential electrode. Its resistance at low frequencies and direct current may reach about 5 ohms/cm 2 for a deposit of about 2 coul/cm 2 but increases rapidly with either more or less plating. Gelatin has been found to be the most satisfactory and widely used electrode for alternating current and transient purposes and may have an impedance less than 1 ohm/cm^2 at 1 kcy/sec after a deposition of about 10 coul/cm^2.

The hybrid electrode was made by first depositing a heavy layer of silver chloride along with isoelectric gelatin on silver in 1.0 M KCl with 10 or more coulombs per square cm. at 2 ma/cm2 to give a resistance of more than 300 ohm/cm.2. More reproducible electrodes were obtained by anodizing in sets of six at 4 ma. per electrode for 24 hours. This corresponds to about 36 x 10^{-4} equivalents of silver deposited. To remove absorbed contaminants, a 10 day washing period with frequent changes of distilled water was used. After this, the six electrodes were chloridized in series, using 1 M KCl at 4 - 6 ma. for 1 hour. Thus about 1.5 x 10^{-4} equivalents of silver chloride was formed, i.e., about 5 per cent of the silver layer was changed to silver chloride.

Electrodes were prepared both in the presence and in the absence of oxygen. In all cases, intercomparison measurements established good reproducibility within each set, and also with members of the other sets (0.02 mv.). By intercomparison of a number of these a suitable pair could be selected for the EMF measurements. The completed electrode then had an equilibrium potential that was somewhat less than that of the original silver-silver chloride with an impedance of a few ohm per square centimeters at 20cy/sec or less. This impedance value is comparable to a properly prepared saturated calomel electrode which is considered by some as an ultimate standard.

An additional gelatin film was deposited from a KCl solution, without greatly altering the potential, however, the impedance increased rapidly as if an additional layer of silver chloride were being laid down. With the current flow reversed (that is, in the direction to remove the silver chloride), the potential remained reasonably constant until a charge was passed approximately equal to that used to deposit the original silver chloride-gelatin layer. Beyond this point the impedance remained unchanged at high frequencies but rose at low frequencies and the electrode potential was poorly defined and unstable, as if the silver chloride had been completely removed, leaving the gelatin coating intact. When the electrode was again plated with silver chloride the stable resistance and potential were promptly restored. Cycles of chloride-gelatin deposition and removal have been repeated, within and about the ends of the useful range, without obvious deterioration of the electrical or mechanical characteristics of this hybrid electrode.

The anodized coating was white, smooth and velvet-like in appearance. Occasionally a set would be obtained in which the silver chloride gelatin film did not wet uniformly. These always resulted in erratic electrodes which gave irreproducible data.

When the electrodes were chloridized, using 0.1 N hydrochloric acid and the conditions cited above, uniform deep pink electrodes resulted, although at times a non-uniform coloring or freckling was noted. According to this data, about 1.6 x 10^{-4} equivalents was changed to silver chloride, i.e., about 1 per cent. With electrodes anodized in hydrochloric acid it was found that with higher current densities (e.g., 3 ma.) during the plating, the silver would deposit uniformly at first, but in a short time would tend to form "trees". The use of the lower plating currents and stirring in the cathode chamber ensured smooth, uniform silver-silver chloride electrodes. The electrodes thus obtained were found to have moderately good reproducibility (0.03 mv.) and would not greatly change in potential over a period of days.

The gelatin coated electrode thus utilizes the best properties of both silver-silver chloride and may be used from direct current to high frequencies so long as the silver chloride and gelatin content is not exhausted.

No specific explanations of the structure or operation of this hybrid gelatin electrode are offered, and no more detailed description or further investigations of its properties are planned.

CHARACTERISTICS OF GELATIN

Gelatin is composed entirely of amino acids joined in polypeptide linkages to form linear polymers. Since it is derived from collagen it is properly classed as a derived protein but is sometimes grouped with the albumoids. It gives typical protein reactions and is hydrolyzed by all of the proteolytic systems to yield its amino acid or peptide components.

In some respects the insoluble collagen may be considered as an anhydride of gelatin, and the formation of soluble gelatin is thus regarded as a hydrolysis into the characteristic heterogenous molecular pattern of gelatin. Gelatin molecules then represent various sized molecules, each a fragment of the collagenous chain from which it was derived. Gelatins from acid treated precursors have a higher isoelectric point inasmuch as many of their carbonyl groups exist in amide form. Alkali treatment of the precursor hydrolyzes the amide, frees the carboxyl and lowers the isoelectric point.

Gelatin is not a complete protein in that it is lacking in the essential amino acid tryptophan. To the extent of this limitation its amino acid complement is available for supporting protein nutrition as shown by experimental study.

Gelatin is a hydrophyllic colloid producing heat reversible gels. When placed in cold water it does not dissolve but swells due to hydration. Some solutes of low molecular weight may diffuse out of the swollen gelatin particle but it remains as a discrete particle. It is claimed that it imbibes water until the gelatin-water ratio approaches that value present in the original solution that was chilled and gelled prior to drying in its manufacture.

If the hydrated gelatin is warmed it goes rapidly into solution by reason of the rupture of the molecular aggregates or micelles which are characteristic of the gel form. Strictly speaking a gelatin solution is a macromolecular colloid dispersion.

Gelatin is a typical hydrophyllic colloid and like other members of that group it can be used to "stabilize" many colloids belonging to the hydrophobic group. In using gelatin as a protective colloid it must be remembered that, quite unlike the gums, it is amphoteric and that it therefore bears either a positive or a negative charge, depending upon it pH and its isoelectric point. This means that the gelatin at some pH values behaves as a cationic agent and at other pH values as an anionic agent. It is this property that makes gelatin a particularly valuable colloid for rendering stable and reversible an otherwise unstable and quasireversible silver chloride layer. As has already been explained the isoelectric point of a given gelatin is established by the nature of the treatment given its precursor.

POLAROGRAPHIC STUDIES OF STABILITY OF ELECTRODES

CURRENT DENSITY MEASUREMENTS

The polarized-depolarized character of several electrode systems was studied by measuring the polarographic behavior (current voltage curve) in a supporting electrolyte of 1N sodium chloride. The experimental electrodes were made both the cathode and anode in the polarographic circuit and various reference electrodes were studied. The current density was measured in the region of potential of +0.5 volts to -2.0 volts. Table 1 gives a comparison of the current density of the electrodes versus platinum, versus themselves and versus a glass membrane saturated calomel electrode. It may be observed that when the current density of the experimental electrodes are measured versus platinum and themselves, the order of decreasing current density is as follows: Gelatin coated > Mennen-Great Batch > anodized silver > Beckman. An exact area of the Tursky electrode could not be obtained because of the sponge effect created by the manufacturer. Interesting and radical changes may be observed in the behavior of the various electrodes versus the saturated calomel reference electrode (glass membrane type). This type of calomel is not suitable for controlled polarographic measurements since they are designed for use with high input impedance vacuum tube measuring circuits. This calomel is, however, suitable for potential measurements (Table 5) using a BOONTON SENSITIVE D. C. Meter (Model 95A).. Polarographic measurements may be made versus a calomel if a type developed in this laboratory is used. Electrolytic contact is made by means of a salt bridge with a porous fritted glass filter. Electrical contact is made through the bottom thus minimizing the large electrical resistance. Compared with a typical glass membrane calomel electrode, this electrode has a relatively small resistance (on the order of a few thousand ohms).

POTENTIAL MEASUREMENTS

Examination of the data in Table 2 also reveals that the anodized silver-silver chloride gelatin electrode gives the low values of a potential using both a calomel (glass membrane) and a replica electrode. The Mennen-Great Batch and anodized silver may be observed to give slightly higher value of potential. The silver-silver chloride pelleted electrode gives a potential of 2.0 millivolts greater than the anodized silver electrode if a calomel reference is used whereas the Beckman electrode is comparable to the anodized silver if a replica electrode is used as the reference system. The Tursky and Luccina electrodes may be observed to give high values of potential. Silver in combination with acrylic resins as methyl, ethyl, butyl, etc. may be observed to give low values of potential. When low concentrations of Acrawax C are combined with silver powder, low values of potential are obtained.

acrylic resins as methyl, ethyl, butyl, etc. may be observed to give low values of potential. When low concentrations of Acrawax C are combined with silver powder, low values of potential are obtained.

TABLE 1

POLAROGRAPHIC MEASUREMENTS

(in NaCl)

Type of Electrode	A Electrode vs. Platinum	B Electrode vs. Electrode	C Electrode vs. SCE
	Current Density $\mu a/cm^2$		
Anodized Ag-AgCl Gelatin	73.5	184.	33.6
Mennen-Greatbatch	69.0	145.	37.7
Anodized Silver	43.7	92.8	34.9
Silver-Silver Chloride Pellet (50-50)	14.9	----	29.9
Beckman	7.3	15.4	72.7
Tursky	----	----	----
Luccina	----	----	----

TABLE 2

POTENTIAL MEASUREMENTS
(in NaCl)

Type of Electrode	Electrode vs. S C E	Electrode vs. Electrode
Anodized Ag-AgCl Gelatin	15.1 mv	340.0 μv.
Mennen-Greatbatch	15.8 mv	600.0 μv
Anodized Silver (Ag-AgCl)	16.4 mv.	1.2 mv
Silver-Silver Chloride Pellet (50-50)	17.1 mv	2.9 mv
Beckman	18.8 mv	1.9 mv
Tursky	88.2 mv	7.4 mv
Luccina	----	17.6 mv
100% Sb	515.0 mv	3.2 mv
100% Cu	220.0 mv	8.5 mv.
100% Sn	505.0 mv	3.0 mv
Ag-Tri-isobutyl methacrylate (80-20)	6.6 mv	625.0 μv
Ag-Ethyl Butyl methacrylate (80-20)	11.0 mv	2.0 mv
Ag-Ethyl Methyl methacrylate (acrylic)	8.1 mv	970.0 μv
Ag-Tri-isobutyl methacrylate (90-10)	10.9 mv	1.4 mv
Ag-Ethyl Butyl methacrylate (90-10)	10.8 mv	530.0 μv
Ag-Ethyl Methyl methacrylate (90-10)	10.1 mv	850.0 μv

Table 2

Page 2

Potential Measurements
(in NaCl)

Type of Electrode	Electrode vs. SCE	Electrode vs. Electrode
Ag-Acrawax C (99-1)	7.4 mv.	280. μv.
Sb-Sb_2O_3 (95-5)	500.0 mv.	2.3 mv.
100% Ag	21.0 mv.	1.1 mv.
Ag-Ag_2O (95-5)	49.0 mv.	2.0 mv.
Ag-Ag_2O (90-10)	51.0 mv.	4.8 mv.
Ag-Ag_2O (50-50)	100.0 mv.	15.0 mv.
Ag-AgI (95-5)	11.2 mv.	250.0 μv.
Ag-AgI (50-50)	5.1 mv.	5.9 mv.
Ag-AgI (90-10)	4.4 mv.	5.4 mv.
Ag-AgI (0-100)	365.0 mv.	49.0 mv.
Sn-$SnCl_2$ (50-50)	440.0 mv.	Dissolution
Quinhydrone (100%)	11.9 mv.	3.2 mv.

SILVER-SILVER BROMIDE ELECTRODES

The stability of the silver-silver bromide electrode was studied using a saturated calomel reference as well as measuring the electrode potential versus itself. The data presented in Table 3 shows that the optimum ratio of silver to silver bromide is 90 to 10 when replica electrodes are used for intercomparison, whereas the measured potentials are essentially the same regardless of the ratio of silver to silver bromide.

TABLE 3

POTENTIAL MEASUREMENTS of SILVER BROMIDE

Electrode Composition	Electrode vs. SCE	Electrode vs. Electrode
	(mv,	v)
50-50 (Ag-AgBr)	30.1 mv.	-500.0μv.
60-40 (Ag-AgBr)	32.5 mv.	+900.0μv.
75-25 (Ag-AgBr)	36.0 mv.	+460.0μv.
90-10 (Ag-AgBr)	37.8 mv.	-340.0μv.
95-5 (Ag-AgBr)	34.8 mv.	+3.5μmv.

SILVER-SILVER CHLORIDE ELECTRODES

Table 4 presents values for DC potentials (calomel replica electrode) obtained when a pair of electrodes, varying in ratio of silver to silver chloride, were placed in an NaCl electrolyte solution, thereby eliminating the subjects body resistance and gel-skin couples.

The 100% silver electrodes exhibited acceptable resistance readings but generated an EMF out of the question for the authors system. On the opposite end of the scale, high ratios of AgCl to Ag resulted in prohibitively high resistance readings. The DC potentials displayed by Ag/AgCl electrodes were stable for at least 12 hours. No upper time limit has been set.

The optimum concentration of silver to silver chloride may be observed to be in the ratio of 90 to 10 when the potential is measured versus itself. When the electrode potentials are measured versus a saturated calomel electrode an optimum ratio may not readily be determined.

TABLE 4

POTENTIAL MEASUREMENTS
OF SILVER CHLORIDE ELECTRODES

Electrode Composition	Electrode vs. SCE	Electrode vs. Electrode
50-50 (Ag-AgCl)	16.2 mv.	1.2 mv.
25-75 (Ag-AgCl)	7.4 mv.	2.2 mv.
10-90 (Ag-AgCl)	7.0 mv.	2.0 mv.
0-100 (Ag-AgCl)	42.0 mv.	5.3 mv.
5-95 (Ag-AgCl)	8.2 mv.	1.6 mv.
60-40 (Ag-AgCl)	5.9 mv.	3.2 mv.
75-25 (Ag-AgCl)	5.2 mv.	2.5 mv.
90-10 (Ag-AgCl)	1.7 mv.	160.0 µv.

STABILITY OF SATURATED CALOMEL ELECTRODE

In biomedical application of potential measurements we usually work with an electrode that gives the best depolarization characteristics. Although the hydrogen electrode is the primary standard reference it is too inconvenient for practical measurements. The commonest and most generally used reference electrode is the calomel electrode consisting of a mercury electrode in a chloride solution of specified concentration that is saturated with mercurous chloride (calomel).

The potential of matched calomel electrodes (Leeds and Northrup) was measured as a function of time and the data is presented in Table 5. The potential change is the greatest in the first thirty (30) minutes of equilibrization and becomes sensibly constant after that time.

Calomel electrodes, especially the saturated type, have the disadvantage of a large temperature coefficient which in most biomedical applications is of great importance. Solid state electrodes such as the silver-silver chloride electrodes are not as sensitive to temperature fluctuations.

TABLE 5

MATCHED CALOMEL VS CALOMEL ELECTRODES

Time (min.)	Potential (microvolts)
3	279.
5	338.
7	365.
10	400.
15	420.
20	435.
25	458.
35	478.
42	480.
45	480.

THE EFFECT OF DISSOLVED OXYGEN ON ELECTRODE POTENTIAL

The effect of dissolved oxygen and purging with nitrogen on the electrode potential is illustrated in Table 6. The presence of oxygen may be observed to increase the electromotive force. This is probably due to the fact that a mixed potential corresponding to a silver-silver chloride and silver-silver oxide is obtained when the electrodes are exposed to oxygen. This mixed potential is slightly lower than that reported for the deareated solution, however the values reported for the nitrogen purged solution are more nearly representative of the true electrode potential, which by definition is independent of environmental conditions.

TABLE 6

Composition	Electrode vs. SCE (millivolt)	
	Areated	Deareated (N_2)
50-50 (Ag-AgCl)	5.1 mv.	16.2 mv.
25-75 (Ag-AgCl)	3.9 mv.	7.4 mv.
10-90 (Ag-AgCl)	5.6 mv.	7.0 mv.

[illegible]

RESISTANCE MEASUREMENTS

The resistance of an electronic conductor (i.e. a conductor which obeys Ohms law) was determined by using a Bruel and Kjaer deviation bridge. Flight electrode paste* was placed between a matched pair of electrodes and the resistance measured after allowing 10, 15, and 20 minutes equilibration time. Resistance values typical of many electrodes systems are given in Table 7 .

* give a reference to define exact contents, characteristics, method of use, etc.

