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## **ELECTROCHEMICAL CARBON DIOXIDE SENSOR**

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## FOREWORD

This program was carried out for the Aerospace Medical Research Laboratories by Ionics Incorporated, 65 Grove Street, Watertown, Massachusetts 02172 under Contract No. AF33(615)-3261 in support of Project No. 6373, "Equipment for Life Support in Aerospace," Task No. 637302, "Respiratory Support Equipment." Mr. Ints Kaleps of the Biotechnology Branch, Life Support Division, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio was the contract monitor.

The principal investigator for Ionics was Mr. Frank B. Leitz, Senior Engineer in the Bionomics Section of Ionics' Research Division assisted by Mr. Bernard I. Sohn, Project Chemist. The work was carried out under the supervision of Mr. Wayne A. McRae, Vice-President Research and Mr. Daniel L. Brown, Manager Contract Research. The research sponsored by this contract was performed between October 1965 and October 1966.

This report has been reviewed and is approved.

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## ABSTRACT

The purpose of this program was to develop a novel carbon dioxide sensor based on obtaining changes in the electrical resistance of anion-exchange resin proportional to the ambient partial pressure of carbon dioxide. The change in resistance is due to the increased ionization of a weakly ionized base in the presence of a slightly acid gas. A laboratory program was conducted to evaluate the response of various types of weak-base ion-exchange polymers to carbon dioxide concentrations in the range of 0 to 4%. The optimum material consisted of a condensation polymer of resorcinol, formaldehyde and triethylenetetramine. A laboratory model of the CO<sub>2</sub> Sensor was fabricated using these sensing elements in the form of small, thin strips. In order to minimize the effects of humidity and temperature, the model contained two sensing elements, one being a reference. A guard chamber has been provided to absorb any strongly-acid gases. Electrical readout is made on a balancing potentiometer with an earphone detector. The Sensor is small (about 50 cubic inches), weighs less than 6 ounces, has a power requirement of less than 0.5 watts, and its operation is independent of gravity.

*Contrails*

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## SECTION 1

## INTRODUCTION

The object of this work was to develop a novel carbon dioxide sensor based upon measurable changes in the electrical properties of weak-base anion-exchange resins as the ambient carbon dioxide partial pressure changes. Such an instrument should be small, rugged, gravity independent and provide rapid, accurate, reliable results at low cost.

Ion-exchange resins are of two major types: cation and anion. In a cation-exchange resin, there is a polymer matrix containing fixed anionic groups and mobile cations. Under concentration or electrical gradients, these cations can move, while the immobile anions remain fixed. In an anion-exchange resin, the situation is reversed and the mobile ions are the anions.

Anion-exchange resins, in turn, are of two types: strong and weak bases. A typical strong-base resin is  $R-N(CH_3)_3^+ + OH^-$  where R represents the polymeric network. As indicated, the active groups of a strong-base resin are normally highly ionized. A weak-base resin is one which is normally little ionized, such as  $R-NH_3OH$ . The ionization constant for a weak-base resin is of the order of  $10^{-5}$ .

The weak-base resin will equilibrate reversibly with carbon dioxide in the atmosphere to form an ionized bicarbonate. The reactions are:  $R-NH_3OH + CO_2 \rightleftharpoons R-NH_3^+ + HCO_3^-$ . As in any such reversible equilibrium reaction, a change in the concentration of one of the components will result in a change in the others which is based, assuming equilibrium is achieved, on thermodynamic factors. Thus, the amount of bicarbonate formed will be a function of the partial pressure of carbon dioxide in the atmosphere surrounding the resin. In the hydroxyl form the resin is little ionized while in the bicarbonate form it is highly ionized. Therefore, in the hydroxyl form the electrical conductivity, which results from the motion of the ions only, is low because of the absence of available mobile ions. In the bicarbonate form, however, there is present a substantial quantity of mobile anions and the electrical conductivity is thereby increased. Since the number of bicarbonate ions is a reversible direct function of the carbon dioxide partial pressure, the electrical resistance is also a reversible direct function of the carbon dioxide partial pressure and can be determined from the electrical conductivity of the resin.

On this basis, a carbon dioxide sensor can be operated by measuring the electrical conductivity of a weakly-basic anion-exchange resin. This report covers the investigation of these phenomena to demonstrate the feasibility of such an instrument.

## SECTION II

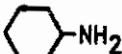
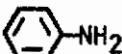


### DEVELOPMENT OF SENSOR ELEMENT

The sensor element developed under this contract is a thin sheet of water-wet weak-base polymer. In this report, this will be referred to as a "membrane" although its configuration was varied during the investigation.

Weak-base resin polymers generally have a nitrogen in the mer-group, with a pair of electrons which can accept a proton. The strength of this bond depends on the structure surrounding the nitrogen and determines how basic the compound will be. In the following table a number of simple weak bases are tabulated with their dissociation constants (K) in water at 25 C.

TABLE I

DISSOCIATION CONSTANTS OF WEAK BASES

Compound	Structure	K
Ammonium Hydroxide	$\text{NH}_4\text{OH}$	$1.7 \times 10^{-5}$
Methyl Amine	$\text{CH}_3\text{NH}_2$	$4.4 \times 10^{-4}$
Dimethylamine	$(\text{CH}_3)_2\text{NH}$	$5.2 \times 10^{-4}$
Trimethylamine	$(\text{CH}_3)_3\text{N}$	$5.5 \times 10^{-5}$
Cyclohexylamine		$4.4 \times 10^{-4}$
Aniline		$3.8 \times 10^{-10}$
Piperidine		$1.6 \times 10^{-3}$
Pyridine		$1.7 \times 10^{-9}$

These data indicate that while there is comparatively little difference in basic character ( $K \approx 10^{-4}$ ) between primary, secondary, and tertiary amines, compounds with a double bond on the  $\alpha$  carbon that can have resonant structures are considerably weaker bases ( $K \approx 10^{-9}$ ).

If the membrane is too strongly basic, the device will always be conductive. If, however, it is too weakly basic, then only a small fraction of the sites will be ionized and the conductivity will always be low. Apparently a compromise should be made in the basic nature of the membrane, but this can only be determined experimentally.

A variety of polymers were studied. These consisted of various formulations of two condensation polymers and two addition polymers. Initial evaluation of membranes were performed on thin rectangular strips with cloth backing.



## Liquid-Phase Evaluation (Acid/Base)

A simple preliminary evaluation of different polymers was made. The AC-resistance was measured under two conditions: (1) equilibrated with strong base (1N NaOH) when the membrane was minimally ionized, (2) equilibrated with strong acid (1N HCl) when the membrane was fully ionized. A large difference in resistance, at least ten-fold, was used to indicate a potentially highly sensitive element. Membranes which showed only a small change in resistance were considered unsuccessful candidates and not subject to further testing.

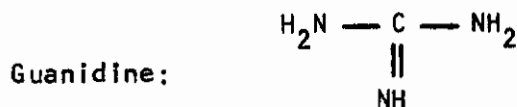
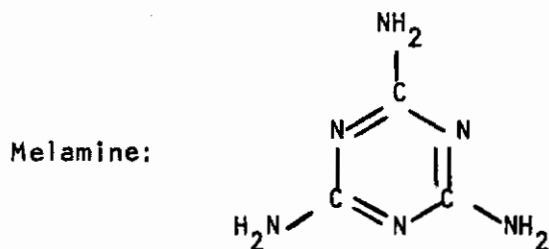
Preliminary evaluation of the membranes consisted of a comparison of fully-ionized to minimally-ionized resistance. Test strips 1.9 cm by 7.6 cm were cut from the membranes.

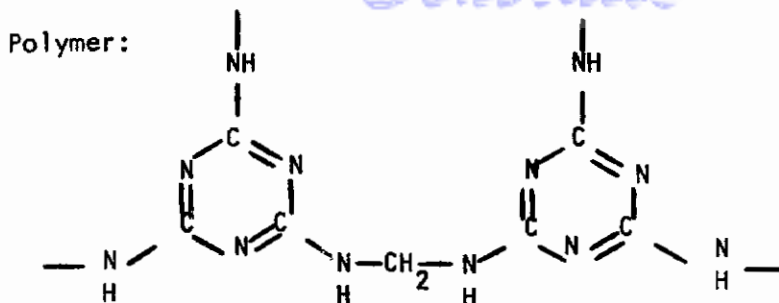
Test strips were separately equilibrated with NaOH and HCl by shaking for periods of about 20 minutes with 1N, 0.1N and 0.001N sequentially. The concentrated solution was used for rapid and complete conversion. The more dilute solutions were then used to suppress either high surface conductivity or hydrolysis.

Resistance at various points in the membrane strips was measured using circular platinized probes 0.123 cm<sup>2</sup> in area. The membrane thickness was 0.050 ± 0.005 cm. The measurements were taken at 1000 cps with an Industrial Instrument RC16B1 conductivity bridge. Six data points were taken on each membrane. Some scatter was observed, but the highest reading was never twice the lowest. An arithmetic mean of the six values was calculated.

### Preliminary Evaluation of Type I Polymers

The system, melamine-guanidine-formaldehyde was arbitrarily selected for first evaluation. Structures and a hypothetical polymer are given below:





The polymer can generally be described by fixing three mol ratios: melamine/guanidine, melamine + guanidine/formaldehyde and melamine + guanidine/water. Five formulations were selected. These allowed evaluation of the effect of each ratio while providing a reasonably wide range of values of each. The formulations are given in Table II below:

TABLE II  
FIRST PASS FORMULATIONS-TYPE I

	Formulation				
	1	2	3	4	5
Melamine	50.8gm	34.0gm	17.0gm	50.8gm	50.8gm
Guanidine Hydrochloride	0	12.9gm	25.8gm	19.2gm	19.2gm
Formaldehyde 34% soln.	100ml	100ml	100ml	100ml	100ml
HCl 37% soln.	36.5ml	24.3ml	12.2ml	36.5ml	36.5ml
Water	60ml	60ml	60ml	35ml	60ml
Melamine/guanidine mol ratio	3/0	2/1	1/2	2/1	2/1
Melamine + guanidine/formaldehyde mol ratio	1/3	1/3	1/3	1/2	1/2
Melamine + guanidine/water mol ratio	0.049	0.052	0.055	0.086	0.072

The hydrochloric acid was added to increase solubility of the melamine and was added in 10% excess of a mol to mol ratio. Polymerization was carried out at 80 to 85 C for 15 hours. Four membranes were made from each formulation, two on 4 oz/yd<sup>2</sup> (.0133gm/cm<sup>2</sup>) dynel cloth and two on 8 oz/yd<sup>2</sup> (.0266 gm/cm<sup>2</sup>) glass cloth.

Casting of the membranes proved difficult. The monomer mix had to be heated in a vented area to dissolve the melamine and guanidine. The mixture turned from a white paste to an almost clear liquid at about 75°C. At 80 C polymerization can occur very rapidly. Several samples set up as they were being clarified. A satisfactory technique was finally determined:

Heat the mixture in a well stirred vessel until only the largest crystals remain undissolved. Immediately plunge the vessel into an ice bath. Let undissolved material settle out and let gas bubbles, from the stirring, escape. A brief cooling period allows time for casting a tray of membranes before the mixture thickens.

# Contrails

The membranes produced did not have very good physical appearance. There were frequent spots where polymer did not fill in the cloth interstices. Formulation 3 failed to polymerize even after an additional 8 hours at 110 C. The performance characteristics of Type I polymers are presented in Table III.

TABLE III  
PERFORMANCE OF FIRST PASS-TYPE I

		<u>Formulation</u>			
	1	2	3	4	5
Resistance in base (ohms)	8850	1000	-	421	326
Resistance in acid (ohms)	446	150	-	92	98
Resistance ratio	19.8	6.6	-	4.4	3.3

Four general conclusions could be drawn:

- Type I polymers appear promising. The highest resistance ratio is almost twice the selected goal.
- The presence of guanidine is undesirable. It provides sites which are more strongly basic than the melamine. These lower the base resistance and, hence, the base/acid resistance ratio. Compare 1 and 2. In high concentrations it does not readily form a sufficiently crosslinked polymer.
- Lowered formaldehyde content is desirable. Compare 2 and 5.
- Lower sol water content is desirable. Compare 4 and 5.

These conclusions led to the second pass formulation tabulated in Table IV.

TABLE IV  
SECOND PASS FORMULATIONS-TYPE I

		<u>Formulation</u>				
	6	7	8	9	10	11
Melamine	32gm	25.5gm	16.9gm	32gm	25.5gm	16.9gm
Formaldehyde 36%	50ml	50ml	50ml	50ml	50ml	50ml
HCl 37%	35.8ml	18.2ml	12.2ml	35.8ml	18.2ml	12.2ml
H <sub>2</sub> O	0	0	0	0	0	0
Melamine/formaldehyde mol ratio	1/1.5	1/3	1/4.5	1/1.5	1/3	1/4.5
Melamine/water mol ratio	1/11.9	1/8	1/5.8	1/20.8	1/20.8	1/20.8

These formulations encompass the previous best performer, No.1, which was repeated as No. 10. A melamine-formaldehyde ratio of 1/1.5 is stoichiometric for complete condensation.

# Contrails

All formulations gave good looking membranes except for number 9, which was more like the early polymers, perhaps due to the high water content. The same treatment and measurement procedures were used. Data are given in Table V.