TABLE 7

Electrode	Resistance (ohms) 10 min.	15 min.	20 min.
AgCl Gelatin (matched pair)	12.75	13.23	13.53
Ag anodized in 1N NaCl (small)	24.97	32.84	36.30
Luccina	219.96	237.60	244.65
Mennen Greatbatch	9.42K	9.32K	9.00K
Beckman	21.54	22.11	22.00
100% Cu Pwd. "A"	6.0	5.5	6.0
100% Sb	7.5	7.8	7.6
95-5 $Sb-Sb_2O_3$	7.5	7.5	7.5
100% Sn (1)	15.00	15.48	15.88
100% Sn (2)	13.68	14.01	14.24
99-1 Ag-Acrawax C	2.7	2.8	3.0
80-20 Ag-Acrylic Powder	5.2	7.8	7.8
90-10 Ag-Ethyl Butyl Copolymer	2.2	2.5	2.65
80-20 Ag-Ethyl Butyl Copolymer	1.8	2.0	2.2
90-10 Ag-Tri-isobutyl Methacrylate	2.2	2.6	3.0
80-20 Ag-Tri-isobutyl Methacrylate	2.5	2.8	3.0

TABLE 7, PART II

Electrode	Resistance (ohms) 10 min.	15.min.	20 min.
	Ag-Ag$_2$O		
95-5	42.72	44.70	45.64
90-10	101.2	94.2	91.6
50-50	109.9	112.5	115.9
	Ag-AgI		
95-5	2.4	2.5	2.6
90-10	2.6	3.0	3.9
50-50	2.5	2.8	3.0
0-100	3.995K	3.036K	2.805K
	Ag-AgBr		
95-5	2.6	2.9	3.0
90-10	2.6	2.6	3.0
75-25	3.2	3.2	3.4
60-40	2.8	2.85	2.95
50-50	2.6	2.75	2.9
	Ag-AgCl		
90-10 (Anodized)	9.23	9.38	9.59
90-10	3.1	3.3	3.2
75-25	3.2	4.0	4.0
60-40	2.8	3.4	4.0
25-75	2.6	3.5	4. → 6.0
5-95	16.95	23.43	24.20
0-100	2.277K	2.066K	1.914K

PRESSED DISC ELECTRODE METHODOLOGY

The use of silver-silver chloride pressed disc as an effective substitute for silver sheet has been under study at this laboratory for some time. The insolubility of silver chloride in water and its resistance to chemical attack by a large number of substances have suggested its use over a broad spectrum of analytical applications.

An investigation of the use of pressed thallous bromide, thallous chloride, and silver chloride discs as solid samples supports in EKG and EEG preparation has been reported.(7) Poor results were claimed for the silver chloride disc only on the basis of the discoloration of the material on exposure to light and a single infrared spectrum of a 1% dispersion of the calcite form of calcium carbonate in silver chloride. Contrary to the above report, our studies have shown that the pressed silver-silver chloride disc is effective not only as a support for liquid films but also as a carrier for the analysis of a large number of organic and inorganic solids.

Studies now under way at this laboratory have already shown that the silver chloride pressed disc technique can be of great significance in the investigation of a large number of compounds containing absorbed and/or chemically bound water, e.g., hydrates, clathrates, metal-organic complexes containing water or other highly polar ligands, biochemical substances extracted from animal and vegetable specimens, the structure of solvated molecules and ions, etc. Furthermore, the non-hygroscopic nature of Ag-AgCl is of particular value when hydroxylic compounds are used in a non-reactive environment.

DESCRIPTION:

The improved electrode device differs from the classical electrode in several respects. The direct metal-to-skin contact is eliminated and an ionic-conductive path is substituted, consisting of compatible electrolytic gel which furnishes a conductive bridge between the electrode pellet and the skin surface. The means of supporting the pellet and gel are illustrated in Figure 4. Basically the supporting structure is a lucite housing which is adherred to the skin and after filling the reservoir between skin and pellet with a conductive gel, the housing assembly is put into place with Stomaseal adhesive.

The electrode pellet itself is a mixture of metal powder and/or metal salt in varying weight ratios, finely ground and thoroughly mixed, then compressed in a suitable die under pressure of

40,000 p.s.i. An integral tinned copper wire is imbedded prior to pressing for attachment to a shielded and insulated lead. The pellet is 15 mm. in diameter and approximately 1.5 mm. in thickness (see Figure 4).

EVALUATION:

Other than comfort, size, and other characteristics the prime consideration in such an electrode system are (a) skin-electrode resistance and (b) skin-electrode junction potentials.

EXPERIMENTAL:

The basic technique of producing pressed silver chloride discs is described as follows: Detailed studies have produced some additions and modifications. The drying and screening of reagent grade silver chloride powder (Mallinckrodt) was wholly unnecessary and, indeed, detrimental for the production of good discs. Storage of the silver chloride in a desiccator is also unnecessary (no water bands were detected in the infrared spectra of silver chloride discs which were subjected to approximately 1 year of constant use without desiccation). The soft, elastic characteristic of the silver chloride crystals allow good pellets to be pressed at pressures as low as 8,000 p.s.i., thus, eliminating the need for an elaborate hydraulic press.

The corrosive effect of silver chloride on the metals used in the disc sample holder were eliminated by using nylon and/or zirconium dies. The disc sample holders were constructed of Teflon and wafer-thin, circular, highly polished Teflon discs were inserted in the die above and below the powdered sample to be pressed. In addition, discs made of nylon or Teflon used in the pellet die functioned as effective die-mold release agents.

(a) Preparation of Sample

Sample preparation techniques differ in individual cases and depend on the type and amount of sample available. Good pellets can be obtained with samples weighing 1/2 to 1 milligram mixed with powdered Ag-AgCl and pressed into 1.5 millimeter pellets.

The AgCl should be ground to at least 200 mesh, since the smoothness of the pellet depends on the fineness of the AgCl. 325 to 400 mesh AgCl is available commercially and is recommended for good quality pellets. The desired amounts of Ag and AgCl and sample are then thoroughly mixed by grinding together in a micropulverizer or mechanical vibrator. Sample concentrations of 5% in Ag-AgCl are typical but may vary in individual cases.

(b) Making the Pellet

The sample and matrix having been ground and mixed are now ready for pressing in a precision evacuable die. The selection of the proper die depends on the amount of sample available and the selection of the gauge depth depends on the concentration and type of sample.

The final pellet thickness is equal to approximately 1/2 the gauge depth. The equivalent cell thickness -

$$\frac{\text{weight of sample} \times \text{density of AgCl}}{\text{weight of AgCl} \times \text{density of sample}}$$

THE PROCEDURE FOR MAKING THE PELLET IS AS FOLLOWS:

1. Place the die on the gauge block over the selected depth with the polished side of the plunger and die up, and press the plunger down until it rests on the bottom of the gauge block groove.

2. Tighten the thumb screw to lock the plunger in place.

3. Fill the space in the die, provided by the depressed plunger, with the sample and Ag-AgCl mixture, and scrape off any excess mixture by running a straight edge along the face of the die. Be sure that the mixture completely and evenly fills the hole; otherwise the pressed pellet will be spotty.

4. Place the polished side of the die base plate over the sample, and hold firmly against the die, while turning the die over and placing it in the die clamp. Tighten the Allen screws on the die clamp, until

die and die base place are firmly clamped.

5. Loosen the thumb screw before applying pressure on the plunger.

6. If the vacuum chamber is used, place the die and the die clamp on the centering pin in the base plate of the chamber over the die. Slide the chamber plunger down until it rests against the die plunger, and attach a vacuum pump to the valve on the side of the vacuum chamber. Evacuate for approximately three minutes (1 - 5 mm Hg) and close the valve.

7. Place the vacuum chamber or the die, if vacuum chamber is not used in a hydraulic laboratory press and apply the desired load. (Note: Total load in pounds = hydrostatic pressure x area of hydraulic ram.) This corresponds to an ultimate pressure on plunger and pellet of approximately 50,000 p.s.i.g. since

$$\text{p.s.i.g.} = \frac{\text{Total load (pounds)}}{\text{Cross sectional area of plunger}}$$

Maintain pressure for approximately three minutes.

8. Remove the die from the vacuum chamber and the die clamp and place on the pressure pad with the pellet down against the pad. Place the die and pressure pad in the press and apply slight pressure until the pellet is forced out against the pressure pad which cushions the shock and prevents the pellet from breaking.

9. Using tweezers, place the pellet in the milled out section of the lucite housing and cement into

place with Scotchcast #8.

(c) Care of Equipment

It is not practical to make the die plunger so tight as to prevent some of the fine Ag-AgCl powder from working around the plunger while pressing. Therefore, the die should be taken apart and thoroughly cleaned with alcohol and water and dried after each pellet is pressed and before storing in a dry place. AgCl has a corrosive action on most stainless steels which can be hardened.

(d) Matrix Problems

Choice of the silver powder and silver chloride are of great importance. AgCl powder must have a small particle size to get closest-close packing of the particle but not so small that the rate of water absorption will be too great. The matrix must be finely ground and intimately mixed with the sample. It has been shown in this work that a particle size below 10 microns is good, and even very much smaller particles are desirable, but these are often impractical to produce and difficult to work with because of extremely rapid water absorption. The insidiousness of water vapor cannot be overlooked and precautions must be taken to remove it at every step.

Additional factors affecting the pelleting technique are absorption of the sample by the matrix and actual chemical reactions between matrix and sample. When a mixture of two compounds is to be pressed into a disc, their mutual reactivity must be considered since mixed crystals are easily found between Ag-AgCl and some samples. For example benzoic acid is easily changed to silver benzoate.

Consideration must also be given to labile substances such as azides which may well decompose during pressing. Even more stable compounds have been known to break down during disc preparation. The decomposition products can wreak havoc with electrode stability unless the breakdown has been considered.

The converse situation is also true that in some cases where decomposition occurs in solution the Ag-AgCl is fine. Apart from reactions with the halide, the procedure for making pellets has also been shown to give rise to polymorphism and crystalline distortion. For example, it has been shown in this laboratory that benzil when ground for a long time loses its crystallin state and becomes amorphous.

EXTRACTING THE PELLET

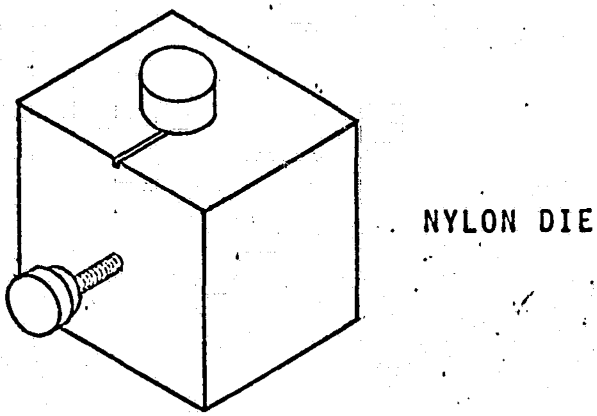


Fig. 3

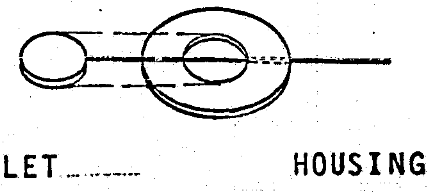


Fig. 4

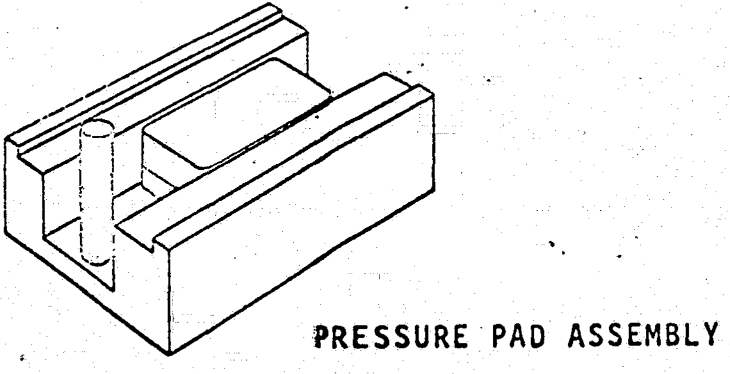


Fig. 5

PRESSING THE PELLET

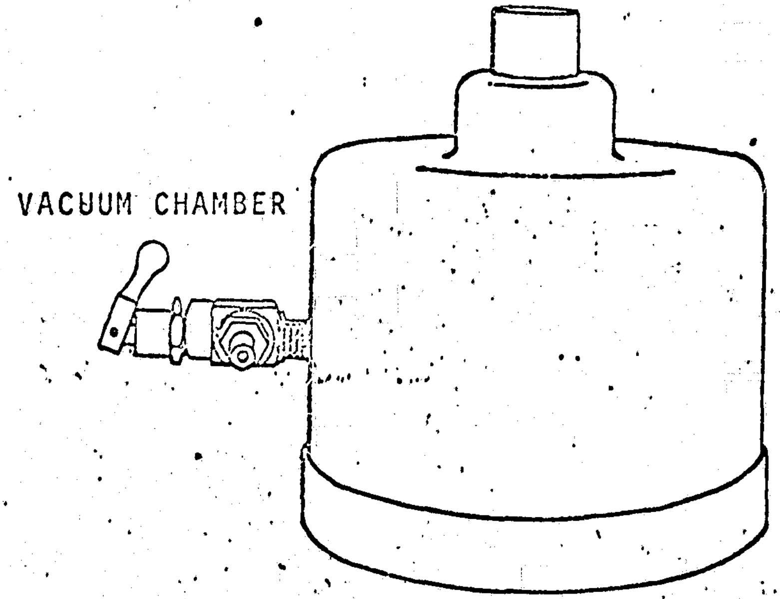


Fig. 6

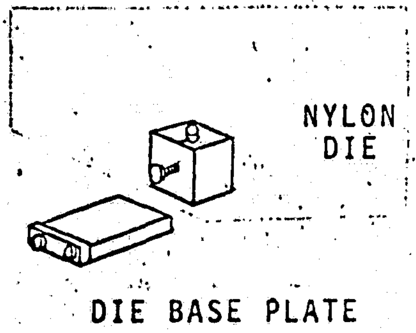


Fig. 7

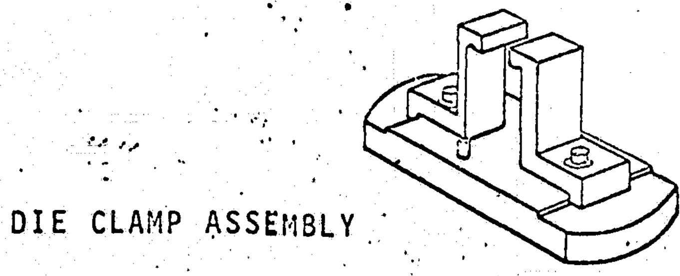


Fig. 8

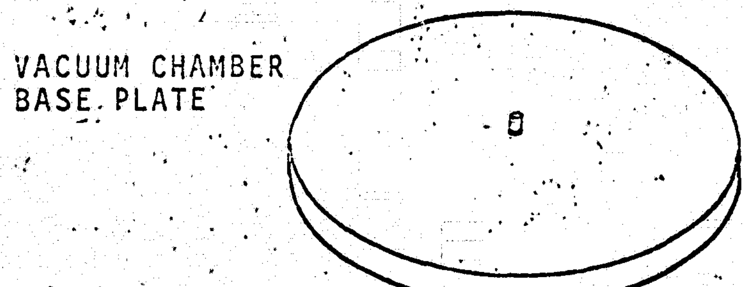


Fig. 9

SUMMARY

Excellent qualitative and quantitative data was obtained on a large number of materials which were combined in the pellets.

The question of whether the appearance of small amounts of water in a pellet is a result of disc preparation of a result of the hydroscopicity of matrix material (Ag-AgCl) was solved by observing the characteristic infrared spectra. No water bands of consequence was observed in the spectral curve.

Exceptional control of concentrations of solids in the pressed disc is made possible by this method. a homogenous distribution of all samples was observed.

The plasticity of the silver-silver chloride suggests its use as a good inorganic binder for large amounts of solid samples.

Most discs contained concentrations of Ag-AgCl high enough to produce pellets opaque to visible light, however, some were transparent in the infrared region of 2.5 to 16 microns and produced exceptional solid state infrared spectra. These spectra were helpful in eliminating the errors inherent in making up new samples, especially with reference to slight changes in concentration as well as evaluating the dispersion characteristics.

Contrary to popular belief, the photodecomposition of silver chloride does not readily take place. The darkening of silver chloride on exposure to visible and ultraviolet radiation does not appear to effect the transmission of infrared radiation to any appreciable extent. Silver chloride discs which were exposed to fluorescent lighting for a period of 10 days showed no significant changes in the base line.

The inertness of a silver-silver chloride material as well as the extreme simplicity and reproducibility of pressing pellets suggest its use as a valuable matrix material for a wide category of compounds to be used in pressed disc methodology.

ANOMALOUS BEHAVIOR OF ELECTRODES

It is observed that electrode design is not of great importance in reducing the amount of motion artifact or noise at the electrode.