TABLE V  
PERFORMANCE OF SECOND PASS-TYPE I

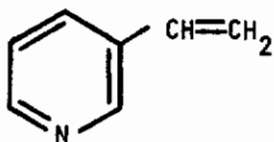
	Formulation					
	6	7	8	9	10	11
Base Resistance (ohms)	26,800	13,300	14,300	11,200	13,000	12,800
Acid Resistance (ohms)	196	524	333	215	231	636
Resistance ratio	137	25.3	43.0	52.1	56.2	20.0

This pass produced an outstanding polymer. Even if the membrane were only fractionally ionized by 4% CO<sub>2</sub>, the top of the sensor range, there should be sufficient sensitivity left. The difference in performance between 1 and 10, identical formulation, was due to improved mixing and casting techniques; a difference was easily seen in the physical specimens.

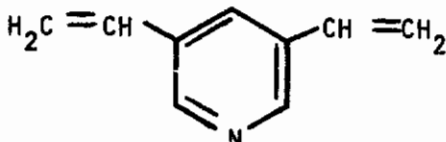
## Evaluation of Type II Polymers

The second system evaluated was an addition polymer of vinylpyridine (VP) crosslinked with divinylpyridine (DVP). To expand the range of capacity of this polymer, styrene (VB) and divinylbenzene (DVB) were added to some of the formulations. Diethylbenzene (DEB) was used as non-polymerizable to provide porosity in the polymer. Structures and a hypothetical polymer are given below. In these structures the functional groups are drawn in the meta position although the monomers used are not limited to these isomeric forms.

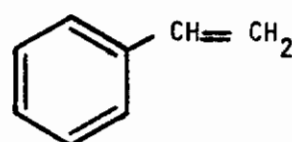
Vinylpyridine



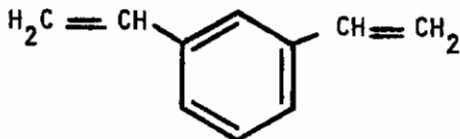
Divinylpyridine



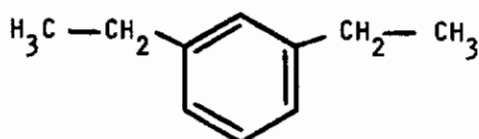
Styrene



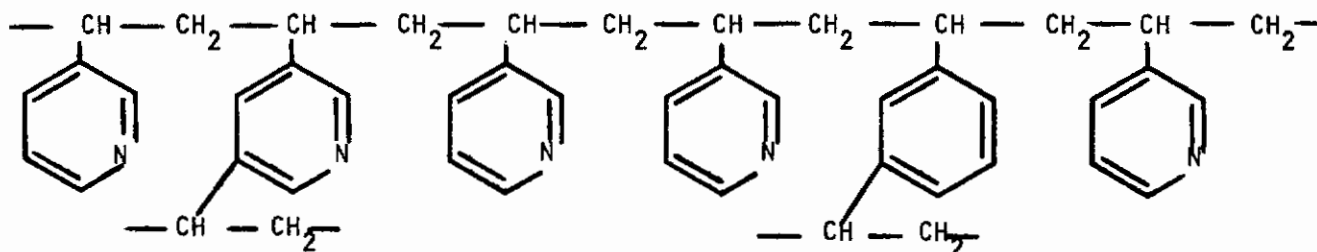
Divinylbenzene



Diethylbenzene



# Hypothetical Polymer



The composition of the polymer is established by fixing the mol fraction of monomers which are crosslinking (divinylpyridine and divinylbenzene) and the mol fraction of monomers which are nitrogen containing (divinylpyridine and vinylpyridine). These percentages are approximate since the divinylpyridine is not a pure material and only an approximate analysis is available. The nonpolymerizable, expressed as volume fraction of the mix, was held constant at 40%, a value which is commonly used in styrene-type polymer films. A constant quantity of catalyst, benzoyl peroxide, was used in the polymerizations as shown in Table VI.

TABLE VI  
FIRST PASS FORMULATIONS - TYPE II

	Formulation					
	12	13	14	15	16	17
Divinylpyridine	6 ml	4 ml	2 ml	4 ml	0	0
Vinylpyridine	0	0	2 ml	1 ml	2 ml	3 ml
Vinylbenzene (Styrene)	0	0	0	0	0.5 ml	0.5 ml
Diethylbenzene	4 ml	4 ml	4 ml	4 ml	4 ml	4 ml
Divinylbenzene	0	2 ml	2 ml	1 ml	3.5 ml	2.5 ml
Benzoyl Peroxide	0.05 gm	0.05 gm	0.05 gm	0.05 gm	0.05 gm	0.05 gm
Percent Crosslinking	30	48	39	33	50	36
Percent Nitrogen - containing compounds	100	66	66	83	33	50

Membranes were cast on 4 x 4 inch pieces of dynel cloth (4 ounce/yd<sup>2</sup>). Of the membranes obtained in the first pass, only numbers 16 and 17 seemed to make reasonably good polymers while 13, 14 and 15 were very porous and limp. Number 12 did not polymerize.

The membranes were cut into 3 x 3/4 inch test strips. To remove the nonpolymerizable material the membranes were sequentially shaken in ethylene dichloride (EDC), methanol, and water. They were then equilibrated in solutions of NaOH and HCl by shaking sequentially for about 20 minutes in 1N, 0.1N, 0.01N and 0.001N solutions. The more concentrated solutions were used for conversion to the desired ion, while the more dilute solutions were used to suppress either high surface conductivity or hydrolysis.



Resistance was measured at six points on the test strip using circular platinized probes  $0.123 \text{ cm}^2$  in area. The membrane thickness measured  $0.050 \pm 0.005 \text{ cm}$ . The measurements were taken at 1000 cps with an Industrial Instruments RCIBI conductivity bridge. Table VII below gives averages of the data obtained.

TABLE VII

PERFORMANCE OF FIRST PASS-TYPE II

		Formulation				
	12	13	14	15	16	17
Resistance in base (ohms)	-	14,151	16,616	6,283	30,916	46,666
Resistance in acid (ohms)	-	5,150	1,416	883	1,608	1,833
Resistance ratio	-	2.7	11.7	7.1	19.2	25.5

The initial assumption that high capacity, i.e., high nitrogen content, is required seems to have been disproven. The polymers performed best which had 50% or less nitrogen-containing monomers. It may be fortuitous that these also produced structurally the best polymers. Within the range tested, variation of fraction crosslinking had little effect. The formulations of the second pass spanned a lower range of nitrogen content and the same range of crosslinking as shown in Table VIII.

TABLE VIII

SECOND PASS FORMULATIONS - TYPE II

	<u>Formulation</u>					
	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>
Divinylpyridine	0	0	0	0	0	0
Vinylpyridine	2 ml	2 ml	3 ml	4 ml	6 ml	6 ml
Diethylbenzene	8 ml	8 ml	8 ml	8 ml	8 ml	8 ml
Vinylbenzene	3 ml	6 ml	3 ml	3 ml	0	1 ml
Divinylbenzene	7 ml	4 ml	6 ml	5 ml	6 ml	5 ml
Benzoyl Peroxide	0.1 gm	0.1 gm	0.1 gm	0.1 gm	0.1 gm	0.1 gm
Percent Crosslinking	50.2	28.6	43.0	35.8	43.0	35.8
Percent Nitrogen - containing compounds	16.6	16.6	25.0	33.3	50.0	50.0

All the membranes exhibited good physical characteristics. The performance of the test strips treated as before are given in Table IX.

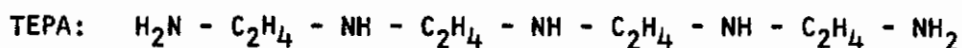
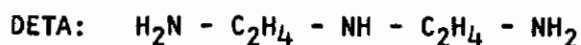
TABLE IX  
PERFORMANCE OF SECOND PASS - TYPE II

	Formulation					
	18	19	20	21	22	23
Resistance in base (ohms)	29,720	91,780	60,400	51,000	38,200	44,400
Resistance in acid (ohms)	752	1,260	638	550	404	303
Resistance ratio	39.5	72.8	94.8	92.7	94.5	146.5

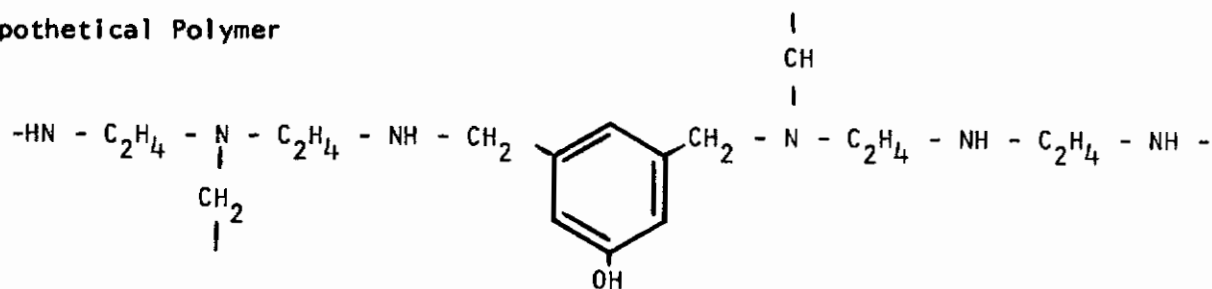
The performance of almost all of these polymers is very good. The optimum formulation has a nitrogen content between 25 and 50%. There is a slight preference for lower fraction crosslinking, perhaps 35%, although this effect is small.

#### Evaluation of Type III Polymers

The third system evaluated was a condensation polymer of diethylenetriamine (DETA) tetraethylenepentamine (TEPA) phenol ( $\phi$ OH) and formaldehyde structures are as follows:



Hypothetical Polymer



The formulation is established by fixing three ratios:  $\text{N}/\phi\text{OH}$ ,  $\text{N} + \phi\text{OH}/\text{HCHO}$  and  $\text{N} + \phi\text{OH}/\text{H}_2\text{O}$ , where the component N is either DETA or TEPA. The  $\text{N} + \phi\text{OH}/\text{HCHO}$  ratio is defined in terms of reaction stoichiometry. The stoichiometric reaction mol ratios are 2 DETA/5 HCHO, 2 TEPA/7 HCHO and 2  $\phi\text{OH}/3$  HCHO. The formulations were selected for one-at-a-time variation of each of the ratios as presented in Table X.

TABLE X  
FIRST PASS FORMULATIONS - TYPE III

	Formulation					
	24	25	26	27	28	29
DETA	12.6 ml	25.2 ml	10.9 ml	9.72 ml	12.6 ml	0
TEPA	0	0	0	0	0	23.0 ml
HCHO (37%)	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml
$\phi$ OH	0	0	2.5 gm	4.4 gm	0	0
H <sub>2</sub> O	0	15.8 ml	1.3 ml	2.5 ml	15.8 ml	0
N/ $\phi$ OH	4/0	4/0	4/1	4/2	4/0	4/0
N + $\phi$ OH/HCHO	5/2 (stoich)	5/4 ( $\frac{1}{2}$ stoich)	10/23 (stoich)	6/13 (stoich)	5/2 (stoich)	7/4 ( $\frac{1}{2}$ stoich)
N + $\phi$ OH/H <sub>2</sub> O	0.139	0.139	0.139	0.139	0.0695	0.139

Samples were prepared on 4 x 4 inch dynel as before. Formulations 24 through 28 yielded tacky, liquid polymers even after prolonged polymerization (1 week) at 80 C. Some of the DETA mixtures, such as formulation 24, formed gelatinous polymers at room temperature. On heating, the polymer liquified irreversibly such that cooling did not cause the polymer to gel.

Formulation 29, the only mixture which used TEPA, set up as it was being mixed.

Since no testable membranes were obtained, the second pass formulations were based on the desire to obtain some sort of solid film. This meant the elimination of DETA, which apparently is not too willing to polymerize under the present conditions. To prevent premature polymerization, the relative amount of formaldehyde was decreased and the amount of water increased. The same ratios of amine to phenol were used. (See Table XI.)

TABLE XI  
SECOND PASS FORMULATIONS - TYPE III

	Formulation					
	36	37	38	39	40	41
DETA	0	0	0	0	0	0
TEPA	58 ml	29 ml	16.5 ml	23 ml	19.3 ml	29 ml
HCHO	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml
$\phi$ OH	0	0	0	2.9 gm	4.8 gm	0
H <sub>2</sub> O	6 ml	24 ml	6.5 ml	23.4 ml	23.4 ml	35.5 ml
TEPA/ $\phi$ OH	4/0	4/0	4/0	4/1	4/2	4/0
TEPA + $\phi$ OH/HCHO	1/1	1/2	1/3.5 (stoich)	1/2	1/2	1/2
TEPA + $\phi$ OH/H <sub>2</sub> O	0.07	0.07	0.07	0.07	0.07	0.04



Formaldehyde and TEPA can react rapidly with the evolution of considerable heat unless the temperature of the mix is kept low. Consequently it was necessary to prechill the reactants, keep the mixing vessel in an ice bath and add the formaldehyde solution dropwise to keep the mix from prematurely polymerizing.

Apparently due to the decrease in formaldehyde content, all polymers obtained were tacky liquids except number 38, which had the highest formaldehyde content. This mixture formed a fine appearing film. When the equilibration procedure was started, it was discovered that this polymer was soluble in water.

In the third pass, the relative quantities of phenol were increased to increase the crosslinking in the polymer and decrease the solubility. (See Table XII.)