Apparatus was constructed wherein the electrodes were subjected to a constant friction and shear motion which would be comparable to lateral movement of the body or clothing. Experiments on these electrodes have shown that the gelatin coated electrodes have good sensitivity to mechanical effects if the proper gel strength is used in the electrode paste. For example, 10X Ringer's solution alters (dampens) the amplitude of the signal by approximately seven percent whereas a viscoelastic gel containing 10X Ringer's, alters the amplitude by only two percent and does not appreciably change the noise level from that of a three percent Natrosol solution. The noise level of electrodes which have been shielded in part, as the Beckman electrode, are essentially the same as the gelatin electrode when they are compared at the optimum viscosity of the thixotropic mixture. The thixotropy of the gelled solution thus determines the amount of motion artifacts rather than geometric design of the electrode system.

SENSITIVITY AND STABILITY OF VARIOUS CLASSES OF ELECTRODES

Because the silver-silver chloride electrode has found increasing use as a secondary reference electrode, studies were undertaken in this laboratory on the reproducibility and stability of the various types of electrodes. The results for different classes of compounds are presented in the following section. The initial (V_0), final (V_f), and average (V avg.) potentials are given to illustrate the sensitivity of a given electrode system (2 hour period). The average slope (μv/sec.) is recorded to demonstrate the stability of an electrode pair over a two hour period.

MEMBRANE ELECTRODES

All of the membrane electrodes described are prepared from clays, natural or synthetic polymers. The use of membrane materials in flight electrodes represents one of several purposes of this development and the principal goal has been to develop materials which give high sensitivity and selectivity to biological systems.

A discussion of the factors governing the sensitivity and non-ideality of membrane materials is given merely for the purpose of interpretation and prediction of electrode characteristics.

CONCEPT OF MEMBRANE ELECTRODES

The simplest concept of an ion selective membrane is that the membrane is regarded as a porous diaphragm throughout which there is an even distribution along the pore walls of one particular species of fixed ionized or ionizable groups.

Membranes can be made to exclude certain cations and anions and permit the diffusion of others is its most important feature. Although simple ionic species, such as sodium, potassium, calcium, etc., do not differ greatly in size, some discrimenation is possible, particularly if the membrane pores are small and inelastic. This type of channel is commonly found in clays and some natural gums. For example, Zeogel is sensitive to uni-valent electrolytes but insensitive to divalent cations. Further refinement of this ion sieve property is obviously possible. It has been shown that under certain conditions bentonite will quantitatively take up (exchange) sodium and potassium ions but totally exclude magnesium ions which evidently cannot penetrate the windows of the "cage like" character of bentonite. Veegum behaves similarly. (See discussion.)

PLANT HYDROCOLLOIDS

The natural plant hydrocolloids commonly known as water soluble gums or stabilizers, form an interesting and widely used group of carbohydrates derived from plant sources. Chemically, these unique products may be classified as anionic or nonionic polysaccharides or salts of polysaccharides. They have the common property of forming viscous solutions, or more accurately, colloidal sols and gels in water. The ability to improve body, convey elasticity and texture, impart emollient properties, and to stabilize the silver-silver chloride matrix material were some of the major factors considered in the selection of the plant hydrocolloids. A discussion of the characteristics of the individual gums follow along with a presentation of the data in Table 8.

GUAR GUM - The guar molecule is essentially a straight chain mannon branched at quite regular intervals with single membered galactose units or alternate mannose units. The long straight chain nature of this molecule, combined with its regular side branching, is unique among the natural colloids and should be beneficial as an ion-exchange material to be incorporated in a reference electrode system. The molecular weight is of the order of 220,000.

AGAR-AGAR - is insoluble in cold water, however it is unique from the standpoint of being completely reversible hydrocolloid. Agar is believed to be a linear polygalactose sulfuric ester. It is likely that Agar is a calcium polygalactopyranose complex. Calcium, magnesium, sodium and potassium seem to be basic constituents.

GUM ARABIC is a complex mixture of calcium, magnesium and potassium salts of arabic acid. Arabic acid is a complex of galactose, rhamnose, arabinose and glucosonic acid. The molecular weight is of the order of 240,000.

GUM TRAGACANTH consists of a soluble portion tragacanthen, and an insoluble portion, borsorin, the latter constituting 60% to 70% of the total. Tragacanthen consists of a ring containing three molecules glucosonic acid and one molecule arabinose with a side chain of two molecules of arabinose. Gum tragacanth contains small amounts of cellulose starch and protein substances.

GUM GHATTI is an amphorous translucent water soluble complex polysaccharide. It has good film forming properties and is a good binder for silver-silver chloride powders.

LOCUST BEAN GUM is a polysaccharide built up of a main chain of mannose units with short branching single galactose units. The molecular weight is about 310,000. The materials may be precipitated by some electrolytes (particularly polyvalent ions).

This insolubility may be helpful in preventing the migration of silver ions. These materials show no tendency toward synersis.

GUM KARAYA is a complex polysaccharide of high molecular weight. A molecular weight as high as 9,500,000 has been reported. On hydrolysis it yields galactose, rhamnose and galactorinic. Gum Karaya occurs as a partially acetylated derivative.

TABLE 8

PLANT HYDROCOLLOIDS

Composition	V_o	V_f	V avg	Average Slope μv/sec
A-Arabic Gum (95-5)	+540.0μv	-355.0μv	+93.0μv	+.13
	-94.0μv	+185.0μv	+46.0μv	+.01
A-Douglas Clearsol Gum (95-5)	-225.0μv	+15.9μv	-105.0μv	+.01
	+30.0μv	+76.0μv	+53.0μv	
A-Gum Ghatti #1 (95-5)	+245.0μv	+220.0μv	+233.0μv	+.01
A-Guar Gum, Pwd. Type M.M. (95-5)	+155.0μv	+138.0μv	+146.0μv	+.02
A-Irish Moss, Pwd (95-5)	-170.0μv	-300.0μv	-235.0μv	+.03
A-Karaya Gum, N.F. Superfine #1 (95-5)	+530.0μv	+330.0μv	+430.0μv	+.03
A-Talha Gum (95-5)	-680.0μv	-1.6mv	-420.0μv	
	-40.0μv	+60.0μv	+10.0μv	+.02
A-Tragacanth Gum (95-5) (Pwd. U.S.P.-L)	+27.0μv	-10.0μv	+9.0μv	+.05
	+320.0μv	+2000.0μv	+1160.0μv	
A-Locust Bean Gum Type D-400 (95-5)	-3.1 mv	-1.0mv	-2.5mv	+.15
A-Agar-Agar Pwd. U.S. Type MK-80	-520.0μv	-140.0μv	-330.0μv	+.04

CLAYS

All of the clays shown give low values of potential. Zeogel (modified montmorillanite) may be observed to give stability and resistivity over long periods of time. (Figure 10)

When silver powder is combined with Bentone 34 in the proper concentration an extremely stable electrode system results. This may possibly be explained on the basis of the solubility of the Bentone 34 since it is prepared by adsorption and/or reaction of a long chain quarternary ammonium compound. VEEGUM (Isomorphous silicates) may be observed to give a very stable, sensitive electrode. Its desirable properties are probably related to its unusual tube or rod-like structure in contrast to the familiar plate structure of high aluminum silicates (montmorillanites). The distortion of the plate to a rolled up tube or rod takes place wherever magnesium has substantially replaced aluminum in the crystal lattice. The greater size of the magnesium ion causes a crystal strain resulting in the unusual structure.

TABLE 9

CLAYS

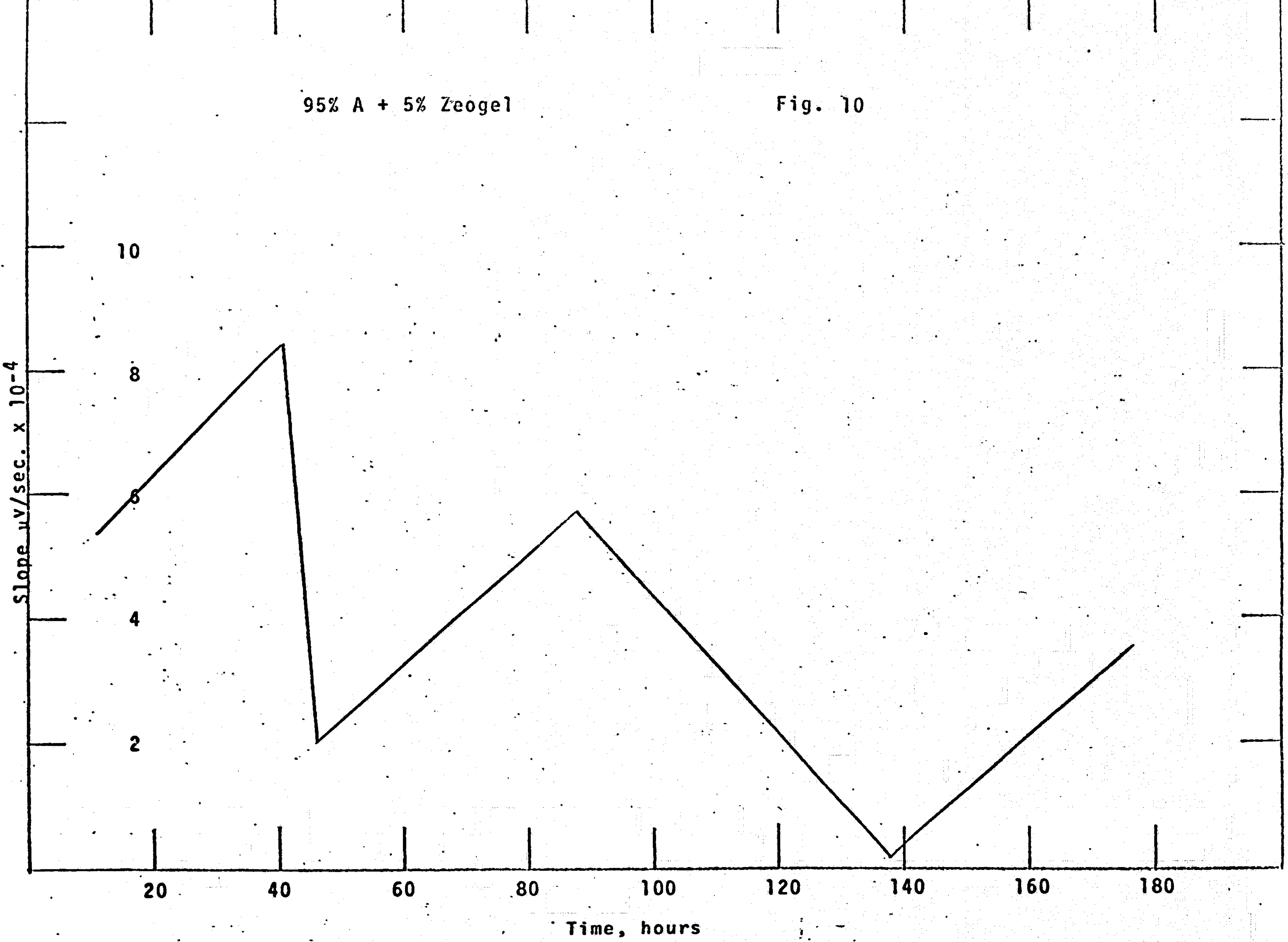
Composition	V_o	V_f	V Avg.	Average Slope µv/sec
A-Zeogel (95-5)				
24 hour run	+910.0µv	-500.0µv	+205.0µv	-.050
	-360.0µv	+9.5µv	-175.0µv	+.35
	-280.0µv	-6.8µv	-144.0µv	
	+150.0µv	-5.7µv	+72.0µv	
14 day run	+52.0µv	-62.0µv	-5.0µv	+.0011
Ag-Zeogel (95-5)	-475.0µv	-335.0µv	-405.0µv	+.038
	+57.0µv	+101.0µv	+79.0µv	
Ag-Zeogel (99-1)	+1.0mv	-320.0µv	-405.0µv	-.314
	-125.0µv	+75.0µv	-25.0µv	
Ag-Bentone 34 (95-5)	-890.0µv	-820.0µv	-855.0µv	-.005
Ag-Bentone 34 (99-1)	+26.0mv	+555.0µv	+1.78mv	
	-620.0µv	-56.0µv	-338.0µv	+1.58
A-Bentone 34 (95-5)	+630.0µv	+320.0µv	+425.0µv	-.062
	+290.0µv	-180.0µv	+55.0µv	
	-490.0µv	-380.0µv	-435.0µv	
A-Bentonite, Wyoming (95-5)	+37.0µv	+20.0µv	+29.0µv	+.030
	-286.0µv	-38.0µv	-162.0µv	+.030
	+46.0µv	-16.0µv	+15.0µv	
A-Veegum (95-5)	-79.0µv	-66.0µv	-72.5µv	-.04
A-Quebracho (95-5)	-143.0µv	+13.2µv	-64.0µv	-.47

HYDROPHYLLIC COLLOIDS -
MINERALS - SYNTHETIC WAXES

POLYVINYLPYROLIDONE (PVP) - This material has wide solubility and compatibility characteristics. PVP may be easily combined with silver and its salts to give a homogenous matrix. It is not known whether PVP forms molecular adducts with metal and/or metal ions. However, it is shown to be an effective electrode paste material. PVP is physiologically acceptable and compatible with body fluids.

SODIUM CARBOXY METHYLCELLULOSE (NaCMC) - This material is a long chain polymer which contains reactive hydroxyl groups to bring about solubility in water. Cellulose gums do not readily deteriorate or depolymerize by hydrolytic or oxidative degradation. From these observations it is apparent that gums of this type should be valuable as ion exchange membrane materials to be incorporated into standard reference electrodes. Toxicity studies conducted on cellulose gums have shown them to be physiologically inert. Cellulose gums are compatible with a large number of anions and cations. There are some complex interactions of ionizing salts with hydrophyllic colloids which make this chain of compounds particularly interesting as electrode materials.

NATROSOL JR is a non-ionic water soluble polymer derived from cellulose (hydroxyethyl ether). The structure



95% A + 5% Zeogel

Fig. 10

of the cellulose molecule is composed of anhydroglucose units. The hydration rate of natrosol has been inhibited so that when exposed to water the particles separate and form a uniform dispersion. This feature may retard the migration of high molecular weight species, such as proteins. No toxic effects observed.

Most water soluble natural and synthetic gums are easily attacked by bacteria. When such gums are combined with heavy metal solts such as silver, they are generally resistant to microbiological degradation. ASP-400 is a selected particle size white crystal of hoolinite that have been pressed to remove moisture, sand, mica and natural contaminants. These non-hygroscopic products are essentially inert and insoluble under normal conditions.

COLLOIDAL ALUMINA - These particles consist of submicroscopic fibrils of boehmite AlOOH approximately 5 millimicrons in diameter and 100-500 millimicrons long. Because of the interlocking and chemical banding of the fibrils this material should be valuable as ion-exchange material.

CELITE SUPERFLOSS - Diatomaceous silica or diatomate as it is commonly called is a powder consisting of fossalized remains of plants known as diatoms. The highly absorptive capacity of materials make it a natural filtering aid. This is due to a series of channels and voids formed by the particles themselves. The physical structure of the individual diatoms particles thus helps explain why Celite Superfloss should be an excellent ion exchange material to be incorporated into a silver-silver chloride matrix. Because of the irregular shape and generally spiney structure, the particles interlace and overlap forming countless microscopic openings that permit only the passage of simple electrolytes while screening out high molecular materials such as complex proteins.

ACRAWAX "C" is a virtually insoluble material in all solvents at ambient temperatures. Infrared examination of Acrawax "C" indicates that the material is a chain substituted amide. The concentration of Acrawax with silver gives a very stable reproducible electrode system of low potential values. This idea of incorporating into the matrix material (Ag-AgCl) an insoluble synthetic wax is shown to offer high chemical specificity.

BARIUM SULFATE - Membranes composed of insoluble materials such as barium sulfate should be specific for certain environments (eg. sulfate and barium ions).

TABLE 10

HYDROPHYLLIC COLLOIDS - MINERALS - SYNTHETIC WAXES

Composition	V_o	V_f	V avg.	Average Slope μv/sec.
A-PVP-K-90 (95-5)	+390.0μv	+1.65mv	+970.0μv	+.09
Ag-PVP-K-90 (80-20)	+200.0μv	+55.0μv	+127.0μv	
A-NaCMC (95-5)	-360.0μv	-20.0μv	-190.0μv	+.46
A-Natrosol JR (95-5)	+710.0μv	+18.0μv	+369.0μv	-.03
Ag-$BaSO_4$ (95-5)	+330.0μv	-257.0μv	+37.0μv	+.24
A-ASP 400 (95-5)	-590.0μv	-121.0μv	-355.0μv	+.06
A-$BaSO_4$ (95-5)	+330.0μv +420.0μv	-257.0μv +460.0μv	+36.0μv +440.0μv	-.099
A- Cab-O-Sil (95-5)	+115.0μv	-340.0μv	-112.0μv	+.19
A-Celite Superfloss (95-5)	-252.0μv	+360.0μv	+56.0μv	+.08
A-Baymal (Colloidal Alumina) (95-5)	-2.3mv	-1.5mv	-1.9mv	-.09
A-Acrawax "C" (95-5)	+1.43mv	+1.29mv	+1.36mv	-.012
Ag-Acrawax "C" (99-1)	-20.0μv -56.0mv	+280.0μv +280.0μv	-150.0μv	+.04

ACRYLIC POLYMERS

Selective membranes have been prepared from cross linked polymethyl methacrylate and combinations thereof. Some of the acrylic compositions shown in Table 11 may be observed to give low potentials and good reproducibility. (eg. copolymers of ethyl-methyl methacrylate). The porosity and permeability of the acrylics may be easily altered by changing the pressure at which it was cast as well as modifying the extent of evacuation.

A copolymer of ethyl-butyl methacrylate may be observed to give low values of potential and moderately stable electrodes. The higher molecular weight methacrylate copolymers (tri-isobutyl) do not give electrode systems which are as effective.

TABLE 11

ACRYLIC POLYMERS

Composition	V_o	V_f	V avg.	Average Slope µv/sec.
Ag-Acrylic Powder (70-30 Ethyl-methyl methacrylate (90-10)	+240.0µv	+237.0µv	+239.0µv	Constant at low values
Ag-Acrylic containing 1% $\mathrm{TiO_2}$ (90-10)	+415.0µv	-850.0µv	-218.0µv	+1.21
Ag-Acrylic Powder (80-20)	-168.0µv	-78.0µv	-123.0µv	+0.42
	-240.0µv	-90.0µv	-165.0µv	
	+540.0µv	+180.0µv	+350.0µv	+0.37
Ag-Tri-isobutyl Methacrylate (90-10)	+1.35mv	+17.1mv	+0.76mv	+.22
Ag-Tri-isobutyl methacrylate (80-20)	+395.0µv	+625.0µv	+510.0µv	
	+6.1mv	+70.0µv	+3.1mv	-2.21
Ag-Ethyl Butyl methacrylate copolymer (80-20)	+5.7µv	+310.0µv	+158.0µv	
	-1.72mv	-2.02mv	-1.87mv	
	+6.9mv	+310.0µV	+3.6mv	+1.71
Ag-Ethyl Butyl Methacrylate (90-10)	+235.0µv	+530.0µv	+382.0µv	
		+162.0µv		+.22
Ag-Lucite 2010 Acrylic Resin (95-5)	-181.0µv	-62.0µv	-121.0µv	+.134
	+660.0µv	+58.0µv	+359.0µv	
A-Lucite 2044 Acrylic (95-5)	+150.0µv	-140.0µv	+5.0µv	-.199
	+1.1mv	+280.0µv	+690.0µv	

MISCELLANEOUS COMPOUNDS

MONSANTO DX-840 is a cross linked ethylene maleic anhydride copolymer which is completely water soluble and as such can be combined directly with silver powder to give a uniform dispersion. The DX-840 resins are capable of preventing or reducing the rate of crystallization of metal ions and/or metal salt combinations. Its high degree of water solubility probably prevents it from being usable electrode material.

AMBERLITE AND SEPHADEX are ion exchange resins and both systems give stable reproducible electrodes. Sephadex is a modified dextran obtained by fermentation of sugar. The linear macromolecules of dextran are cross linked such as to give a three dimensional network of polysaccharide chains. Sephadex is not affected by cations or anions and because it contains multiple hydroxyl groups it is strongly hydrophyllic.

HYSTRENE 5016 is a triple pressed stearic acid and may be observed to give low potentials. The calcium salt (calcium stearate) as well as aluminum hydroxy stearate does not give stable reproducible potentials. Silver lactate dissolved after approximately 15 minutes.

Q-BROXIN is sodium lignosulfonote and give low values of potential as well as stable reproducible behavior. The structure of lignosulfonotes is similar to the hydroxy cellulose derivatives and would be expected to behave comparably with sodium carboxy methyl cellulose.

PARLON is chlorinated rubber and would be expected to be completely inert in a silver-silver chloride matrix. Its low low value of potential and stability is notably due to its insolubility as its ability to permit the diffusion of simple ionic species (e.g. Na, K) but prevent the outward migration of the crystalline silver chloride.

TABLE 12

MISCELLANEOUS COMPOUNDS

Composition	V_o	V_f	V avg	Average Slope μv/sec.
A-Monsanto DX 840 (95-5)	-60.0μv --14.0μv	+580.0μv -241.0μv	+260.0μv -127.0μv	+.308
Ag-Polyvinyl Alc. Resin 165 (95-5)	-880.0μv +240.0μv	+126.0μv +99.0μv	-377.0μv +170.0μv	+.205
A-Polyvinyl Alc. 3098 (95-5)	-1.05mv +560.0 v	-680.0μv +1100.0μv	-865.0μv +830.0μv	+.064
A-Butvar B-73 (95-5)	-650.0μv -170.0μv	-1.01mv -139.0μv	-827.0μv -155.0μv	-.198
A-Ca Stearate (99-1)	+210.0μv +8.5 mv	+2.mv +1.08mv	+1130.0μv +4.8mv	+.190
A-Al hydroxy Stearate (95-5)	+52.5μv	+1.55mv	+801.0μv	-1.03
A-Amberlite (ion exchange resin) (95-5)	-670.0μv	-710.0μv	-690.0μv	+.01
A-Hystrene 5016 (95-5)	+10.0μv +400.0μv	+2.0μv +299.0μv	+6.0μv +315.0μv	+.07
Ag-Ag Lactate		DISSOLUTION		
A-Sephadex C-25 (95-5)	+290.0μv	+490.0μv	+390.0μv	-.04
A-Parlon, Type S-125 (95-5)	+220.0μv	+140.0μv	+180.0μv	+.11
A-Q-Broxin (95-5)	-185.0μv	+142.0μv	-22.0μv	+.07

(Slope becomes 2.78×10^{-5} after one hour.

TABLE 13

MISCELLANEOUS FABRICATED ELECTRODES

Composition	V_o	V_f	V avg	Average slope μv/sec
Luccina Electrode	+18.5mv	+13.2mv	+15.7mv	-21.4
Beckman Electrode	+165.0μv	+174.0μv	+169.0μv	-.08
Mennen Greatbatch	+600.0μv	+510.0μv	+555.0μv	-.04
Tursky	+88.0mv	+31.0mv	+59.0mv	+3.8
Ag-AgCl Gelatin (Silver Sheet)	-40.0μv	-84.0μv	-62.0μv	+.02
Ag Sheet anodized in NaCl	-310.0μv +1.7mv	+400.0μv -4.0μv	+45.0μv +852.0μv	 -.15

COMMERCIAL ELECTRODES

CALOMEL - It is shown in Table 14 that commercial preparations of calomel (eg. Leeds and Northrup) give rise to positive deviations of potentials and are slow to decay. An examination of Figure 11 illustrates the calomels general erraticity when exposed for long periods of time.

QUINHYDRONE - The quinhydrone electrode obtains its equilibrium potential fairly rapidly. However, its electromotive force is too high to be useful as a biological electrode. The quinhydrone is also readily "rolled out" when subjected to simple electrolytes such as sodium chloride. In the presence of high molecular weight compounds, such as proteins, the quinhydrone electrode is a good substrate to affect preferential adsorption.

GOLD ELECTRODE - A 100% gold electrode was studied and found to be outside the stability domain of a satisfactory working electrode. (Table 14, Figure 12). Combinations of gold powder with auric chloride was observed to be extremely corrosive and yield unsatisfactory potentials.

COPPER ELECTRODE - Pure copper powder was observed to give unstable electrode potentials. This instability is probably due to the extreme rapidity in which copper forms an oxide film in air as well as solution. Copper offers a well defined (if unique) structure and should be investigated further.

TABLE 14

COMMERCIAL ELECTRODES

Composition	V_o	V_f	V avg	Average Slope μv/sec.
Calomel Electrode Saturated (24 hour run)	+550.0μv +660.0μv	+6.9mv +6.9mv	+3120.0μv	+.15
100% Cu, Pwd. "A"	-85.0mv	-31.0mv	-58.0mv	
100% Cu (SCE value) Electrode vs Electrode	+209.0mv -8.5mv	+129.0mv	+165.0mv	+3.7
100% Hg_2Cl_2 (pressed pellet)(SCE value E vs E)	+64.0μv +124.0mv +3.2mv	+20.0μv +129.0mv	+42.0μv +126.0mv	-.44 +.90
Quinhydrone	+8.7mv	+1.2mv	+4.5mv	+2.3
100% Au (10 days)	+160.0mv	+108.0mv	+134.0mv	+.49

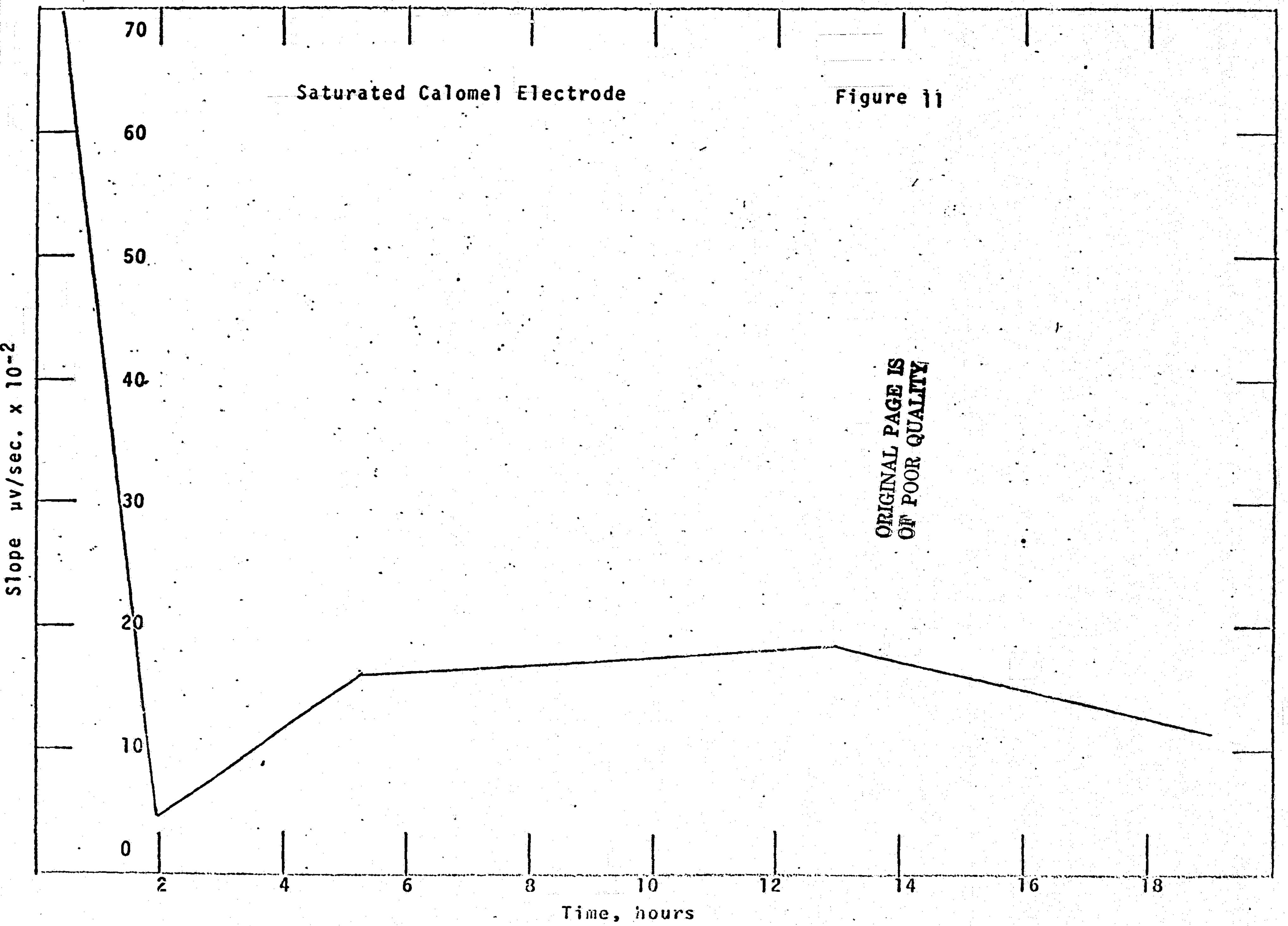
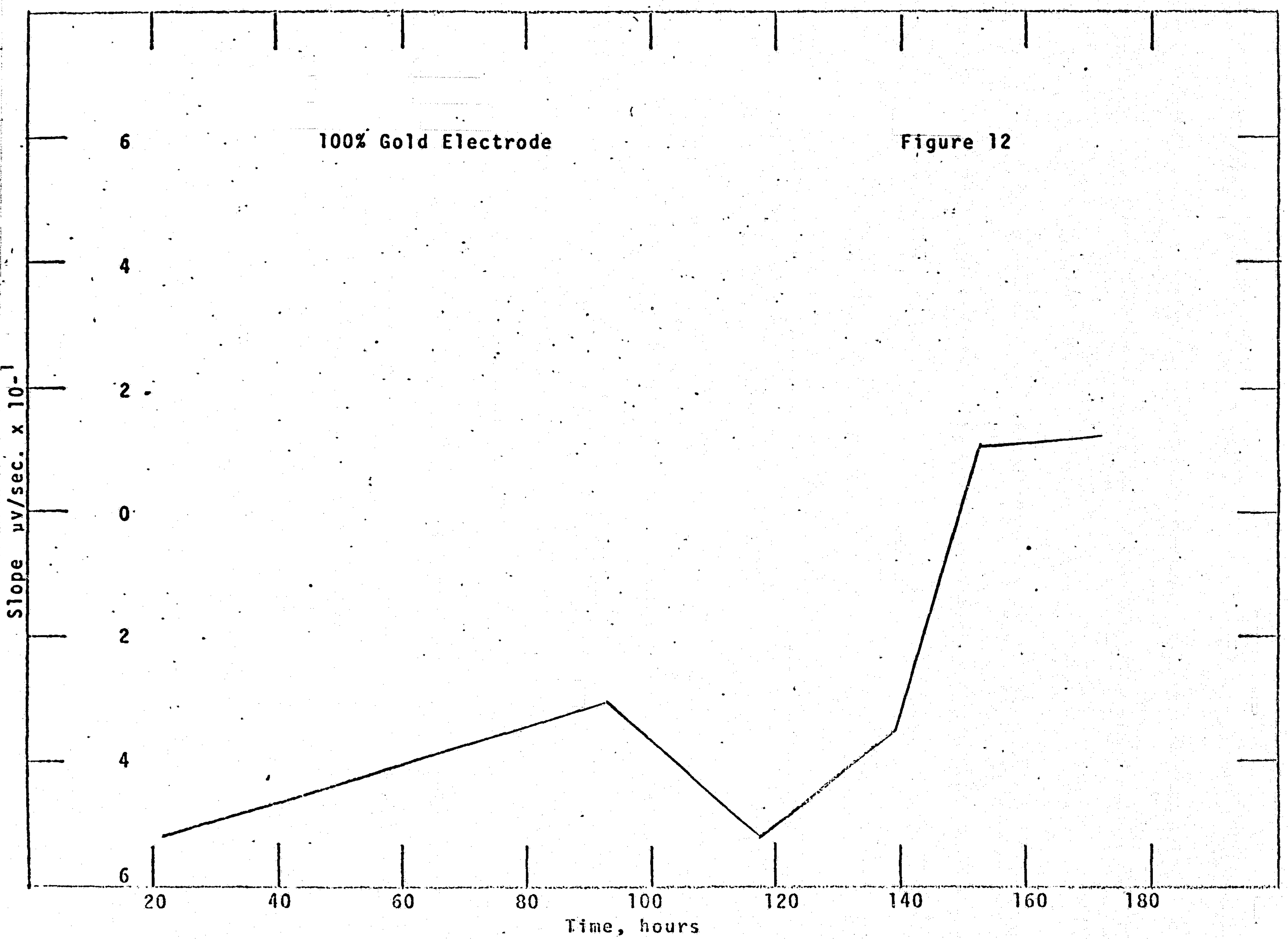


Figure 11

Saturated Calomel Electrode


100% Gold Electrode
Figure 12
Slope µv/sec. x 10-1
6
4
2
0
2
4
6
20
40
60
80
100
120
140
160
180
Time, hours

SILVER-SILVER HALIDE RATIOS

From an inspection of Table 15 it appears that the most desirable concentration to produce a stable reproducible silver-silver chloride electrode is 90 parts silver to 10 parts silver chloride.