TABLE XII  
THIRD PASS FORMULATIONS - TYPE III

	Formulation					
	42	43	44	45	46	47
DETA	0	0	0	0	0	0
TEPA	10.4 ml	7.8 ml	5.1 ml	11.5 ml	7.8 ml	4.7 ml
HCHO	20 ml	20 ml	20 ml	20 ml	20 ml	20 ml
φOH	2.5 gm	3.9 gm	5.2 gm	5.7 gm	7.6 gm	9.1 gm
H <sub>2</sub> O	8.5 ml	8.5 ml	8.5 ml	18.8 ml	18.1 ml	18.8 ml
TEPA/φOH	4/2	4/4	4/8	4/4	4/8	4/16
TEPA + φOH/HCHO	1/3	1/3	1/3	1/2	1/2	1/2
TEPA + φOH/H <sub>2</sub> O	.07	.07	.07	.07	.07	.07

This mix was cast on 4 x 4 inch pieces of dynel cloth and polymerized for 15 hours at 80 C. Good looking polymers were obtained and were evaluated for resistance in NaOH and HCl, samples as described previously. Formulations 42 and 47 however were water-soluble. The performance of the others in this group is given in Table XIII.

TABLE XIII  
PERFORMANCE OF THIRD PASS - TYPE III

	Formulation					
	42	43	44	45	46	47
Resistance in base (ohms)	-	21,600	43,200	19,900	107,000	-
Resistance in acid (ohms)	-	550	1,180	500	1,800	-
Resistance ratio	-	39.3	36.6	39.8	59.4	-

Further variation of the type III polymer (polyamine-phenol-formaldehyde) was attempted to overcome the difficulties in polymer formation. In this pass triethylenetetramine (TETA) was used as the nitrogen-containing compound.



Formulations similar to those in the third pass, except with increased formaldehyde content, were used. (See Table XIV.)

TABLE XIV  
FOURTH PASS FORMULATIONS - TYPE III

	60	61	62	Formulation 63	64	65
TETA	8.0 ml	5.9 ml	15.9 ml	4.0 ml	8.0 ml	2.0 ml
HCHO	20 ml	20 ml	20 ml	20 ml	20 ml	20 ml
$\phi\text{OH}$	5.2 gm	7.6 gm	10.2 gm	2.7 gm	20.5 gm	5.1 gm
H <sub>2</sub> O	12.6 ml	15.8 ml	37.6 ml	0	56.6 ml	0
TETA/ $\phi\text{OH}$	$\frac{1}{1}$	$\frac{1}{2}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{4}$	$\frac{1}{4}$
TETA+ $\phi\text{OH}$ /HCHO	2/9 (stoich)	1/2 (stoich)	4/9 (2 stoich)	1/9 ( $\frac{1}{3}$ stoich)	10/9 (2 stoich)	5/18 ( $\frac{1}{3}$ stoich)
TETA+ $\phi\text{OH}$ /H <sub>2</sub> O	.078	.078	.078	.078	.078	.078

Because of the high reactivity of the formaldehyde with TETA, caution was exercised to prevent premature polymerization while mixing the components.

The membranes were cast on 4 ounce dynel cloth as well as on 1 ounce dacron felt. Their performance characteristics are presented in Table XV.

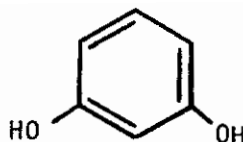
The polymerized membranes were mottled in appearance and adhered tenaciously to the glass plates between which they were cast. Some could not be separated, while most (particularly those cast on 4 ounce cloth) were salvaged only with much difficulty.

TABLE XV  
PERFORMANCE OF TYPE III POLYMER - PASS 4

	60	61	62	Formulation 63	64	65
Resistance in base (ohms)	55,000	25,800	6,160	9,460	5,000	10,400
Resistance in acid (ohms)	880	276	110	548	296	1200
Resistance ratio	62.5	93.4	56.0	17.3	16.9	8.7

A further variant of the type III polymer was one in which resorcinol was substituted for phenol.

Resorcinol:



Only one membrane of this type was prepared as shown in Table XVI.

TABLE XVI

FIFTH PASS FORMULATION - TYPE III

	Formulation 66
TETA	5.2 ml
HCHO	15 ml
$\phi(OH)_2$	11 gm
H <sub>2</sub> O	10 ml
HCl	8.5 ml
TETA/ $\phi(OH)_2$	1/3
TETA+ $\phi OH/HCHO$	3/4
TETA+ $\phi OH/H_2O$	.087

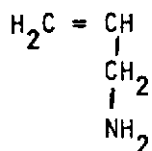
The ingredients were precooled and mixed slowly at 10 C. The polymer was cast onto 2 mil dacron felt, and pressed in a Carver press at 80 C and 2,000 pounds for 15 minutes and then heated for an additional hour at 75 C.

Membranes produced by this method were brownish in color, somewhat transparent, and quite flexible. This sample was produced at a time when the gas-phase testing program was being conducted. Consequently this sample was placed directly in the gas-phase test apparatus and its evaluation will be discussed below. The base-acid resistance ratio was not measured.

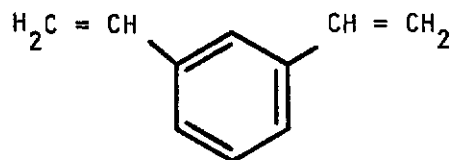
Evaluation of Type IV Polymers

The fourth system tested was addition polymer of allylamine cross-linked with divinyl benzene. This polymer was originally to have been vinylamine crosslinked with divinylbenzene, but the change was made because of the unavailability of vinylamine. Structures are given below.

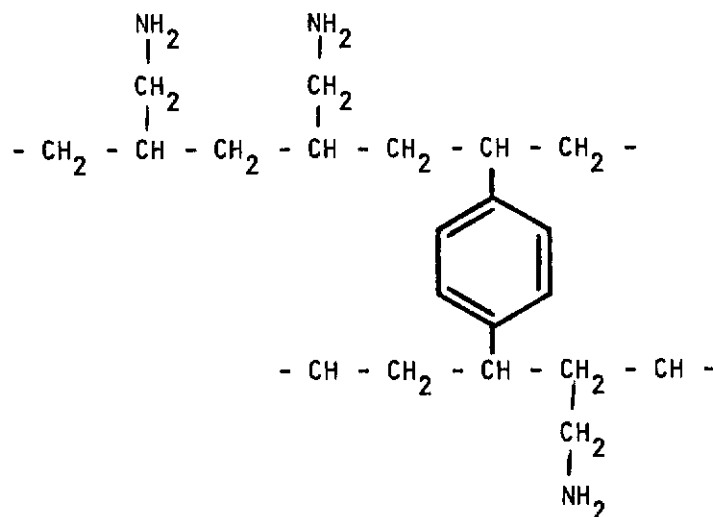
Allylamine:



Divinylbenzene



Hypothetical Polymer



Formulations of this type polymer are specified by fixing the ratio of allylamine (M) to crosslinking agent (DVB) and the fraction of non-polymerizable (NP) since the structures of the various species are dissimilar, mol ratios are used. Two nonpolymerizables, diethylbenzene and hexane, were evaluated. (See Table XVII.)

TABLE XVII

FIRST PASS FORMULATIONS - TYPE IV

	Formulation					
	30	31	32	33	34	35
Allylamine	20 ml	20 ml	20 ml	20 ml	20 ml	20 ml
DVB	4 ml	4 ml	4 ml	8.1 ml	4 ml	8.1 ml
NP	26 ml	20 ml	24.5 ml	28.4 ml	9.8 ml	10 ml
	DEB	DEB	Hexane	DEB	DEB	Hexane
B.Peroxide	0.5 gm	0.25 gm	0.5 gm	0.5 gm	0.4 gm	0.25 gm
M/XL	10/1	10/1	10/1	5/1	10/1	5/1
M + XL/NP	6/4	6/4	6/4	6/4	8/2	8/2

No difficulty was experienced in making the monomer mixes. All of the samples with the exception of numbers 32 and 35 yielded tacky polymers even after the prolonged polymerization. Performance of the usable samples is given in Table XVIII.

TABLE XVIII

PERFORMANCE OF FIRST PASS - TYPE IV

	<u>Formulation</u>					
	<u>30</u>	<u>31</u>	<u>32</u>	<u>33</u>	<u>34</u>	<u>35</u>
Resistance in Base (ohms)	--	--	49,300	--	--	161,000
Resistance in Acid (ohms)	--	--	13,800	--	--	8,960
Resistance Ratio	--	--	3.5	--	--	17.9

A second pass was attempted using only hexane as the NP. Formulations are given below in Table XIX.

TABLE XIX

SECOND PASS FORMULATIONS - TYPE IV

	<u>Formulation</u>					
	<u>48</u>	<u>49</u>	<u>50</u>	<u>51</u>	<u>52</u>	<u>53</u>
Allylamine	20 ml	20 ml	20 ml	20 ml	20 ml	20 ml
DVB	20 ml	4 ml	20 ml	8 ml	2.7 ml	8 ml
N-Hexane (NP)	6.4 ml	4.6 ml	12.7 ml	10.2 ml	9 ml	27.1 ml
B. Peroxide	0.25 gm	0.25 gm	0.25 gm	0.25 gm	0.25 gm	0.25 gm
M/XL	2/1	10/1	2/1	5/1	15/1	5/1
M + XL/NP	8/1	8/1	4/1	4/1	4/1	3/2

The mixtures were polymerized at 80 C for 15 hrs. All of the resulting membranes showed a very low degree of polymerization with only a small amount of polymer clinging to the cloth. Samples were equilibrated in base and acid and resistance ratios were obtained. Formulations 49,50 and 52 yielded polymers which dissolved in the equilibrating solutions and could not be evaluated. Performance of the balance of this group is given in Table XX.

TABLE XX

PERFORMANCE OF SECOND PASS - TYPE IV

	<u>Formulation</u>					
	<u>48</u>	<u>49</u>	<u>50</u>	<u>51</u>	<u>52</u>	<u>53</u>
Resistance in Base (ohms)	35,200	--	--	53,400	--	43,000
Resistance in Acid (ohms)	31,000	--	--	35,000	--	45,000
Resistance Ratio	1.52	--	--	1.52	--	0.96

The very low resistance ratios indicate that the item being measured was essentially a solution-wet piece of cloth. The third pass consisted of the same formulations but with twice the catalyst concentration as indicated in Table XXI.

TABLE XXI

THIRD PASS FORMULATIONS - TYPE IV

	Formulation					
	54	55	56	57	58	59
Allylamine	20 ml	20 ml	20 ml	20 ml	20 ml	20 ml
DVB	20 ml	4 ml	20 ml	8 ml	2.7 ml	8 ml
N-Hexane (N.P.)	6.4 ml	4.6 ml	12.7 ml	10.2 ml	9 ml	27.1 ml
B.P.	0.5 gm	0.5 gm	0.5 gm	0.5 gm	0.5 gm	0.5 gm
M/XL	2/1	10/1	2/1	5/1	15/1	5/1
M + XL/NP	8/1	8/1	4/1	4/1	4/1	3/2

These mixtures, polymerized under the same conditions, gave much better looking membranes. Resistance ratios in this group are given in Table XXII.

TABLE XXII

PERFORMANCE OF THIRD PASS - TYPE IV

	Formulation					
	54	55	56	57	58	59
Resistance in Base (ohms)	36,000	30,000	124,800	28,000	16,400	23,200
Resistance in Acid (ohms)	6,560	4,220	31,600	3,860	2,820	4,780
Resistance Ratio	5.48	7.10	3.94	7.25	5.81	5.81

As a group, type IV polymers yield resistance ratios which are considerably lower than the other three groups investigated.

This polymer type offered considerably less promise than the other types.

Liquid Phase Evaluation (Carbonate/Base)

An attempt was made to develop a rapid liquid phase test which would more closely approximate the sensitivity to be expected in the gas phase when the acid/base test without a mass transfer limitation. However, as indicated below, this attempt was not successful.

To get a closer approximation to the sensitivity which would be expected from membranes when contacted with CO<sub>2</sub>-laden air, base/carbonate resistance ratios were measured for two formulations of each of the four



polymer types. In this ratio, the denominator is the through resistance of the membrane after soaking in a solution in equilibrium with air containing 4% CO<sub>2</sub>. This solution was meant to approximate the surface film on the membrane when exposed to 4% CO<sub>2</sub>.

Membrane strips (1.9 x 7.6 cm) were equilibrated in 10<sup>-4</sup> NaOH and resistance measurements were taken at ten random points on each strip. The same strips were then placed in water through which air containing 4% CO<sub>2</sub> was bubbled. After several hours, the sample strips were removed and resistance measurements were again taken at ten random points. The mean values obtained are as follows in Table XXIII.

TABLE XXIII

BASE/CARBONATE RATIOS OF SELECTED MEMBRANES

Polymer Type	Formulation Number	Base Resistance (K $\Omega$ )	Carbonate Resistance (K $\Omega$ )	Resistance Ratio
I	6	66.4	3.6	18.4
	10	7.3	2.6	2.8
II	20	49.2	20.6	2.4
	23	39.9	23.6	1.7
III	44	48.4	23.8	2.0
	46	83.8	33.9	2.5
IV	32	29.7	12.5	2.4
	35	40.7	18.2	2.2

Except for formulations 6 and 35 the base resistances are similar to those reported earlier. The present readings are higher for 6 and much lower for 35. These readings will be excepted from any generalizations.

The base/carbonate resistance ratios are considerably lower than the base/acid ratios, reflecting the fact that a weak-acid weak-base "salt" is largely unionized. The ratios are all approximately two, indicating that each formulation has some potential sensitivity. However, excepting the suspicious data on formulation 6, far from providing a selection criterion, the data did not even indicate a preference.

Gas-Phase Resin Evaluation

A test rig was designed and built which permitted measurement of the resistance of a piece of membrane fully exposed to a flowing gas stream. This could hold up to twelve test pieces. The membranes were stretched across a gap 6.2 mm wide with a platinum screen electrode making contact at each side of the gap for the full width of the membrane. This creates a current path through the membrane 6.2 mm long with a cross sectional area of 19 mm multiplied by the membrane thickness.