The most desirable concentration for the silver-silver iodide (Table 16) and silver-silver bromide (Table 17) is 95 parts silver to 5 parts of the respective halides. The spread in potential for the iodide and bromide may be observed to be considerably higher than a chloride electrode which is prepared under identical conditions.

TABLE 15

SILVER-SILVER CHLORIDE

Composition	V_o	V_f	V avg.	Average Slope µv/sec.
Ag-AcCl (100-0)	+1.05mv.	+0.89mv	+0.97mv	+.46
Ag-AgCl (90-10)	-160.0µv	-90.0µv	-125.0µv	+.19
Ag-AgCl (75-25)	+2.3mv	+345.0µv	+1321.0µv	+.34
Ag-AgCl (60-40)	+12.1mv	+6.3mv	+9.2mv	-.16
Ag-AgCl (50-50)	-2.88mv	-1.03mv	-1.95mv	+.12
Ag-AgCl (25-75)	+3.3mv +2.2mv	+41.0µv	+1670.0µv	+.10
Ag-AgCl (5-95)	+1.6mv	+1.2mv	+1.4mv	+.07
Ag-AgCl (0-100%)	+3.2mv +2.6mv -5.3mv	+19.0mv	+11.2mv	+8.57 +6.4
A anodized with gelatin	+105.0µv	+145.0µv	+125.0µv	+.17

TABLE 16

SILVER-SILVER IODIDE

Composition	V_o	V_f	V avg	Average Slope μv/sec.
Ag-AgI (95-5)	-370.0 μv	-250.0 μv	-310.0 μv	
Ag-AgI (90-10)	+480.0 μv +5.4mv	+600.0 μv	+540.0 μv	-.09
Ag-AgI (50-50)	+4.25mv +5.9mv	+1.91mv	+3.08mv	-.11
Ag-AgI (10-90)	+5.4mv	-3.4mv	+1.0mv	
Ag-AgI (0-100)	+49.0mv			Constant at low values

TABLE 17

SILVER-SILVER BROMIDE

Composition	V_o	V_f	V avg	Average Slope μv/sec.
Ag-AgBr (95-5)	+860.0 μv +400.0 μv +3.5mv	+140.0 μv +1480.0 μv	+500.0 μv +940.0 μv	+.15 +.36
Ag-AgBr (90-10)	+8.02mv -340.0 μv	+1.07mv	+4.86mv	+.03
Ag-AgBr (75-25)	+12.2mv +460.0 μv	+200.0 μv	+6.2mv	+3.65
Ag-AgBr (60-40)	+7.6mv +.9mv	+88.0 μv	+3844.0 μv	-4.8
Ag-AgBr (50-50)	-500.0 μv +10.0mv	+222.0 μv	+5.11mv	+3.0

SILVER-SILVER OXIDE - ANTIMONY-ANTIMONY TRIOXIDE - TIN ELECTRODES

Admixtures of silver-silver oxide give moderately stable electrodes. The stability of these electrodes depend upon the extent of chemisorption of oxygen into the metal-metal oxide substrate. In some cases extremely thin deformable films of oxygen are formed which readily repair themselves when a breach occurs on the surface. (Table 18)

Antimony electrodes are not readily poisoned and have low electrical resistance. Combinations of these electrodes with membrane materials should offer some interesting possibilities. (Table 19)

Tin electrodes decompose in the presence of stannic chloride. (Table 20)

TABLE 18.

SILVER-SILVER OXIDE

Composition	V_o	V_f	V avg	Average Slope μv/sec.
$Ag-Ag_2O$ (95-5)	+12.8mv	+14.2mv	+13.5mv	+9.1
$Ag-Ag_2O$ (90-10)	+4.8mv	+1.3mv	+3.0mv	+.35
$Ag-Ag_2O$ (50-50)	-38.0mv +15.0mv	-44.0mv	-41.0mv	-5.2

ANTIMONY-ANTIMONY OXIDE

TABLE 19

100% Sb	+3.2mv	+4.1mv	+3.7mv	+.86
$Sb-Sb_2O_3$ (95-5)	+600.0μv	+6.0μv	+303.0μv	+.42
$Sb-Sb_2O_3$ (90-10)	+89.0mv	+8.2mv	+48.0mv	+.59
$Sb-Sb_2O_3$ (60-40)	+130.0mv	+111.0mv	+120.0mv	+2.34
$Sb-Sb_2O_3$ (50-50)	+184.0mv	+153.0mv	+168.0mv	+.78

TABLE 20

TIN-TIN CHLORIDE

Sn (100%)	+300.0μv	+1.6mv	+950.0μv	+8.03
$Sn-SnCl_2$ (50-50)		DISSOLUTION		
$SnCl_2$ (100%)	+90.0mv	-197.0mv	-53.0mv	

ELECTROCHEMICAL BEHAVIOR OF DIMETHYL SULFOXIDE

The resistivity of varying concentrations of dimethyl sulfoxide (DMSO) containing water and sodium chloride is shown in table 18.

TABLE 18

No.	Composition	Resistivity (ohm^{-1}/cm^{-1})
1	DMSO-H_2O (90-10)	>10
2	DMSO-H_2O (70-30)	>10
3	DMSO H_2O (50-50)	>10
4	DMSO-1 N NaCl (90-10)	3.85
5	DMSO-1 N NaCl (70-30)	1.45
6	DMSO-1 N NaCl (50-50)	0.59

Experiments were preformed on measuring the changes in potential when DMSO containing NaCl is transported across synthetic and natural membrane materials. Electrodes (Ag-AgCl) having an area of 1 cm^2 were mounted in a specially constructed vessel that permits the diffusion of the DMSO-salt solution from one compartment to another by means of a membrane material. The potential was measured after 0, 5, 10, and 15 minutes. The data is presented in table 22.

TABLE 22

Teflon Membrane (.001 thickness)

Composition	Time (minutes)			
	0	5	10	15
1 vs 4	8.2 mv.	9.4 mv.	10.1 mv.	12.0 mv.
2 vs 5	4.4 mv.	5.0 mv.	5.1 mv.	5.2 mv.
3 vs 6	17.0 mv.	44.0 mv.	37.0 mv.	31.0 mv.

Chicken Skin Membrane

Composition	0	5	10	15
1 vs 4	162.0 mv.	178.0 mv.	211.0 mv.	269.0 mv.
2 vs 5	200.0 mv.	180.0 mv.	178.0 mv.	176.0 mv.
3 vs 6	83.0 mv.	66.0 mv.	90.0 mv.	109.0 mv.

The potential may be observed to increase with increasing time when a Teflon membrane is used and the ratio of DMSO to water is in the range of 70 to 90 per cent. The potential increases with increasing time when a 90 per cent DMSO solution is used and gives irregular behavior when concentrations of DMSO are 70 per cent or less.

PREPARATION OF FLIGHT ELECTRODE PASTE

(FEP-1)

A. Ingredients for one liter

1. 1 gram methyl-p-hydroxybenzoate
2. 1 gram propyl-p-hydroxybenzoate
3. 60 gram hydroxyethylcellulose Natrosol 250 GR (Hercules Powder Co.0
4. 5.8 grams NaCl (Analytical Reagent Grade)
5. 1 liter deionized water

B. Blending process

1. Add benzoates to one liter deionized water and blend in mixer with plastic coated beaters and glass or plastic container.
2. Add NaCl and blend until dissolved
3. Add Natrosol slowly and blend
4. Blend thoroughly
5. Adjust pH to 7.0 ± 0.1 with pH meter, using 6 N NaOH or HCL
6. Let stand overnight and recheck pH
7. Add food coloring to suit, if desired

C. Storage

1. Use plastic tubes or containers
2. No metal should contact paste
3. This paste provides a high conductivity vehicle that is isotonic to sweat (0.1N NaCl) and will not alter skin resistance. It is non-irritating and non-sensitizing and has

a good shelf life.

2. No metal should come in contact with paste.
3. This paste is ten times isotonic Ringers' solution in ionic content.
4. This paste should have a long shelf life and is non-irritating and non-sensitizing.

CONCLUSIONS

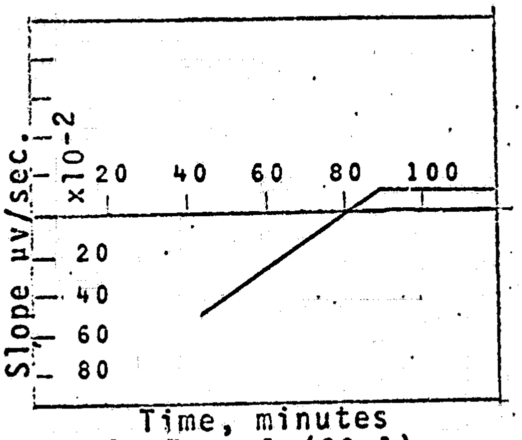
It has been amply demonstrated that water soluble gums, clays, synthetic waxes, polymeric materials are effective membrane materials which can be incorporated into a standard pressed pellet electrode system such as silver-silver chloride.

It has been shown that a hybrid electrode may be prepared by electrolytically coating silver-silver chloride along with a hydrophyllic colloid. This colloid has been found to combine the stable potential and low direct-current resistance properties of a silver-silver chloride electrode with the low frequency impedance characteristics of a gelatinized electrode.

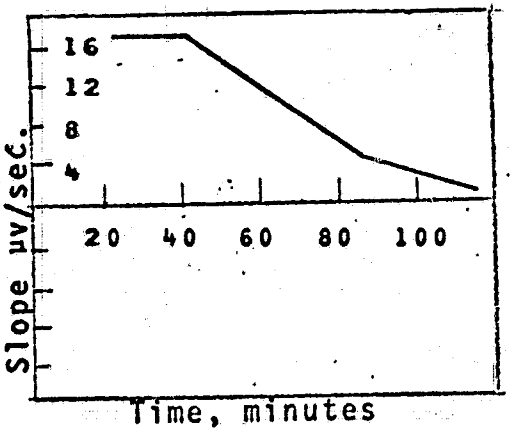
The most important assets of the electrode system described is that they are small and compact, can be used in any orientation and usually do not contaminate any environment to which they are exposed. Furthermore, the colloid coated and membrane electrodes help to prevent flow and movement artifacts and are not readily "poisoned" by materials such as proteins.

APPENDIX

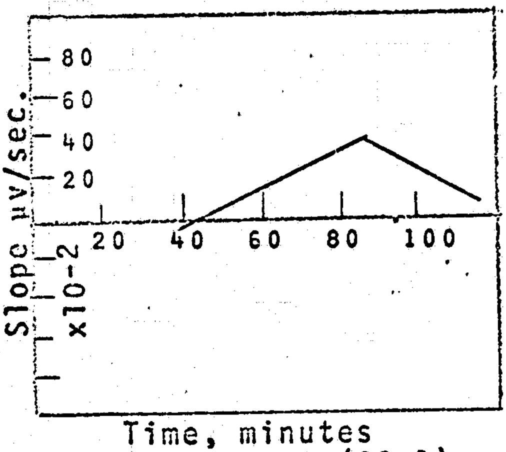
NOMOGRAPHS ON ELECTRODE STABILITY



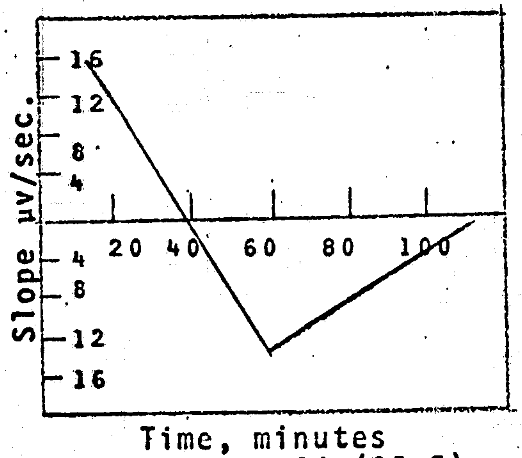
Ag-Zeogel (99-1)



Ag-Zeogel (95-5)



Ag-Bentone 34 (99-1)



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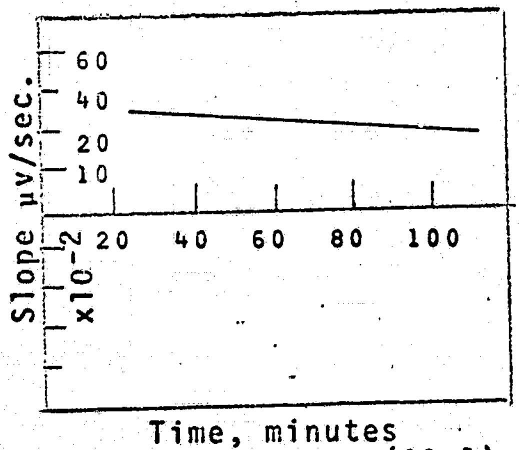
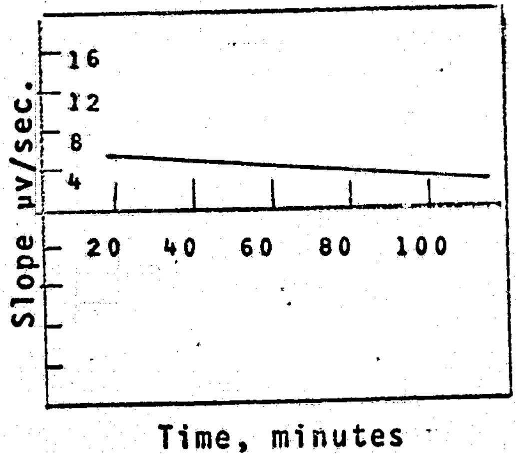
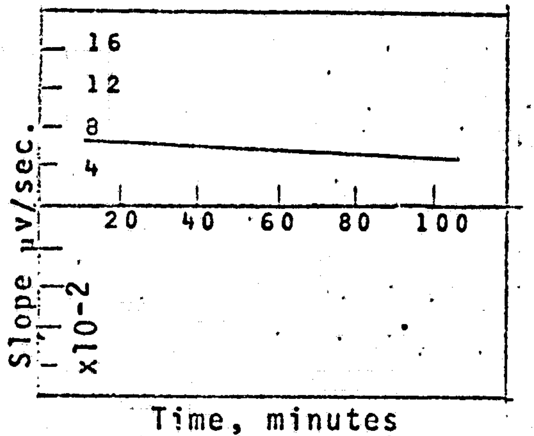


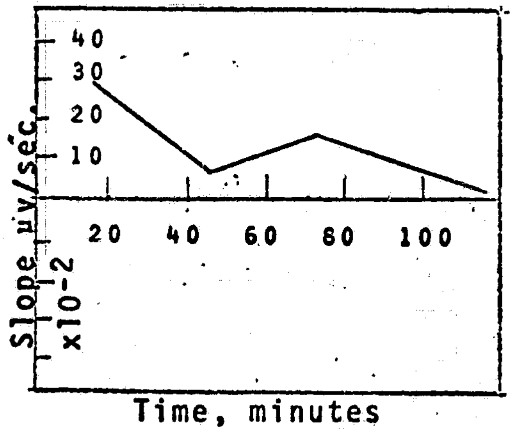
Ag-CaStearate (99-1)



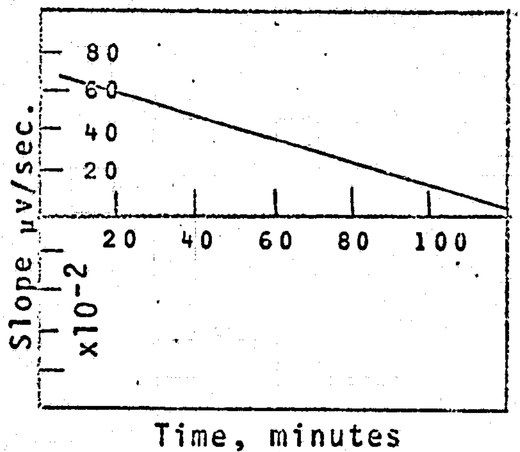
Zeogel



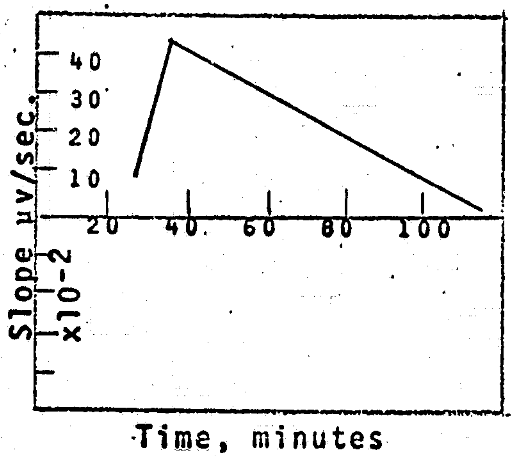
Polyvinyl (Alcohol) 30.98



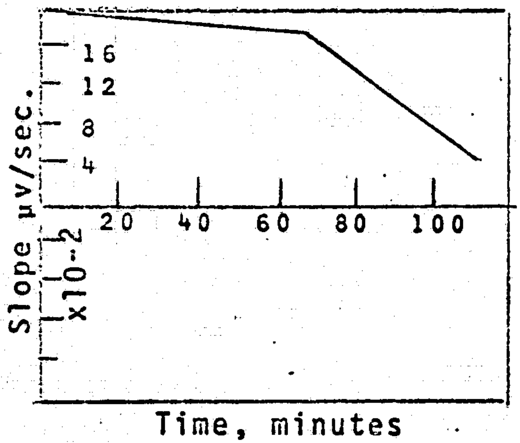
Acrawax C



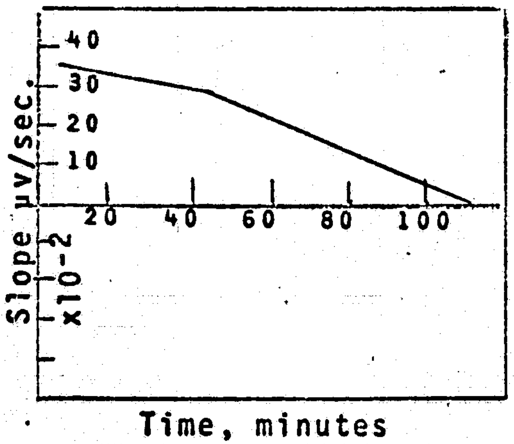
Polyvinyl Alcohol 165



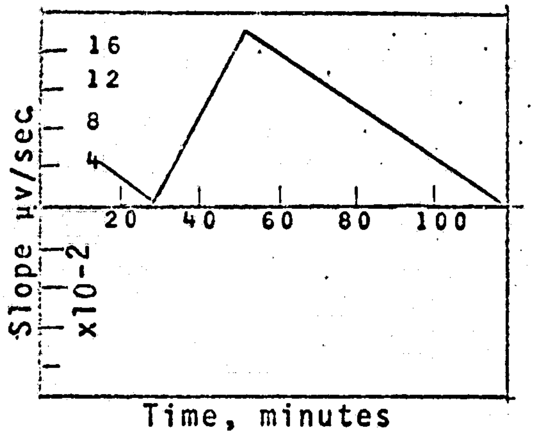
DX-840



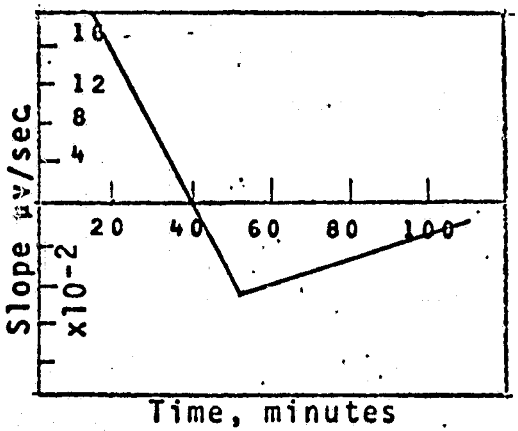
Lucite 2044



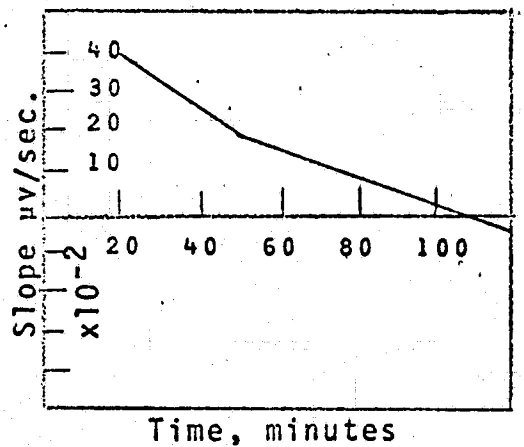
Lucite 2010



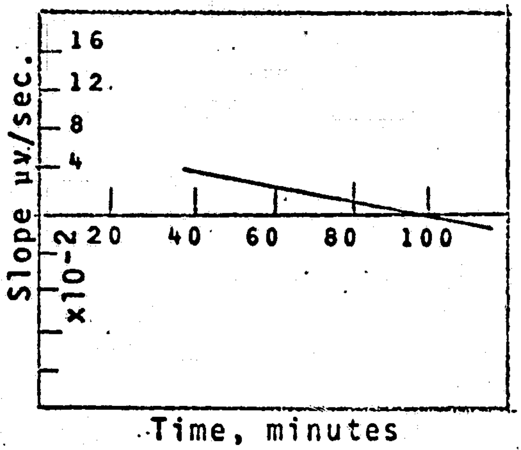
Baymal



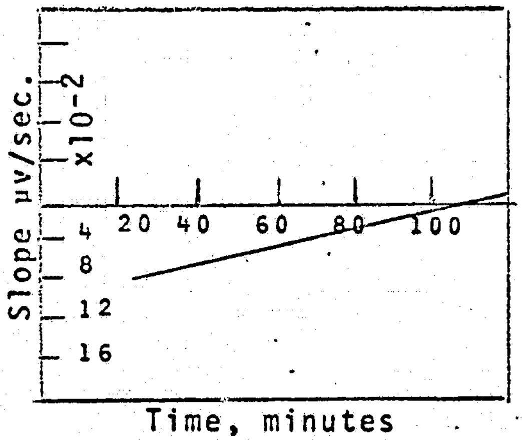
Sephadex



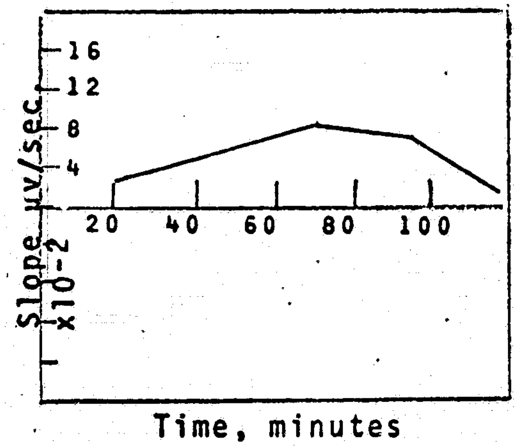
Al Hydroxy Stearate



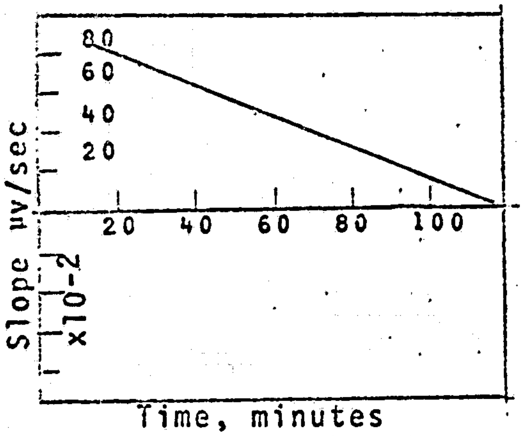
Quebracho



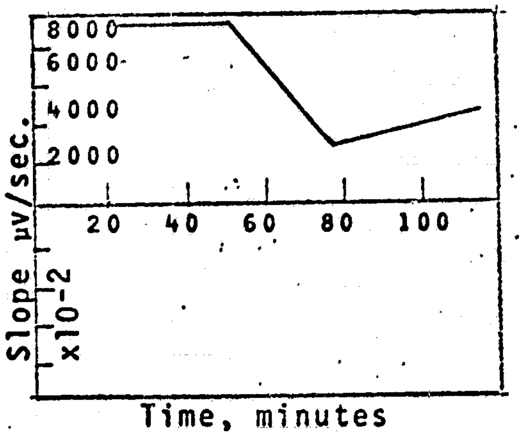
Cabosil



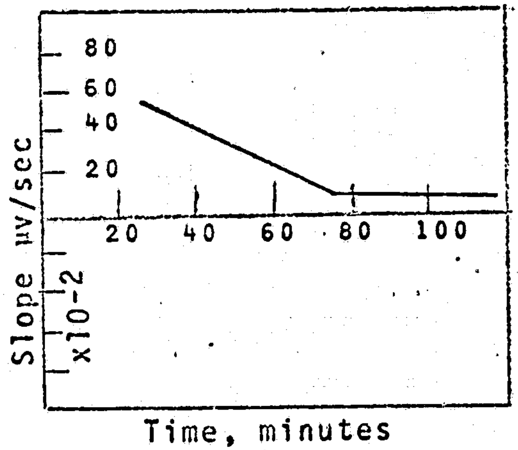
Wax 280



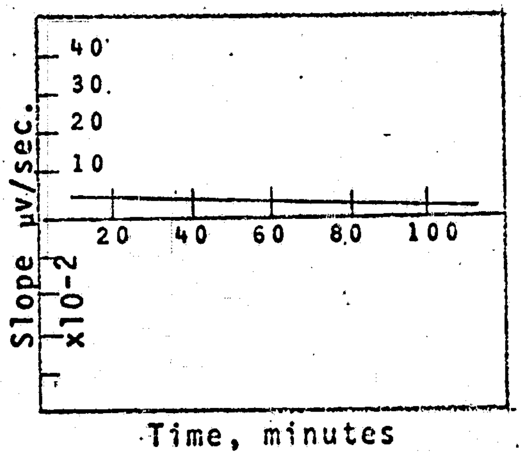
Mennen Greatbatch



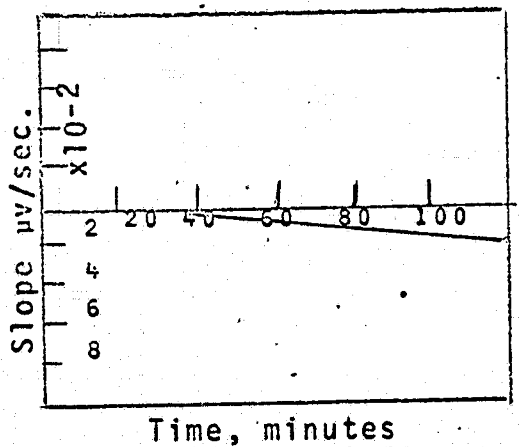
Luccina



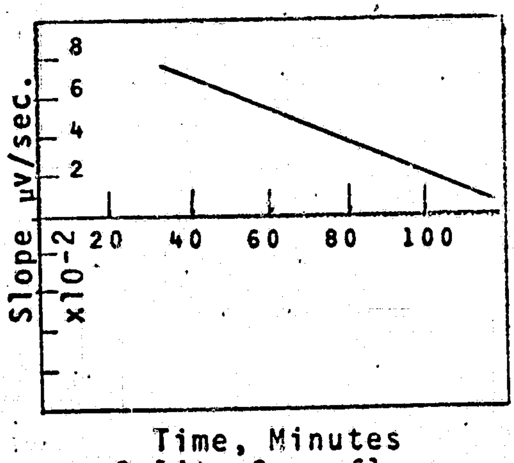
Beckman



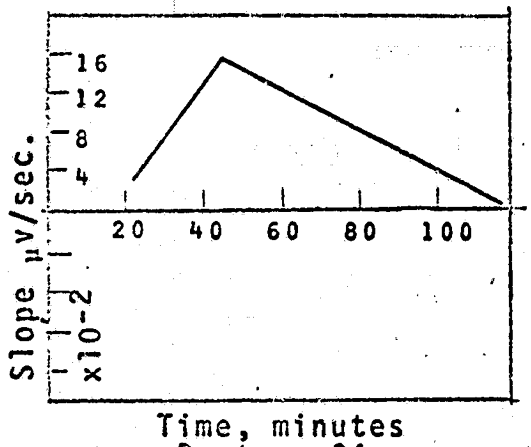
Calomel



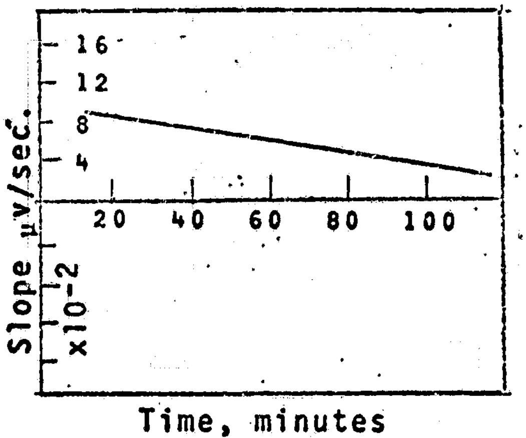
Natrosol 250 JR



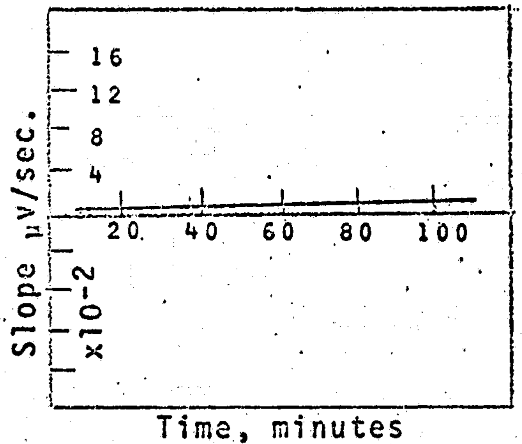
Celite Superfloss



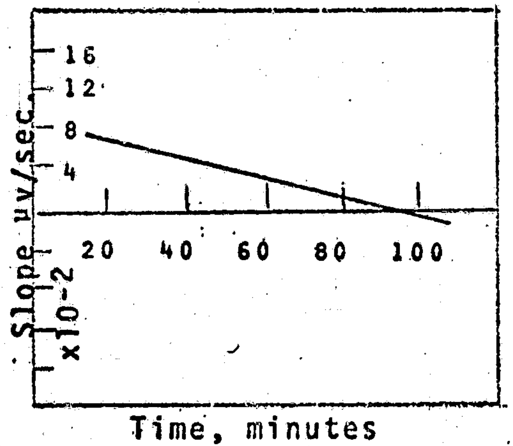
Bentone 34



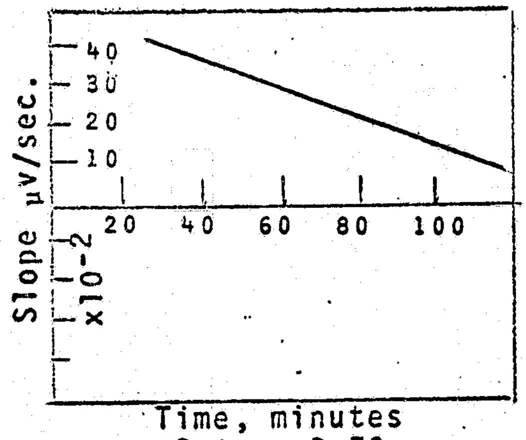
Bentonite



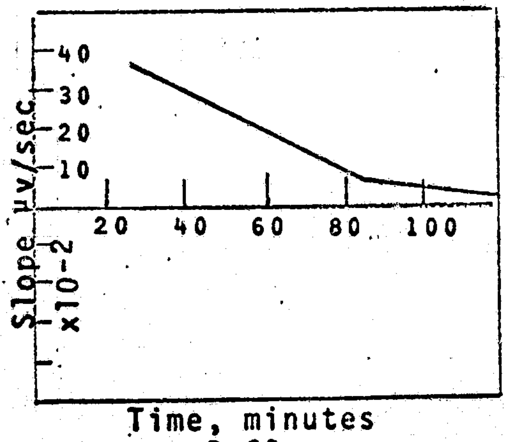