The pairs of electrodes are connected to the conductivity bridge by a selector switch. Temperature, humidity and flow rate of the incoming gas stream can be measured. Readings were taken with CO<sub>2</sub>-free air and air containing 4% CO<sub>2</sub>.

Preliminary results were encouraging. The first readings were taken on the dynel-backed samples used to obtain the base/acid resistance ratios. These showed some tendency to wander with time, but a fairly consistent and reversible drop in resistance of 10 to 20% was observed when the gas stream was changed from air to 4% CO<sub>2</sub>. This is not a large change by comparison to those measured between base and acid equilibration, but a large change is not needed. A drop of 50% in resistance when equilibrated with 4% CO<sub>2</sub> was felt to be more than adequate.

Thin test strips of each of the four polymer types were made for evaluation in the air test rig. The objective of this experiment was to find a polymer-type which could fulfill the following requirements:

a) High Sensitivity - Since most gas-phase tests were conducted with 4% CO<sub>2</sub> in air as test gas, the definition of sensitivity as the ratio of resistance of the membrane in equilibrium with 4% CO<sub>2</sub> in air to the resistance in equilibrium with air will be used. A sensitivity of 50% was desired but not necessary. The use of highly accurate read-out equipment should make a sensitivity of 25 percent entirely adequate.

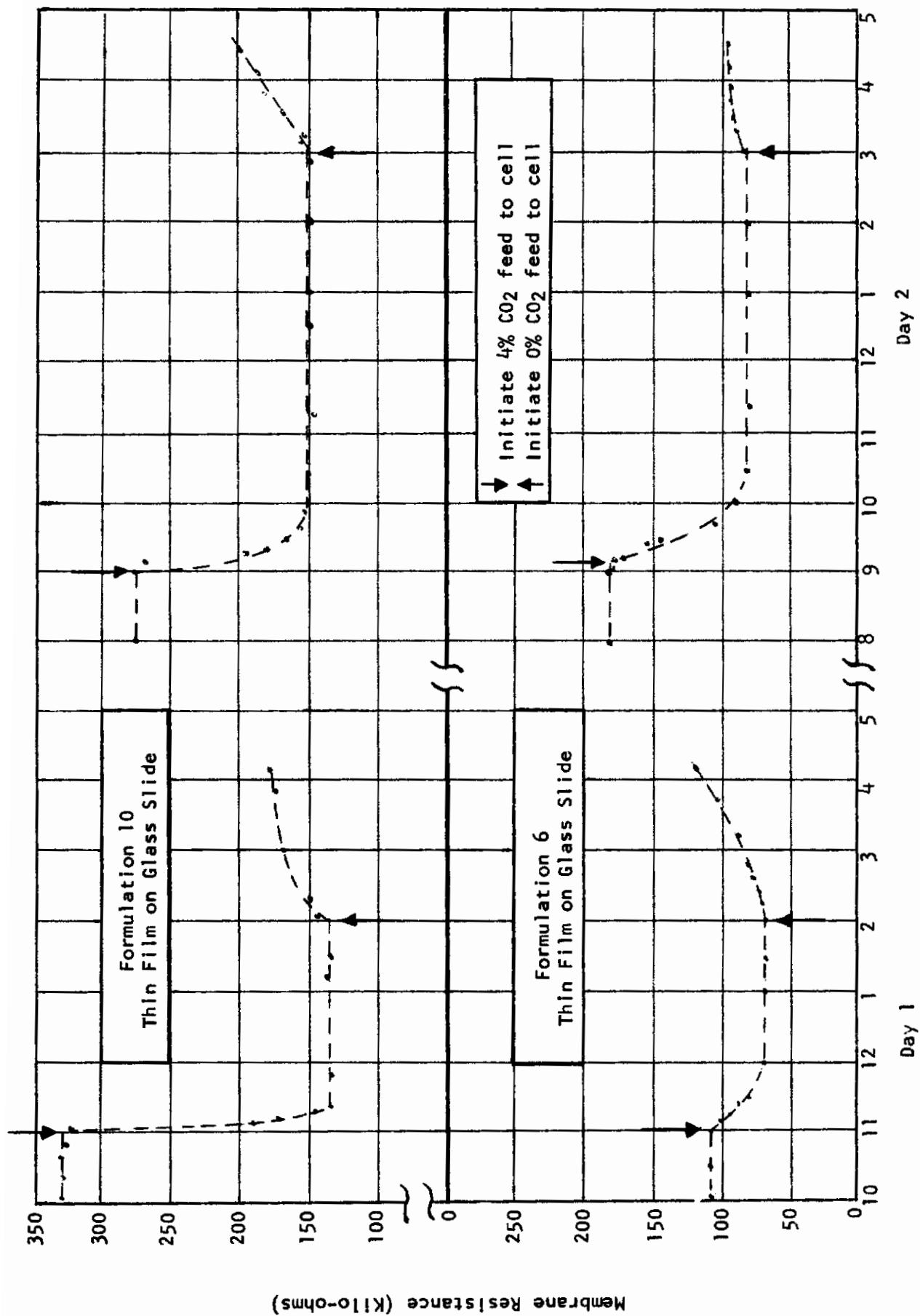
b) Response Time - The time which it takes the membrane to respond from one steady state to another should be minimal. Ideally this should take no more than a few seconds. However it is not unreasonable to assume that response time over the full range of 0% to 4% CO<sub>2</sub> should take on the order of 10 minutes. For the purposes of definition - response time was defined as the time between the change of gas and the point when the resistance is 90% of the way to the new steady state values. If "steady-state" values wander, then both definitions become vague and the values become approximations.

With these objectives in mind, each of the test strips was cycled between CO<sub>2</sub>-free air and 4 percent CO<sub>2</sub> twice over a period of 48 hours. Resistance measurements were taken at frequent intervals and the data are presented in Figures 1 through 5.

Figure 1 shows the performance of two type I polymers (melamine, formaldehyde). This type fulfills the requirement for high sensitivity but is painfully slow to respond. The data show a sensitivity on the order of 50 percent or so but a response time of about one hour for adsorption and six hours or more for desorption. Formulation 10 appears to be slightly preferable to Formulation 6.

Figure 2 is representative of type II polymers (divinylbenzene, vinylpyridine). This polymer shows a considerable improvement over the previous type in terms of response time but the sensitivity leaves much to be desired. It can be seen from the data that the rate of adsorption is on