Douglas Clearsol Gum



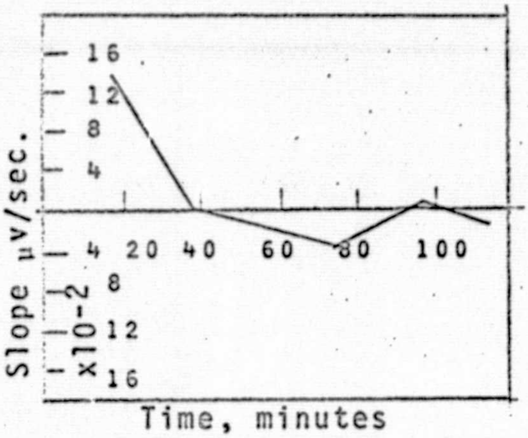
Gum Talha



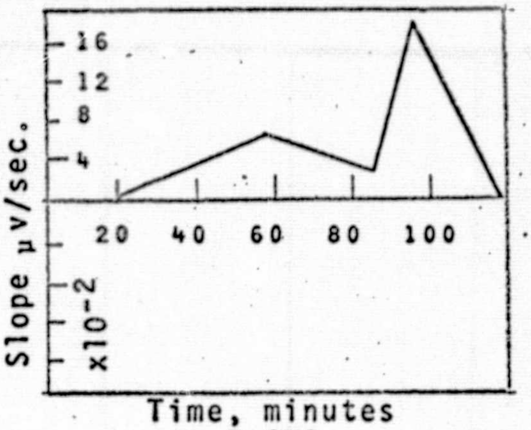
Butvar B-73



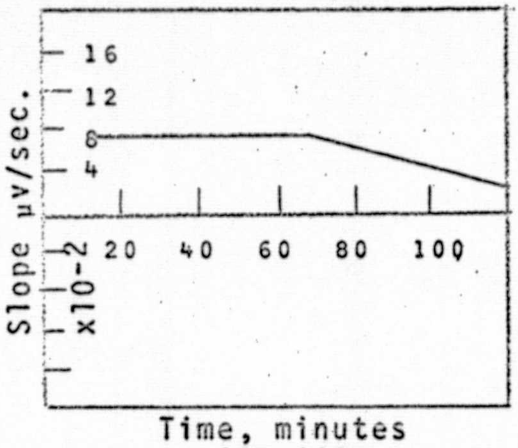
$BaSO_4$



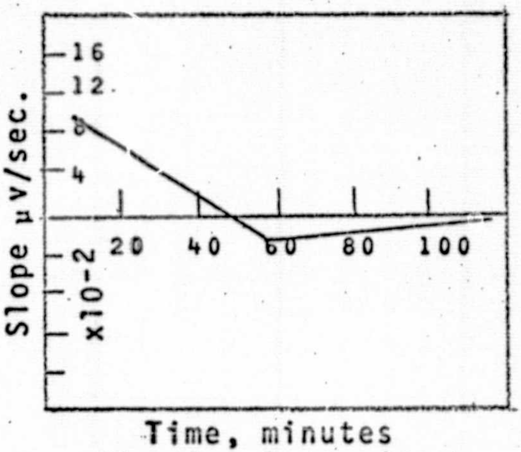
Amberlite RC-D



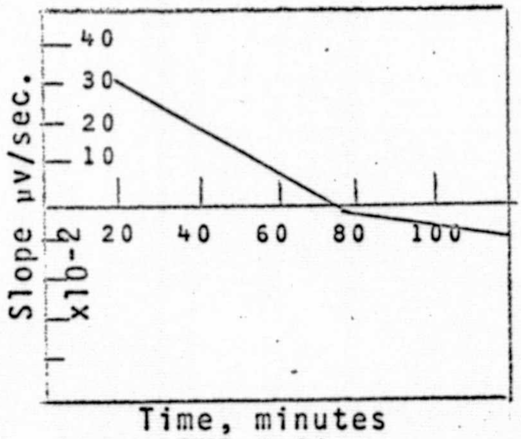
NaCMC



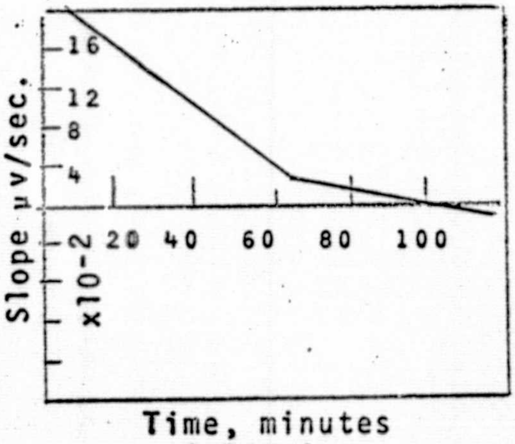
ASP-400



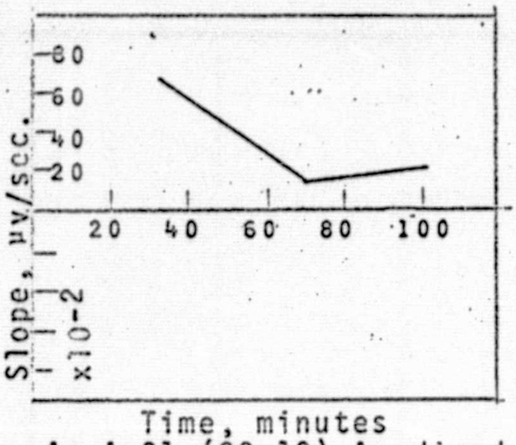
Wyoming Bentonite



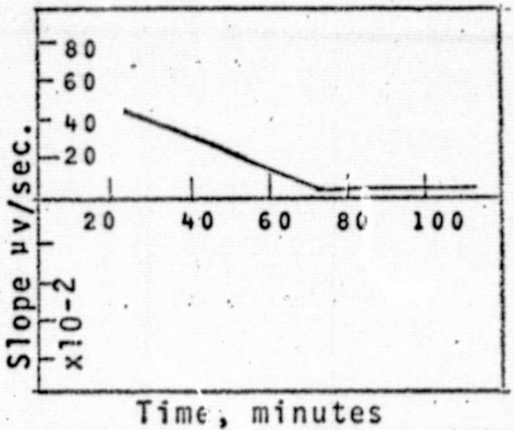
PVP-K-90



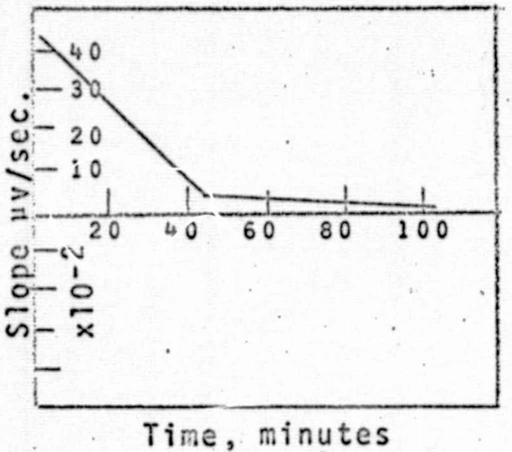
Q-Broxin



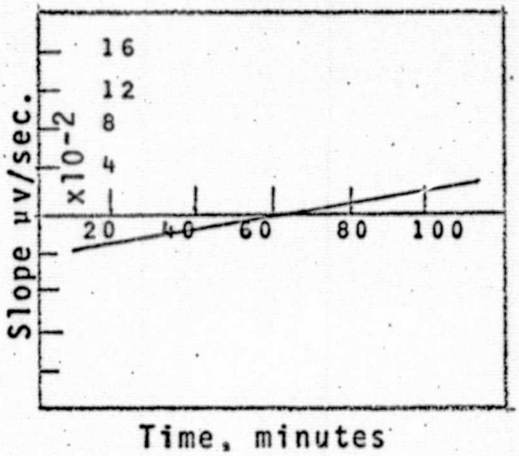
Ag-AgCl (90-10) Anodized



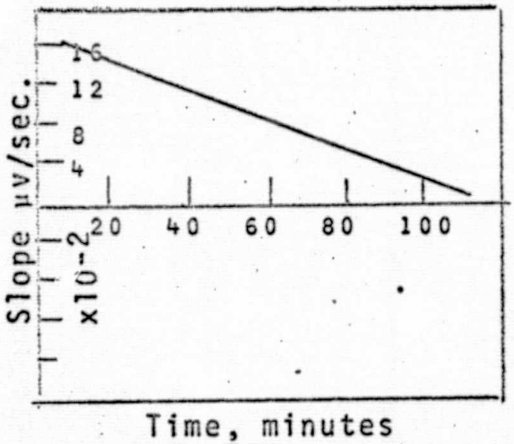
Ag sheet - Anodized with NaCl



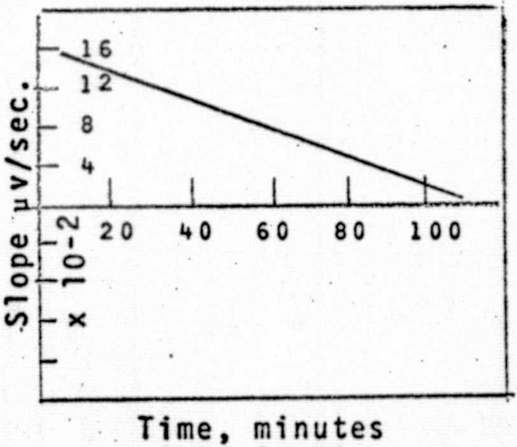
Zeogel



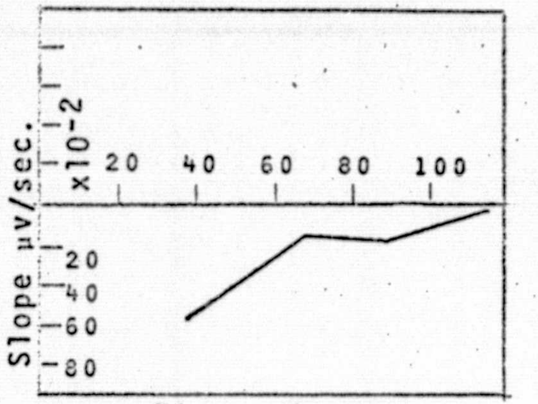
Vee Gum



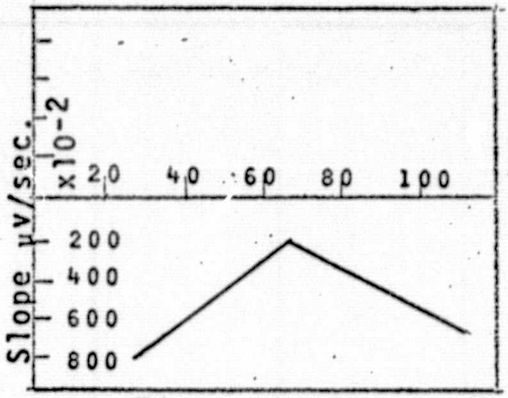
Gum Tragacanth



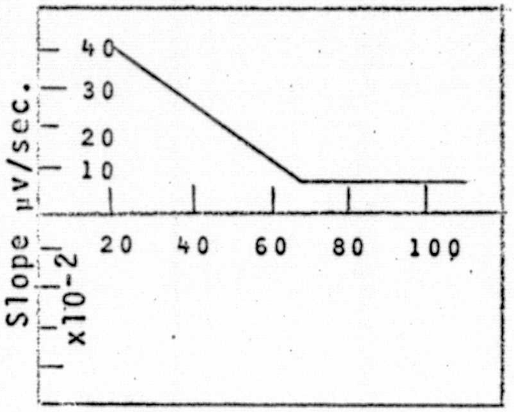
Gum Arabic



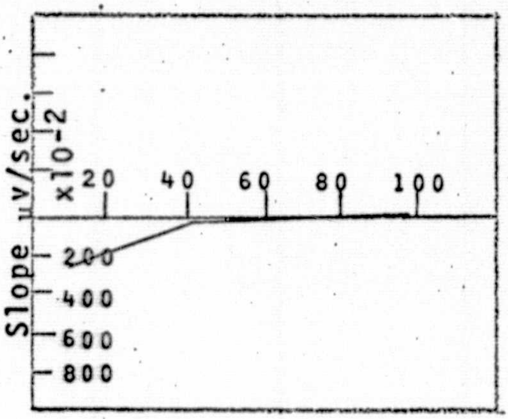
Ag-AgI (50-50)



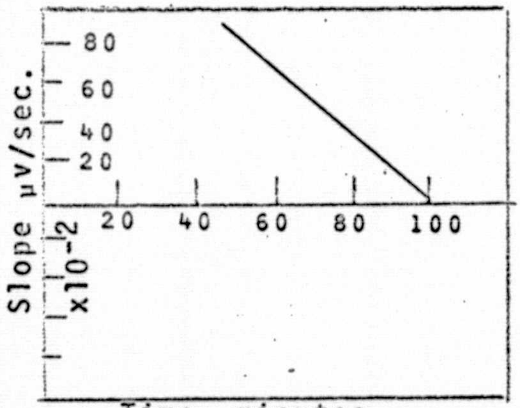
$Ag-Ag_2O$ (50-50)



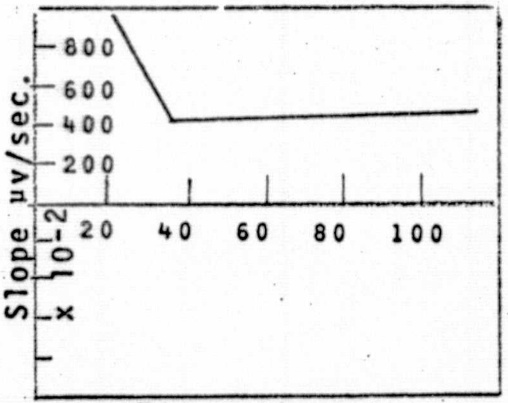
Ag-AgI (90-10)



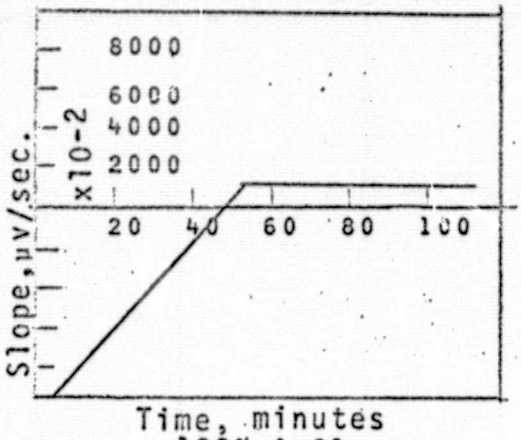
$Ag-Ag_2O$ (90-10)



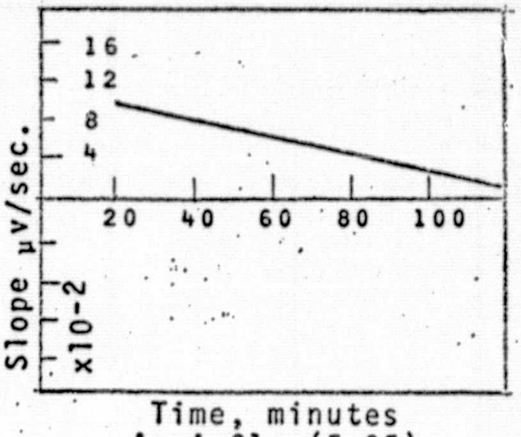
Ag-AgI (95-5)



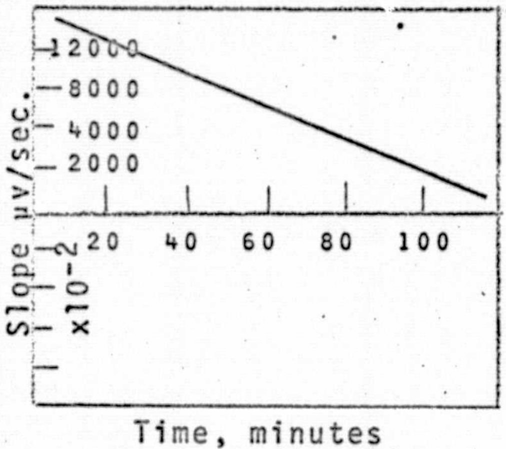
$Ag-Ag_2O$ (95-5)



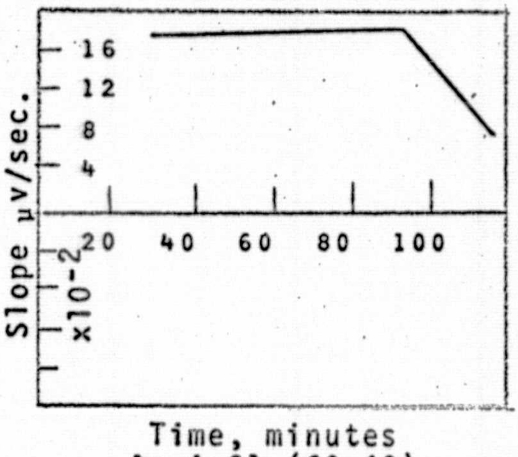
100% AgCl



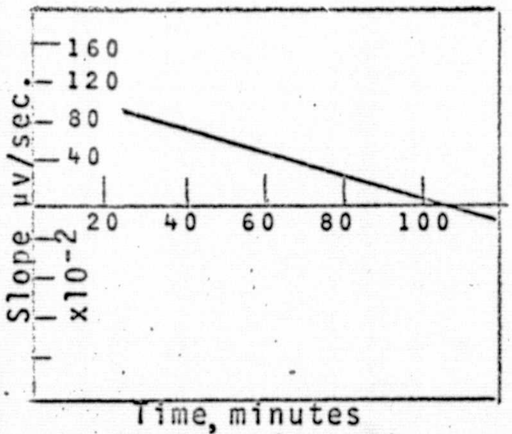
Ag-AgCl (5-95)



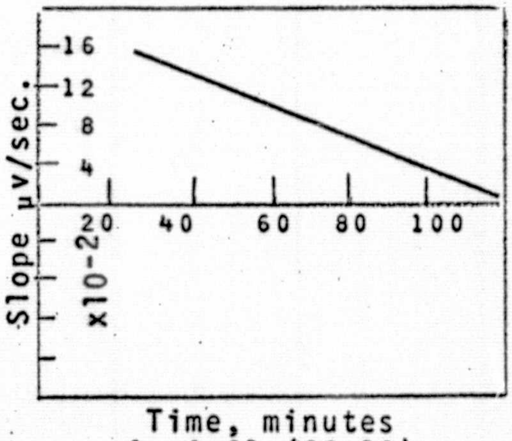
Ag-AgCl (25-75)



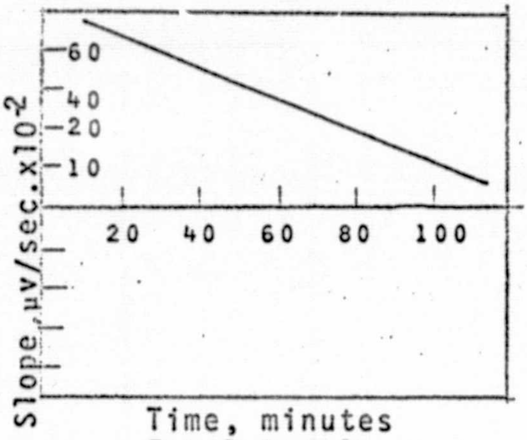
Ag-AgCl (60-40)



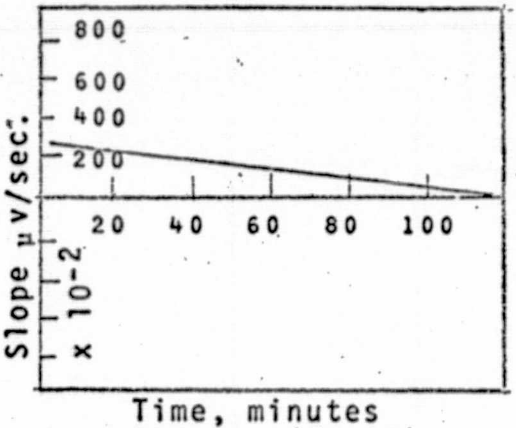
Ag-AgCl (75-25)



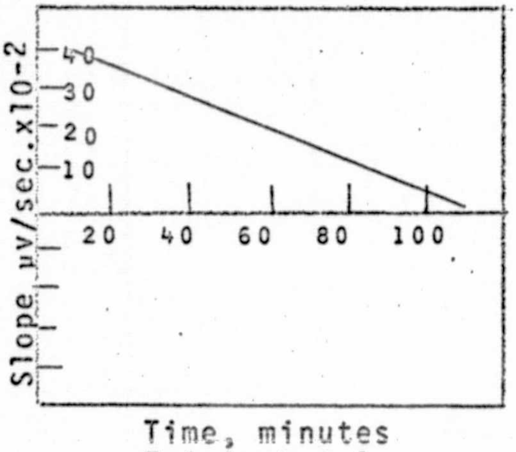
Ag-AgCl (90-10)



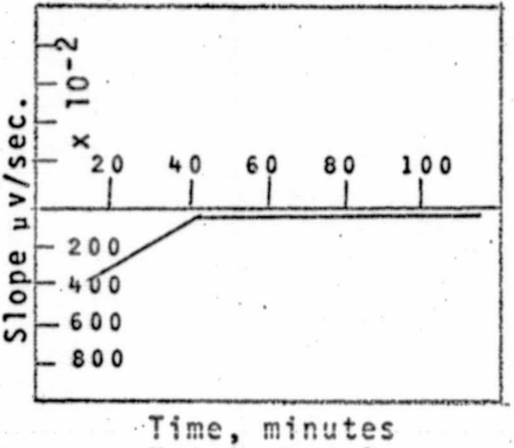
Ethyl-Butyl
Copolymer (90-10)



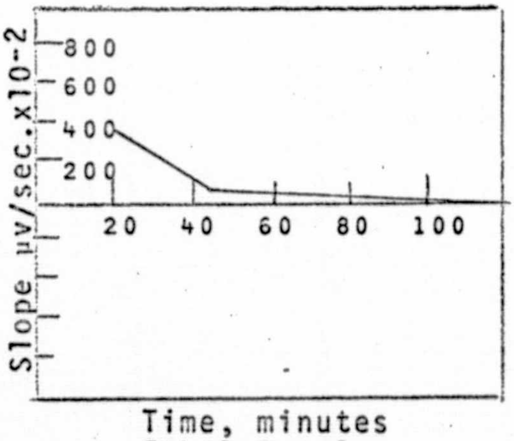
Acrylic (90-10)



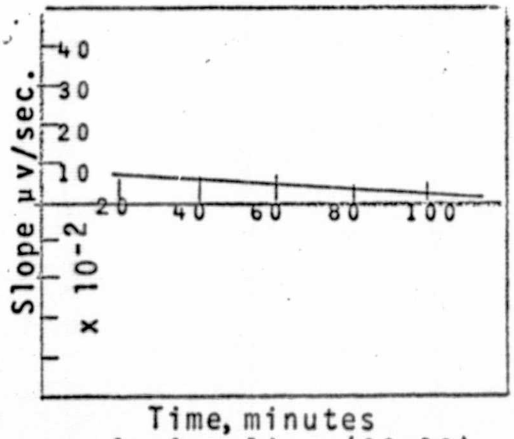
Tri-isobutyl
Methacrylate (90-10)



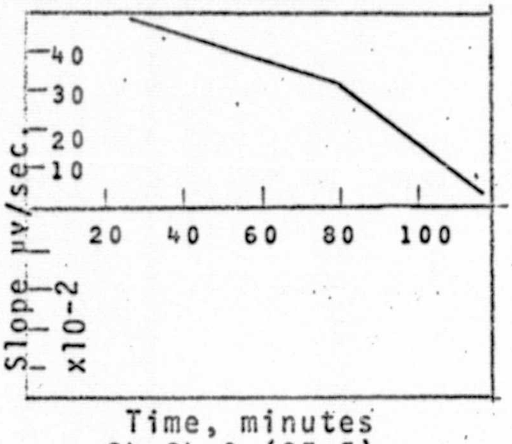
Tri-isobutyl
Methacrylate (80-20)



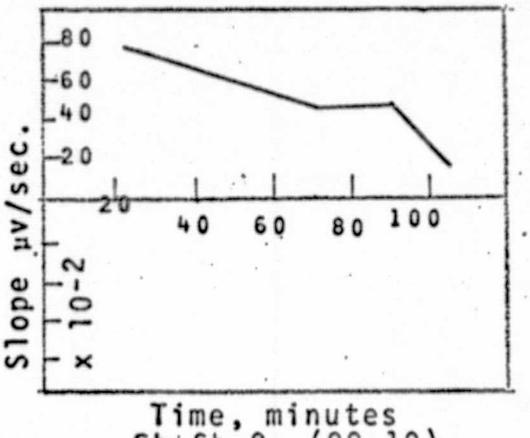
Ethyl-Butyl
Copolymer (80-20)



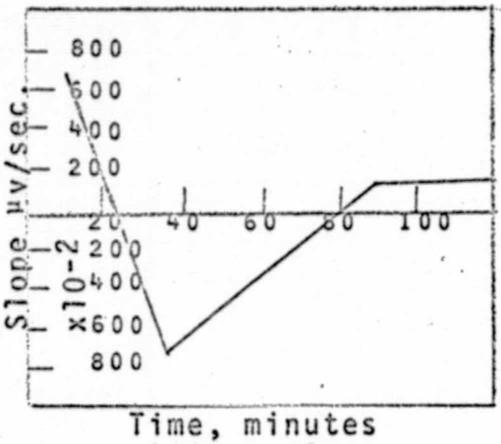
Ag-Acrylic (90-10)
Ethyl-methyl Methacrylate
(70-30)



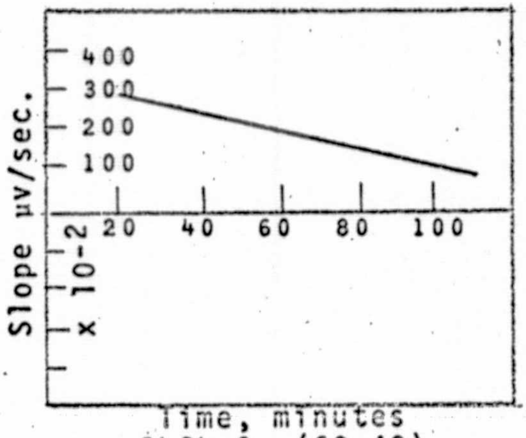
$Sb-Sb_2O_3$(95-5)



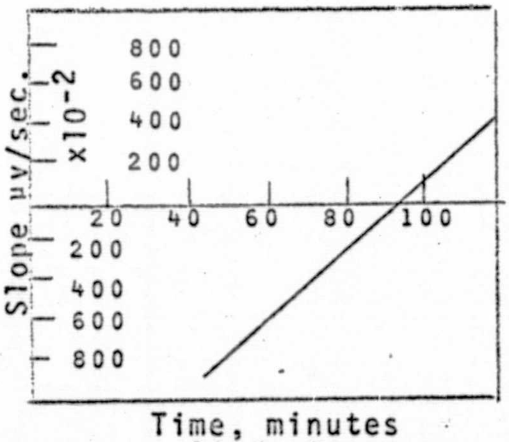
$Sb-Sb_2O_3$ (90-10)



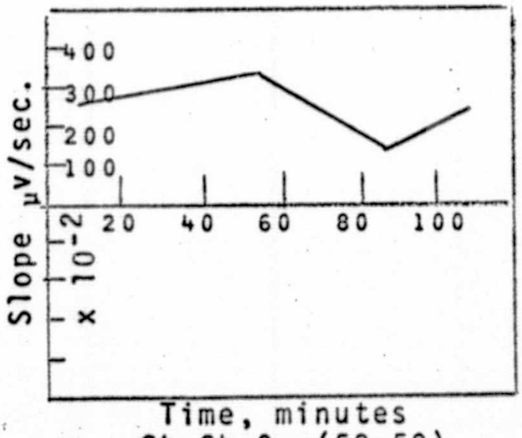
100% $HgCl_2$



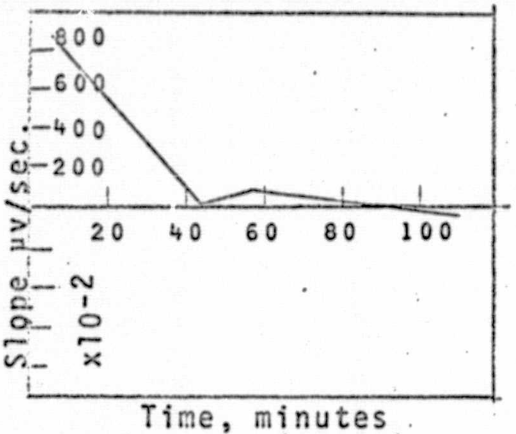
$SbSb_2O_3$ (60-40)



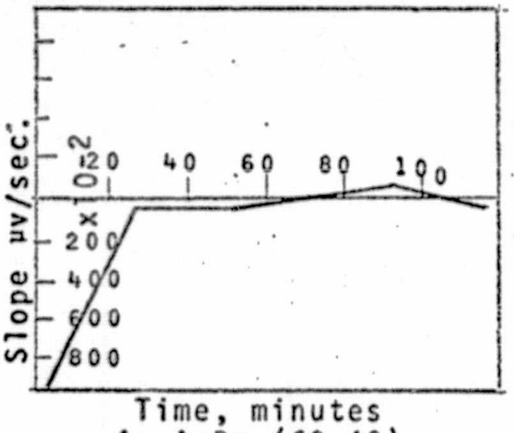
100% Sn



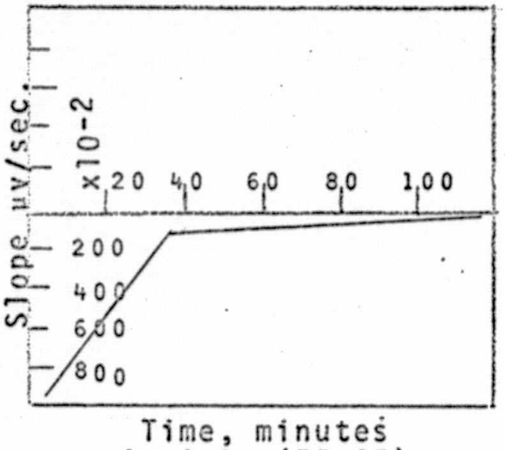
$Sb-Sb_2O_3$ (50-50)



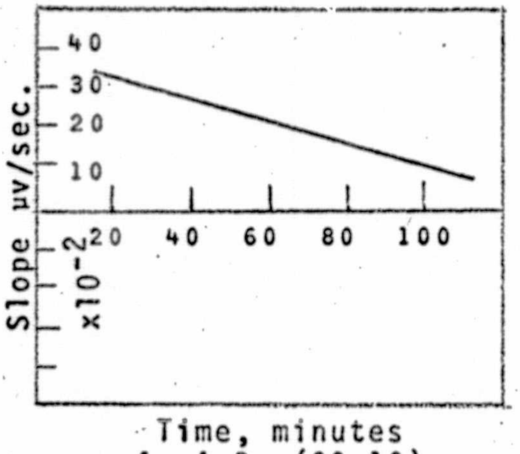
Ag-AgBr (50-50)



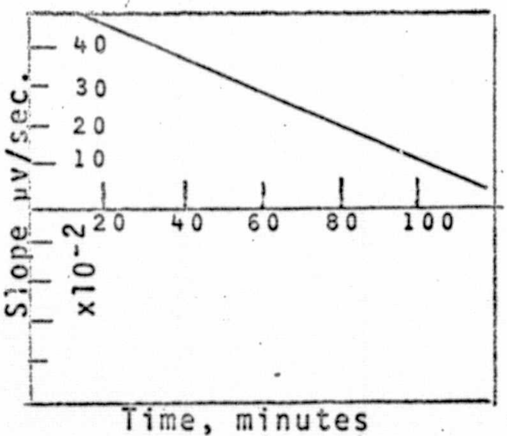
Ag-AgBr (60-40)



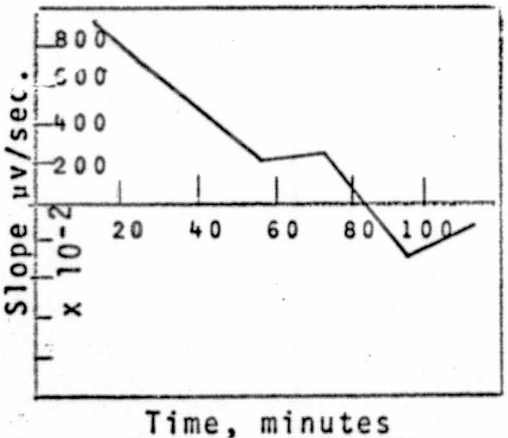
Ag-AgBr (75-25)



Ag-AgBr (90-10)



Ag-AgBr (95-5)



Ag-AgCl (25-75)