**Figure 1. Polymer Type I-Melamine, Formaldehyde**

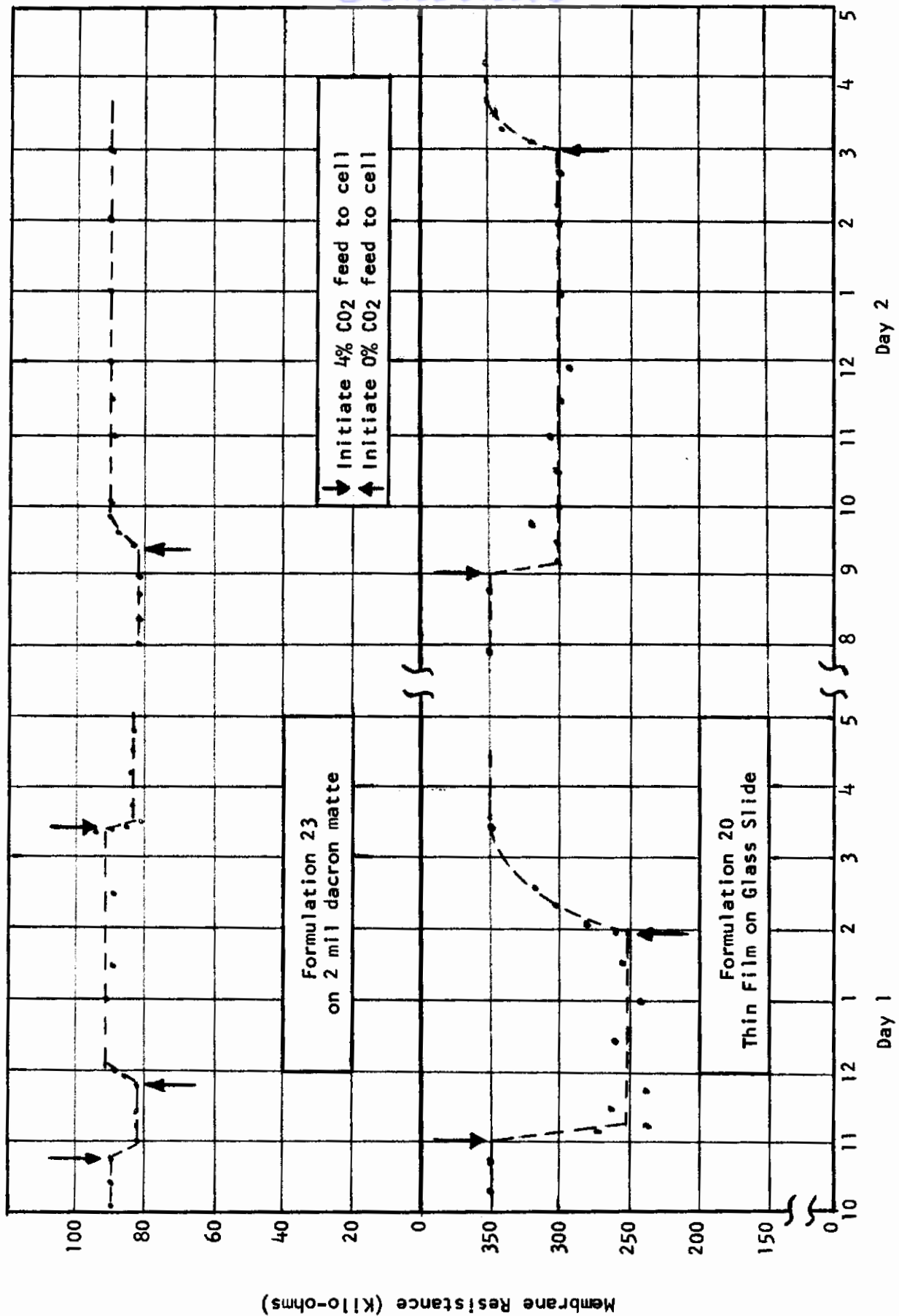


Figure 2. Polymer Type 11-Divinylbenzene, Vinyl Pyridine, Styrene

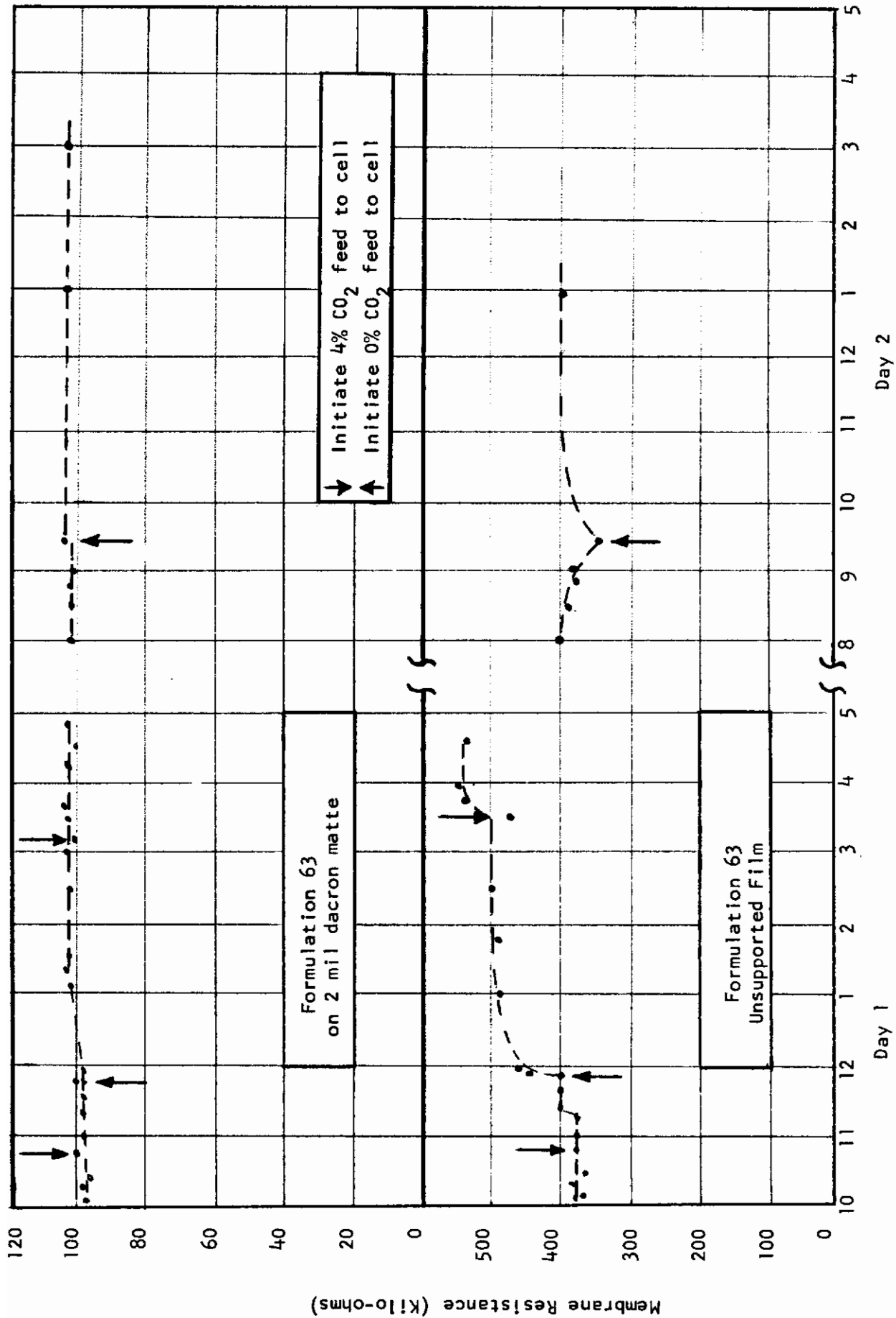


Figure 3. Polymer Type III - Triethylenetetramine, Formaldehyde, Phenol

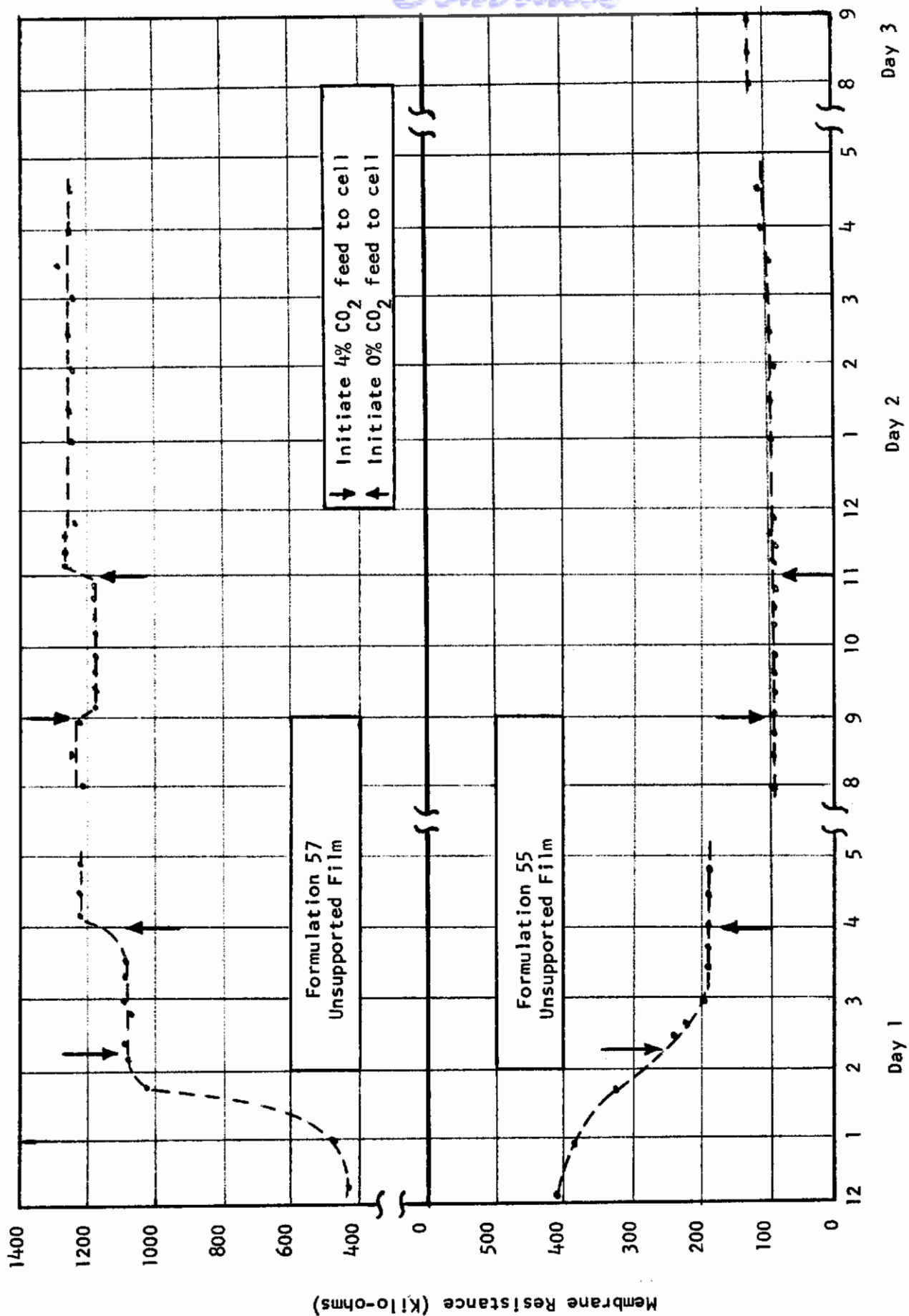


Figure 4. Polymer Type IV - Allylamine, Divinylbenzene

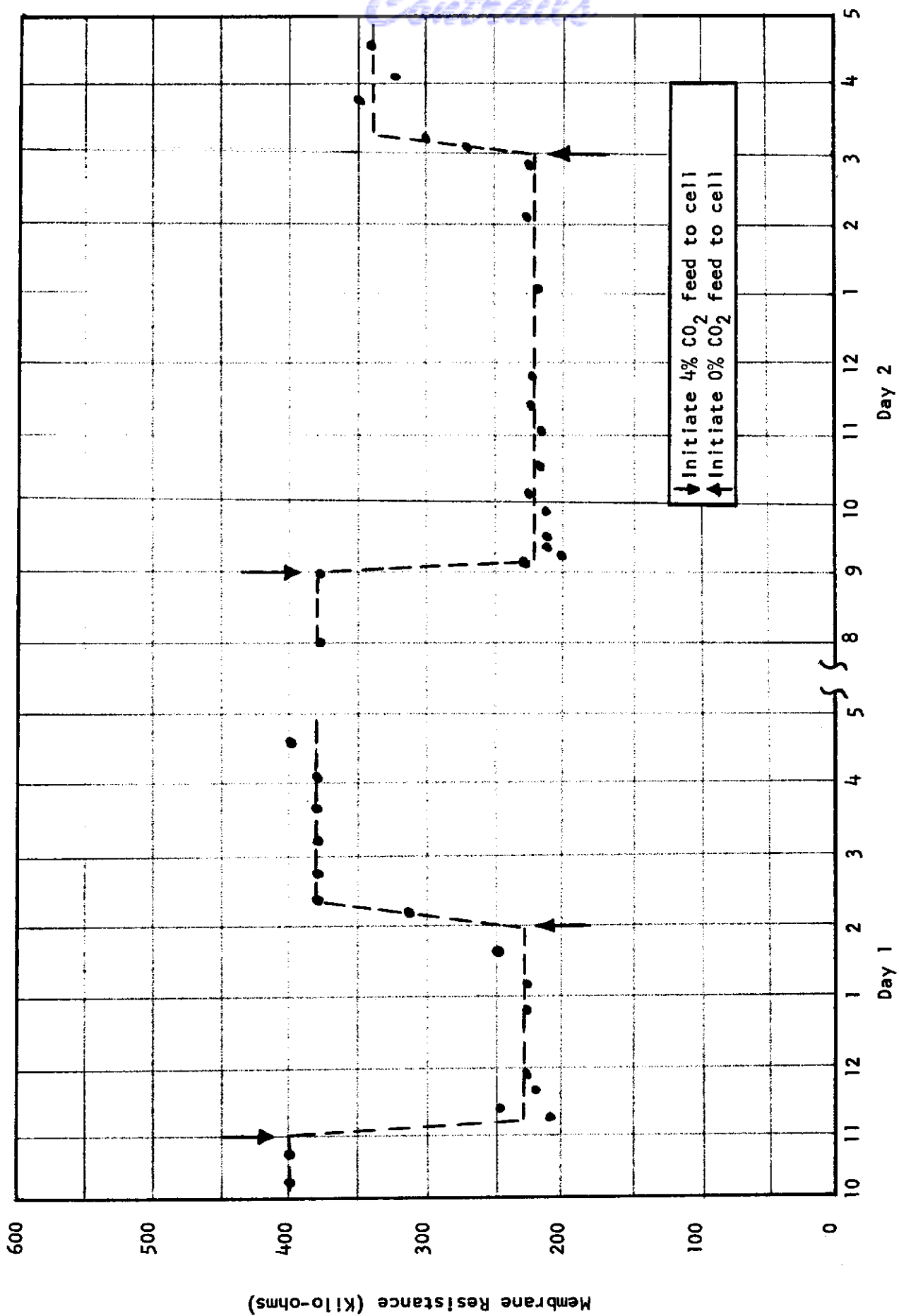


Figure 5. Polymer Type III - Triethylenetetramine, Formaldehyde, Resorcinol

the order of 10 to 12 minutes while the rate of desorption is considerably longer on the order of an hour or so. On the other hand, the sensitivity ranges between 11 percent and 30 percent.

Figure 3 illustrates the behavior of two type III polymers (triethylenetetramine, formaldehyde, phenol). One sample showed no response whatever, the other gave some change in resistance but nothing that could be correlated to CO<sub>2</sub> level in the test gas. Figure 4 shows two formulations of type IV. Neither of these gave any correlatable variation with CO<sub>2</sub> concentration.

Figure 5 shows the variant of polymer type III (Formulation 66) which was prepared by the substitution of resorcinol for phenol. This gave a strikingly different response than other formulations of this type. The sensitivity of this formulation to changes in the test gas from 0% to 4% CO<sub>2</sub> was in the order of 43% while the adsorption and desorption time were both in the neighborhood of 10 to 15 minutes. This was by far the best performance obtained. Further testing of this promising polymer was continued.

## Optimization and Characterization of Type III Polymer

### Replication of Type IIIB Performance

The air test evaluations presented in Figures 1 to 5 demonstrated the superiority of the first Type IIIB (triethylenetetramine-formaldehyde-resorcinol) polymer, particularly in regard to response time. This polymer type is referred to as IIIB to distinguish it from polymers with phenol in place of resorcinol. Before this type could be formally selected, replication tests were necessary to ensure that the performance could be reproduced.

Sample strips of formulation 66 were converted to the base form by treatment with 0.2M Na<sub>2</sub>CO<sub>3</sub>. These were placed in the air test apparatus and resistance measurements were made under conditions of 0 percent, 1 percent, and 4 percent CO<sub>2</sub>. The data in Figure 6 show a plot of resistance as a function of changes in the CO<sub>2</sub> of the gas stream over a two day period.

Although the two test strips were cut from the same membrane, their resistances differ by about 30 percent. This difference is due largely to variations in the thickness of the strips.

A change in the gas stream from 0 percent CO<sub>2</sub> (air-steady-state) to 4 percent CO<sub>2</sub> produces a change in resistance of about 18 percent of the air steady state value, while a change in gas stream from 0 percent to 1 percent CO<sub>2</sub> produces a change of about 6 percent. While this is not the highest sensitivity that has been obtained, it should be sufficient. The steady-state values are reasonably reproducible.

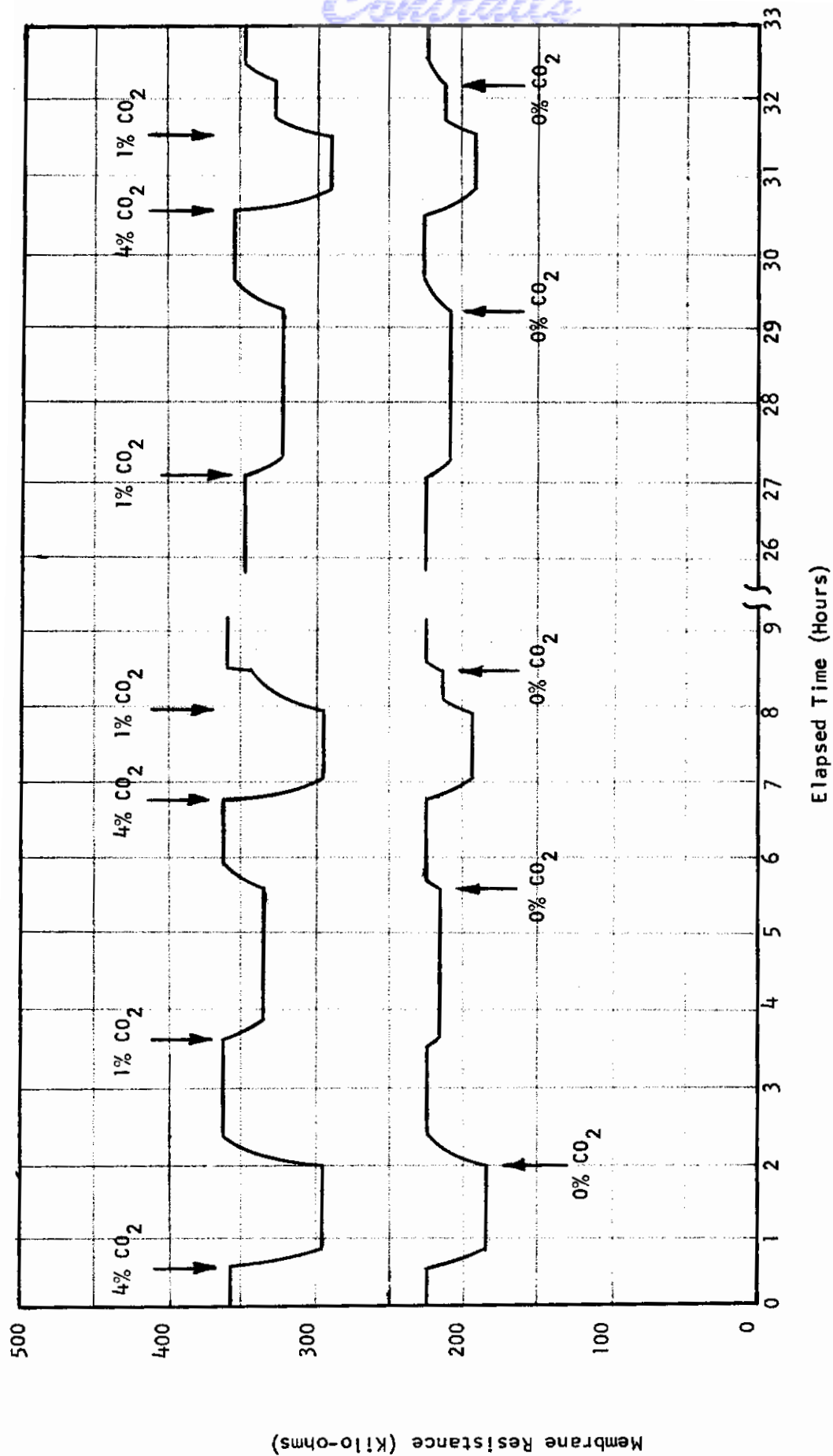


Figure 6. Performance of Formulation 66 in Air Test Apparatus



Rapid response is the chief virtue of Type IIIB membranes. Mean values for response time based on the test strips in Figure 6 are given in Table XXIV.

TABLE XXIV

RESPONSE TIME OF FORMULATION 66 AS A FUNCTION OF CO<sub>2</sub> CONCENTRATION

<u>CO<sub>2</sub> Concentration in Air Stream</u>		<u>Response Time(minutes)</u>
<u>Initial</u>	<u>Final</u>	
0%	4%	13
0%	1%	7
4%	0%	20
4%	1%	15
1%	0%	10

The measured response times can not be explained solely by a diffusion-controlled process. The one-dimensional, unsteady-state Fick's law diffusion equation predicts that response times, defined as they are, should be the same for each of these changes of state. However, the response times are not the same, and the measurements are sufficiently consistent so that it is very unlikely that the observed differences are due to random error. The response time on absorption (increasing the CO<sub>2</sub> concentration in the gas stream) is about half as great as the time required for desorption (decreasing the CO<sub>2</sub> concentration in the gas stream). A smaller change in concentration requires a shorter period of time. This may imply that the reaction of the bicarbonate with the active groups of the polymer is sufficiently slow to affect the rate of migration.

The preoccupation with the controlling mechanisms is justified only if it provides some direction in the search for a formulation with better response times. Since the mechanism could not be elucidated from the data at hand, this search was carried out by a one-at-a-time variation of the component ratios in the formulations. The probability of cross-influence was too great to permit use of a less laborious factorial experimental design.

Variations of Type IIIB Formulation

Several Type IIIB polymers were prepared in which the variables were

- a) the ratio of TETA plus resorcinol to formaldehyde.
- b) the ratio of TETA plus resorcinol to water.

The relative amounts of TETA, resorcinol, and hydrochloric acid were kept constant. The formulations are given in Table XXV.



TABLE XXV

VARIANTS OF TYPE IIIB

	<u>Formulation</u>			
	70	71	72	73
TETA	5.2 ml	5.2 ml	5.2 ml	5.2 ml
HCHO	10 ml	10 ml	15 ml	15 ml
$\phi$ (OH) <sub>2</sub>	11 gm	11 gm	11 gm	11 gm
H <sub>2</sub> O	10 ml	20 ml	5 ml	10 ml
HCl	8.5 ml	8.5 ml	8.5 ml	8.5 ml
TETA/ $\phi$ (OH) <sub>2</sub>	0.35	0.35	0.35	0.35
TETA+ $\phi$ (OH) <sub>2</sub> /HCHO	1.12	1.12	0.75	0.75
TETA/H <sub>2</sub> O	0.029	0.02	0.032	0.025
TETA+ $\phi$ (OH) <sub>2</sub> /H <sub>2</sub> O	0.11	0.077	0.12	0.096

Each formulation was cast on glass cloth (0.037 mm) and also on dacron felt (0.05 mm). The samples were polymerized in a Carver press at 80 C with 910 kgm pressure on a 103 cm<sup>2</sup> piece. The membranes thus produced were quite flexible and strong. Sample strips (19 mm x 76 mm) were cut and conditioned in sodium carbonate. The thickness of the sample strips is given in the following table. The values given represent the mean of 10 measurements taken at random points along each strip.

TABLE XXVI

THICKNESS OF SAMPLE STRIPS IN MILS

<u>Formulation Number</u>	<u>Glass Cloth</u>	<u>Dacron Felt</u>
70	1.0	1.5
71	1.1	1.3
72	1.1	1.3
73	1.1	1.6

Polymerizing the membranes under pressure resulted in a reduction in thickness of about 30 percent of the unpressed backing.

Sample strips of the membranes were placed in the air test apparatus. Response times and sensitivity are summarized in Table XXVII.

TABLE XXVII

PERFORMANCE OF TYPE IIB POLYMERS

Formulation Number	Backing Material	Response Time(Minutes)		Sensitivity Change as Percent of Air Steady State
		Adsorption 0% → 4%	Desorption 4% → 0%	
70	glass cloth	5	23	23
	dacron felt	5	22	12
71	glass cloth	5	33	20
	dacron felt	4	24	12
72	glass cloth	4	23	33
	dacron felt	3	12	17
73	glass cloth	4	12	16
	dacron felt	4	17	25

These data provide three comparisons:

- formulation water content, where 71 and 73 comprise the lower group
- formaldehyde ratio, where 70 and 71 have lower formaldehyde content
- glass cloth vs. dacron felt.

Response Time. Since desorption is slower, response time on desorption was taken as the significant parameter. The high formaldehyde content gave better response time. Water content did not correlate and dacron felt is better except for formulation 73.

Sensitivity. The high formaldehyde group, 72 and 73, had the high sensitivity. Water content did not correlate to sensitivity. Glass cloth gave high sensitivity except for formulation 73.

Appearance. Good appearance also corresponded to high formaldehyde content. While reasonable polymers were obtained from each formulation, 72 and 73 gave samples with much better surface finish than 70 or 71. The rough surface of the latter samples may contain slightly conductive liquid from the pretreatment which could lead to increased response time and loss of sensitivity.

Ion-exchange capacity and water content analyses were carried out on the sample strips on dacron felt. The specimens on glass cloth disintegrated during analysis. The data are given in Table XXVIII.

TABLE XXVIII  
CHARACTERIZATION OF TYPE IIIB POLYMERS

Formulation Number	Capacity Milliequivalents/dry gram of resin	Sample Water Content
70	2.5	37.8%
71	3.1	36.5%
72	4.7	27.2%
73	3.6	48.9%

Formulations 72 and 73 on the average have a higher capacity than do formulations 70 and 71. The water content of the finished polymer does not correlate to formulation water content. However, the range of each variable is not great. The formulations can be separated into three groups by increasing sample water content (72, 70 and 71, 73). The performance factors do not correlate to this grouping either.

Further variants of type IIIB were investigated. Using formulation 73 as the standard, the variants investigated were higher and lower acid (HCl) content, higher formaldehyde content, and higher resorcinol content. The effect of different backing materials was also studied. Formulations are given in Table XXIX.

TABLE XXIX  
FORMULATION VARIATIONS OF POLYMER TYPE IIIB

	Formulation				
	73	74	75	76	77
TETA	5.2 ml	5.2 ml	5.2 ml	5.2 ml	5.2 ml
HCHO	14.8 ml	14.8 ml	14.8 ml	22.6 ml	30.7 ml
$\phi$ (OH) <sub>2</sub>	11 gm	11 gm	11 gm	19.3 gm	11 gm
H <sub>2</sub> O	10.7 ml	4.8 ml	6.9 ml	19.8 ml	0.7 ml
HCl	8.2 ml	15.9 ml	6.5 ml	8.2 ml	8.2 ml
TETA/ $\phi$ (OH) <sub>2</sub>	0.35	0.35	0.35	0.2	0.35
TETA/HCl	0.39	0.20	0.53	0.39	0.39
TETA+ $\phi$ (OH) <sub>2</sub> HCHO	0.75	0.75	0.75	0.75	0.35
TETA+ $\phi$ (OH) <sub>2</sub> H <sub>2</sub> O	0.096	0.096	0.096	0.096	0.096

Formulation 73 was prepared as before.

In formulation 74 the hydrochloric acid content was increased. Other components were kept constant and the amount of water added was adjusted to keep the formulation water content constant.

In formulation 75 the original intent was to have zero acid but attempts to produce such a polymer proved to be futile. With little or no acid in the system, the reaction mixture became strongly basic, causing premature polymerization even at temperatures just above the freezing point of the mixture (-18 C). A minimum of 6.5 ml HCl was necessary to prevent polymerization during preparation at -10 C to -15 C. Even

then the membrane had to be laid and pressed immediately after preparation of the monomer mixture because polymerization occurred within three minutes of preparation.

Formulation 76 had increased resorcinol content. The mol ratios of the other components were kept constant. Formulation 76A had the same component ratios but a different mixing sequence was used.

Formulation 77 was prepared with twice as much formaldehyde as formulation 73. Mol ratios of all the other components were kept constant.

All of the polymers with the exception of formulation 75 were prepared on glass cloth, dacron felt, and 0.2 mil paper. Formulation 75 was prepared on glass cloth only.

The membranes were polymerized for 2 hours in the Carver press at 85 C and 2000 pounds force on a 4 x 4 inch sample.

The following table shows the thickness of the membranes with respect to the backing used.

TABLE XXX

<u>Backing Material Used</u>	<u>Average Thickness of Membrane</u>
Dacron Felt	3.0 mils
Glass Cloth	1.7 mils
0.2 mil Paper	0.7 mils

While glass and dacron backings are commonly used in the preparation of membranes, condenser tissue paper was used here because it represents one of thinnest available materials, which exhibits a reasonable wet strength in spite of its thinness (0.0002 inches). One shortcoming of the paper backing however is its vulnerability to strong acids. Hence in formulation 74 where a large amount of acid was used, the membrane cast on paper disintegrated.

Sample strips of the membranes were converted to the base form with 0.2M  $\text{Na}_2\text{CO}_3$  and rinsed with distilled water. Sample strips  $3/4 \times 3$  inch were tested in the air test apparatus with  $\text{CO}_2$ -free air and air containing 4%  $\text{CO}_2$ . Figure 7 shows the sensitivity and desorption time for different formulations and backing materials.

A number of not too rough correlations can be extracted from Figure 7. Overall, sensitivity is dependent on formulation and independent of backing while response time is a function of backing, and hence thickness but not of formulation.

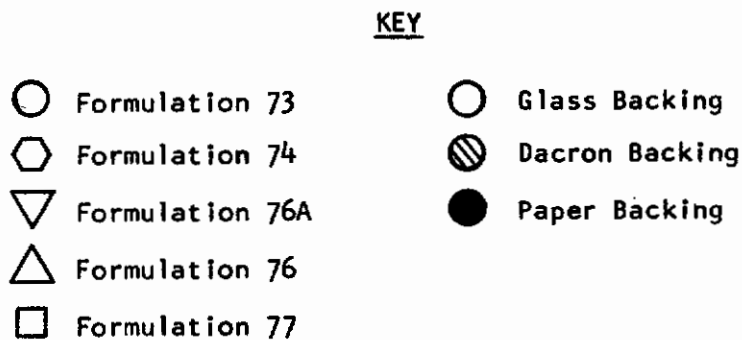
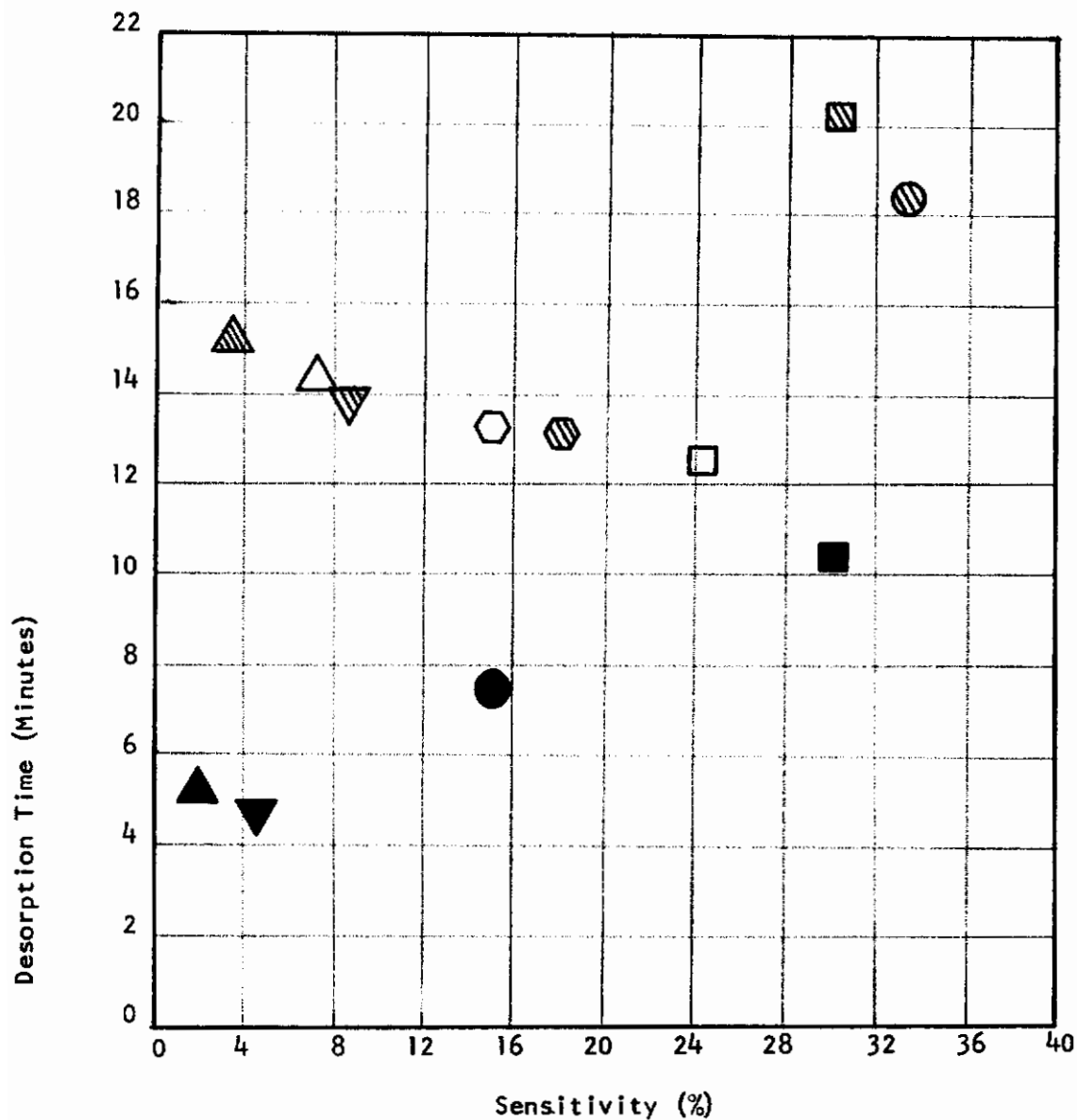


Figure 7. Performance of Polymers as a Function of Formulation and Backing

The sensitivity of 33% and 18 minute adsorption time for formulation 73 on dacron compare closely to the values of 25% and 17 minutes obtained with a nominally identical membrane. This gives an idea of the sort of reproducibility which can be expected.

The data are sufficiently clustered to make ranking of the formulations easy. Formulations 76 and 76A performed identically and showed little sensitivity, 74 is middling, and 73 and 77 are fairly sensitive. There is a wide spread in the data on 73 but this is the only such case.

There is a close relationship between sample thickness and desorption time. The paper samples 0.7 mils thick have an average desorption time of 7 minutes. The 1.7 mil glass-backed samples averaged 13 minutes and the 3-mil dacron-backed samples required 17 minutes. The paper used for the thin membranes is an extremely thin (0.2 mil) tissue manufactured for use in condensers. It also makes reasonably strong thin membranes. The data in Figure 7 indicate without question that this material should be used for the sensor backing.

This left some question in the selection of formulation. Looking at the paper-backed samples, the choice was between formulations 73 and 77. Resistance curves for these membranes are shown in Figure 8. The increase in sensitivity of 77 over 73 is at the expense of a small but very important increase in desorption time. These formulations are the same except for formaldehyde content, which is the last variable that was studied. These formulations were recast along with formulations having intermediate formaldehyde ratios to enable the trade-off to be made accurately. (See Table XXXI).

TABLE XXXI

ADDITIONAL FORMULATION VARIANTS OF TYPE IIIB

	<u>Formulation</u>			
	73	77	78	79
TETA	5.2 ml	5.2 ml	5.2 ml	5.2 ml
HCHO	14.8 ml	30.7 ml	21.8 ml	17.8 ml
$\phi$ (OH) <sub>2</sub>	11 gm	11 gm	11 gm	11 gm
H <sub>2</sub> O	10.7 ml	0.7 ml	6.3 ml	8.8 ml
HCl	8.2 ml	8.2 ml	8.2 ml	8.2 ml
TETA/ $\phi$ (OH) <sub>2</sub>	0.35	0.35	0.35	0.35
TETA/HCl	0.39	0.39	0.39	0.39
TETA + $\phi$ (OH) <sub>2</sub> /HCHO	0.75	0.35	0.50	0.62
TETA + $\phi$ (OH) <sub>2</sub> /H <sub>2</sub> O	0.096	0.096	0.096	0.096



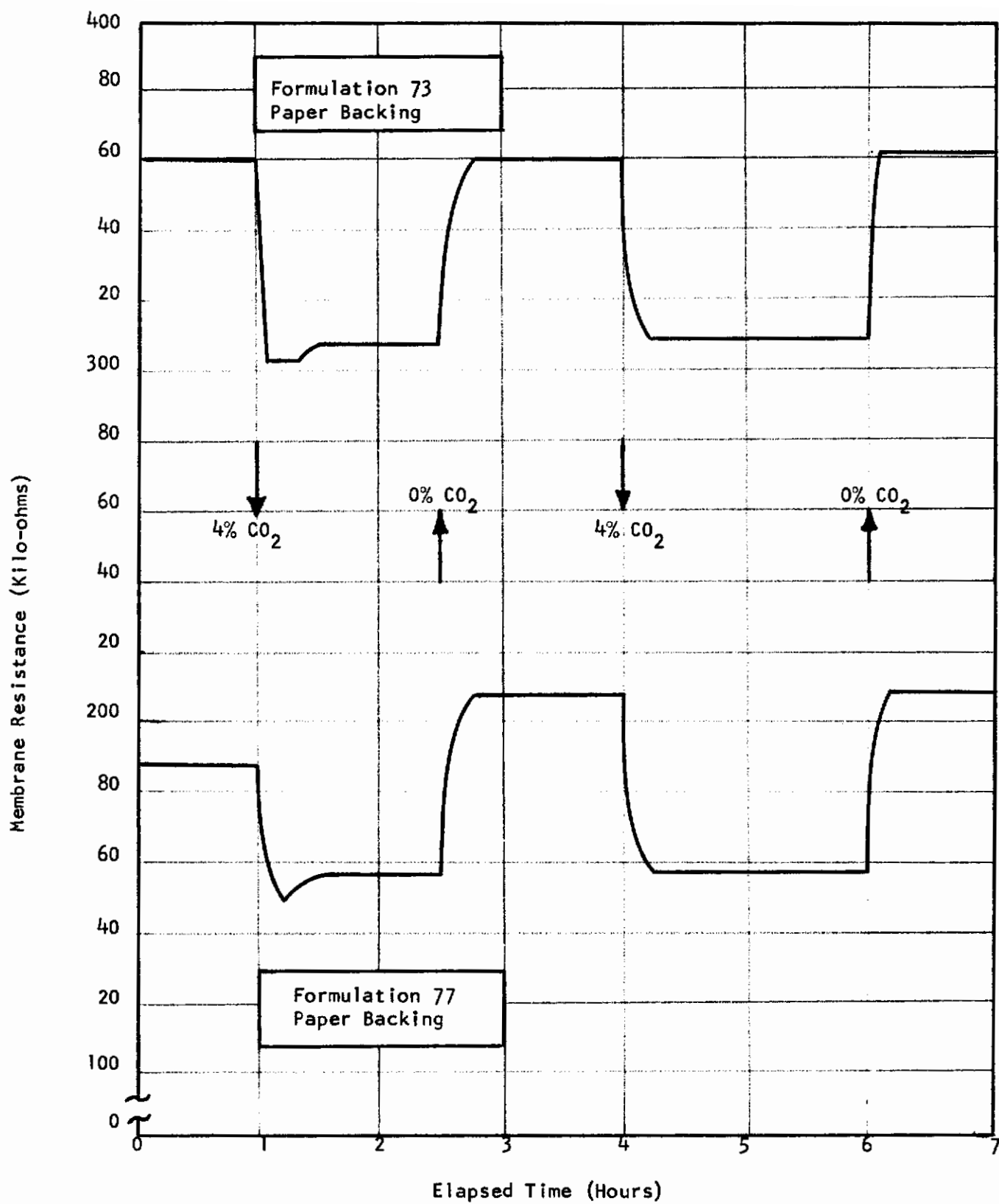


Figure 8. Performances of Formulations 73 and 77 in Air Test Apparatus

Duplicate samples of each of the above formulations were subjected to repeated changes of 0 percent and 4 percent CO<sub>2</sub> in the test apparatus. The response time for all of the samples was about the same-approximately 4 minutes. The sensitivity varied slightly between formulations, however there was considerable variance in sensitivity within a given formulation. All these four formulations were practically identical in performance. On the basis of past data formulation 73 was chosen for the sensor element.

## Effect of CO<sub>2</sub> Partial Pressure and Temperature

With formulation 73 as the sensor polymer, it was necessary to determine the resistance of this polymer at different CO<sub>2</sub> partial pressures and different temperatures. Different CO<sub>2</sub> partial pressures were achieved by equilibrating the membranes in test gas containing 0, 1, 2, and 4 percent CO<sub>2</sub> in air. To avoid the complications of possible thermal gradients, the experiments were carried out in a constant temperature room held at 13, 22, and 43 C. This gave more consistent readings than when the test cell only was thermally isolated.

Five membrane strips were prepared and tested simultaneously. The effective test portion of each strip was about 5mm wide, 4mm long and 0.05mm thick. The resistance of each strip was determined in CO<sub>2</sub>-free air before and after exposure to each of the test gases. The resistance R in the test gas was expressed as a fraction of the resistance R<sub>0</sub> in CO<sub>2</sub>-free air before and after each test. Table XXXII lists the values of (R/R<sub>0</sub>) as well as the average value of R<sub>0</sub> determined for each strip.

The effect of temperature on membrane resistance is shown in Figure 9. Within the accuracy of the data, the resistance of any one membrane in CO<sub>2</sub>-free gas can be expressed in the form

$$\ln R_0 = A - 0.035t$$

where t is the temperature in °C and A is a constant for a given strip. This indicates a 3.5% change in resistance per °C change in temperature. Temperature compensation was built into the sensor by using a dummy membrane maintained at the same temperature as the test membrane but immersed in CO<sub>2</sub>-free air. The variation in resistance among membrane strips at a given temperature is due to variations in thickness and width of the test portions.



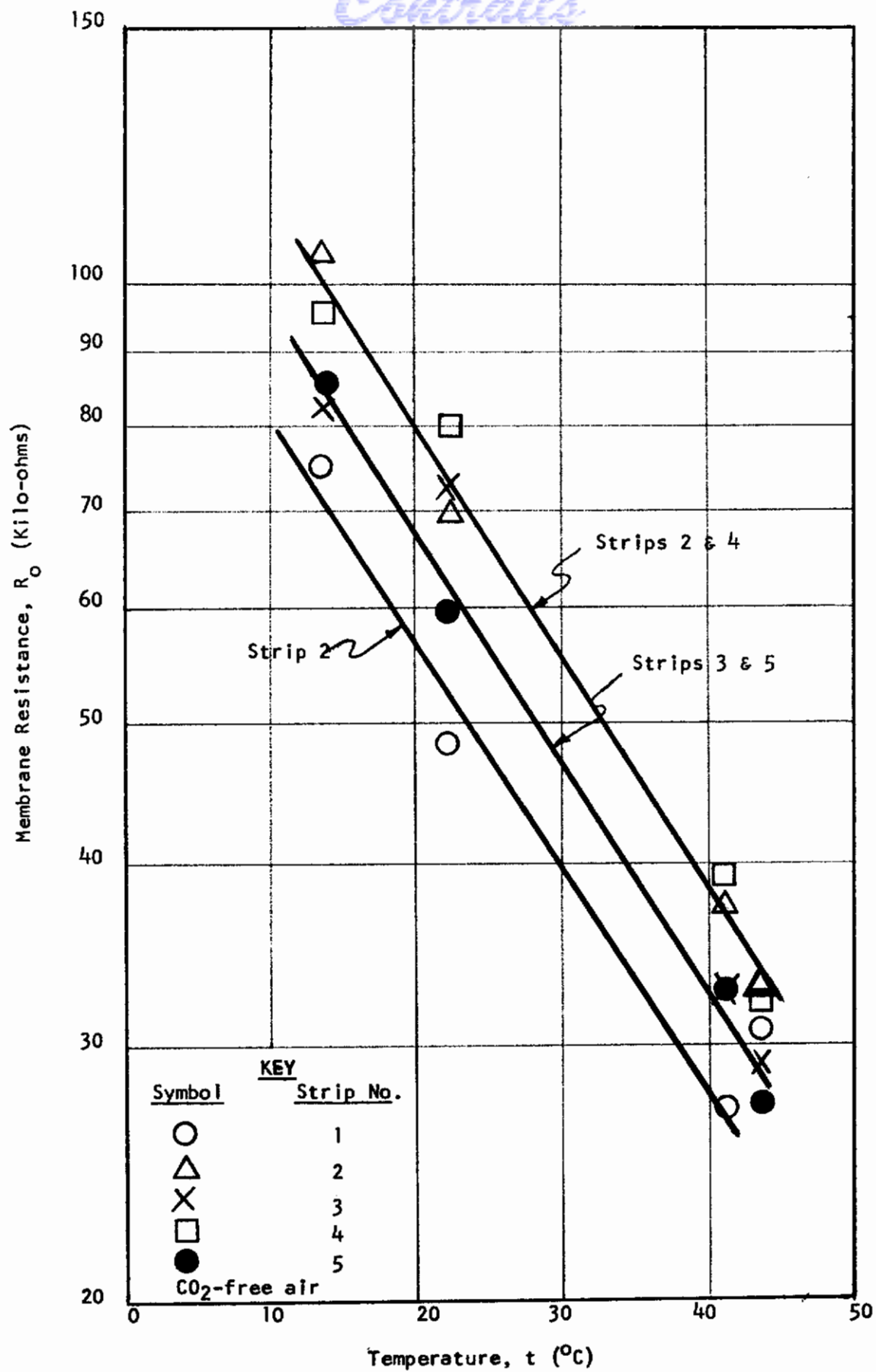


Figure 9. Effect of Temperature on Membrane Resistance

TABLE XXXII  
EFFECT OF TEMPERATURE AND CO<sub>2</sub> CONCENTRATION  
ON MEMBRANE RESISTANCE

Strip No.	Temp. t, C	Resistance R <sub>0</sub> at 0% CO <sub>2</sub> , KΩ	Resistance Ratio, R/R <sub>0</sub>			
			0.5% CO <sub>2</sub>	1.0% CO <sub>2</sub>	2.0% CO <sub>2</sub>	4.0% CO <sub>2</sub>
1	13	75.7	0.973	0.934	0.921	0.894
2	13	104.8	0.995	0.976	0.966	0.946
3	13	85.1	0.982	0.970	0.958	0.946
4	13	96.3	0.969	0.948	0.927	0.907
5	13	88.0	0.977	0.943	0.931	0.909
1	22	49.0	0.960	0.960	0.918	0.854
2	22	69.3	0.972	0.972	0.890	0.824
3	22	73.2	0.973	0.960	0.932	0.861
4	22	80.3	0.981	0.951	0.926	0.850
5	22	60.1	0.983	0.966	0.933	0.900
1	41	27.0	--	--	0.923	0.824
2	41	37.5	--	--	0.916	0.923
3	41	32.0	--	--	0.935	0.909
4	41	39.5	--	--	0.947	0.902
5	41	32.0	--	--	0.903	0.909
1	43	31.5	0.939	0.875	--	--
2	43	33.0	0.969	0.909	--	--
3	43	29.9	0.903	0.896	--	--
4	43	32.5	0.942	0.909	--	--
5	43	27.3	0.944	0.925	--	--

The response of the membrane strips to CO<sub>2</sub> concentration is shown in Figure 10, where the data obtained at 22 C are plotted. (Data obtained at the other temperatures are listed in Table XXXII). Within the accuracy of the data the resistance ratio decreases linearly with an increase in CO<sub>2</sub> concentration and can be expressed as:

$$(R/R_0) = 1 - 0.037c$$

where c is the concentration of CO<sub>2</sub> in the air. This indicates that a change of 1% in CO<sub>2</sub> concentration leads to approximately a 3.7% change in resistance, i.e., has about the same effect on membrane resistance as a 1 C change in temperature. This again highlights the need for temperature control or compensation.

The membrane sensor elements that will be used in the final sensor unit will be considerably thinner than the 0.05mm thick strips used in the tests discussed here. Thinner strips should have a faster response time. They will also have a higher resistance than the 30-100KΩ of the present strips, but the resistances are not expected to be so high as to cause readout problems.

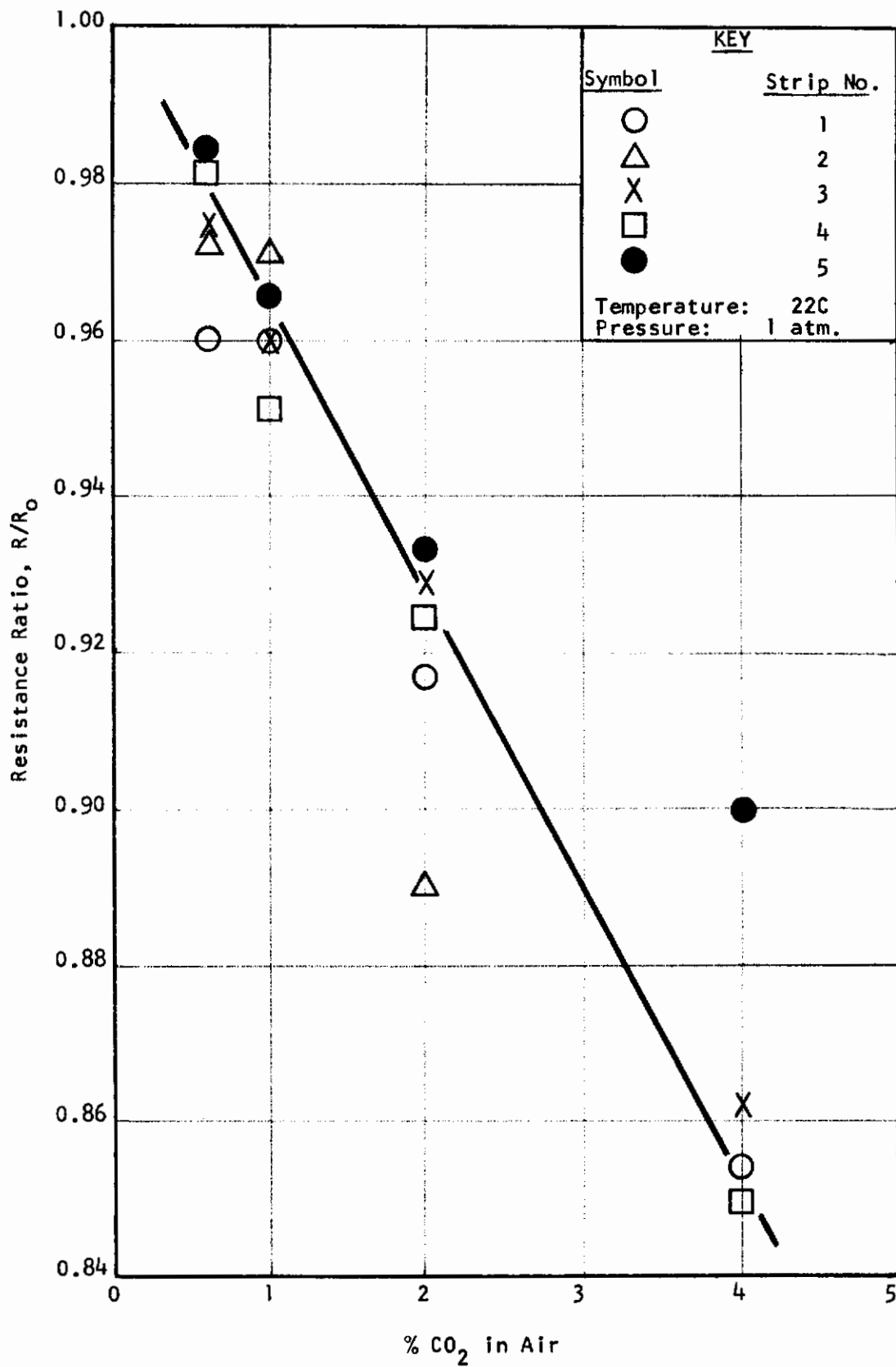


Figure 10. Effect of  $CO_2$  Concentration on Resistance Ratio

SENSOR CELL

System Design

The sensor cell was designed both to take advantage of the membrane properties given in Table XXXII and to comply with the design objectives.

Pertinent design objectives are:

- Temperature independent to 1% for 10C change.
- Pressure independent to 1% for 20 mm change in total pressure.
- Total power consumption below  $\frac{1}{2}$  watt.
- Weight not to exceed 6 oz without readout.
- Detection range of 0-4% CO<sub>2</sub>.
- Ability to cope with weightless conditions.
- Simplicity of design and ease of maintenance.

The average membrane resistance decreases approximately 3% for a centigrade degree increase in temperature; meeting the temperature requirement with a single membrane unit would require significant and probably elaborate temperature compensation. However, the ratio of resistances of two membranes in streams of different CO<sub>2</sub> concentrations is independent of temperature. Consequently a system was devised in which one membrane is exposed to the atmosphere to be tested and another, in close thermal contact, is exposed to a similar stream of gas, but with the carbon dioxide removed.

Since the membrane is actually sensitive to partial pressure of CO<sub>2</sub> the requirement of independence of total pressure makes it necessary to express the CO<sub>2</sub> content as partial pressure. If the readout were expressed in % CO<sub>2</sub>, then the pressure criterion could not be met because, for constant composition, the variation in partial pressure is proportional to the variation in total pressure, i.e., a 20 mm change in total pressure would cause a 2.6% change in partial pressure for the same percentage composition. The relevant physiological quantity is probably partial pressure rather than percentage composition.

The detection range, along with other factors, was used to determine the values of the balancing resistors. Only a widely different range would require a change of resistant values.

There are no unconfined solids or free gas-liquid interfaces in the unit, the only gas-liquid interfaces being on the surfaces where they are controlled by surface tension. Thus the unit will not be affected by weightless conditions.

Both sensor and readout units were designed with the objectives of design simplicity and ease of maintenance in mind.

A photograph of the Carbon Dioxide Sensor is presented in Figure II.

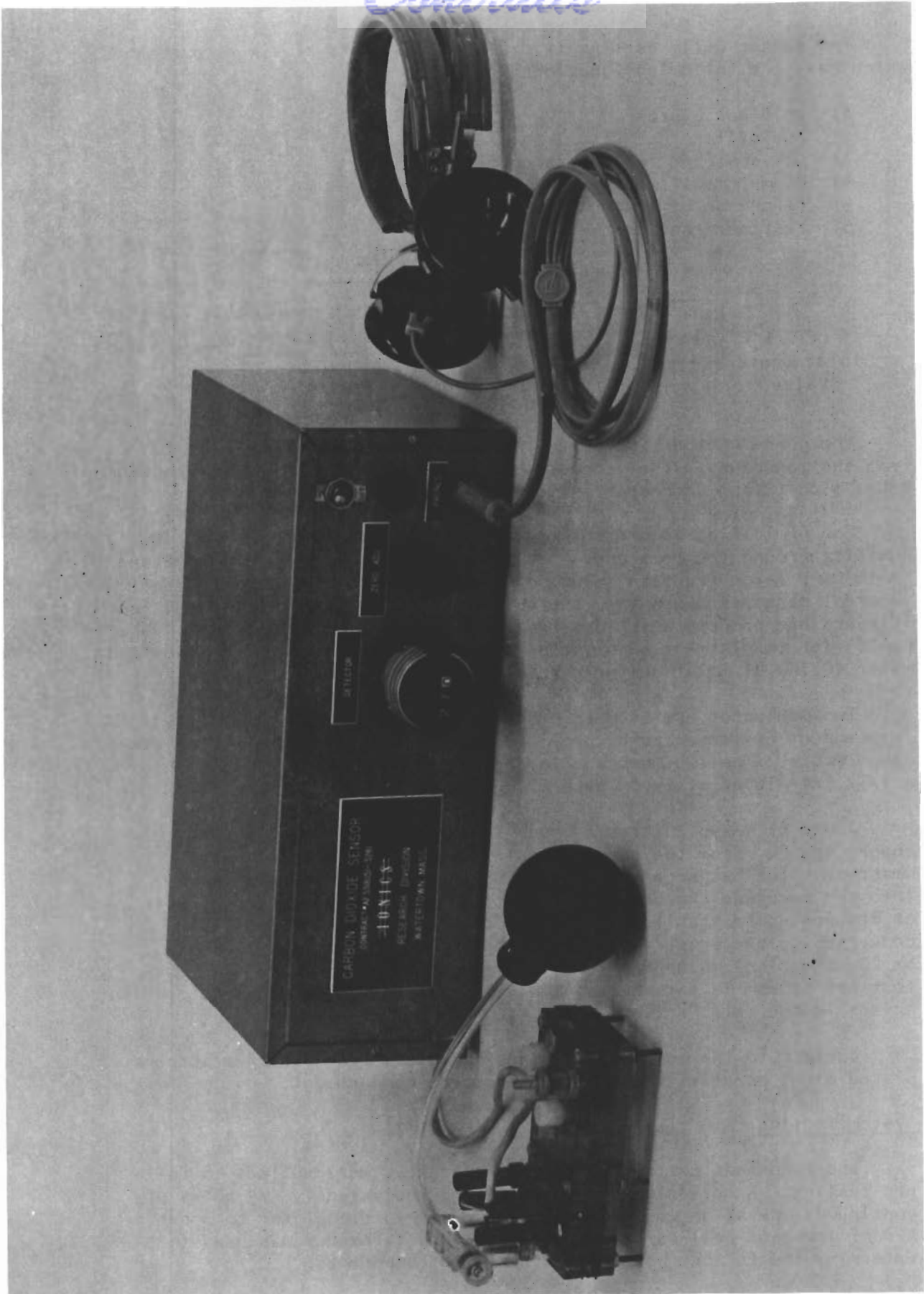
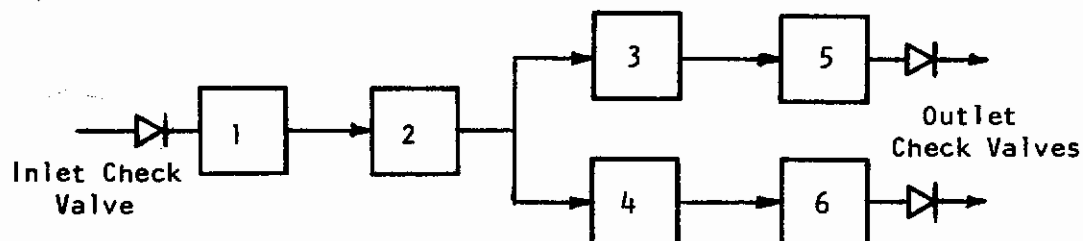


Figure 11. Photograph of Carbon Dioxide Sensor



The sensor cell, as finally designed, consists of six compartments, which have the following functions:

- 1) acid gas guard
- 2) humidifier
- 3) CO<sub>2</sub> absorber for reference membrane
- 4) dummy compartment
- 5) reference membrane chamber
- 6) test membrane chamber



The guard chamber is to keep strong acid gases like SO<sub>2</sub> or HCl from the membranes. The irreversible absorption onto the membrane would cause significant decreases in membrane resistance.

The humidifier is present to maintain an atmosphere of near 100% humidity around the membranes. This is necessary because the membrane contains a large fraction (~30%) of water. If this is removed, the internal stresses cause the membrane to wrinkle and crack. This is an irreversible process which destroys the utility of the membranes. The humidifier consists of a polypropylene felt which is wet with acidified water (0.1-0.01 molar sulfuric acid).

Two membranes are used to produce a unit which is essentially independent of temperature, provided the two membranes are at the same temperature. The two membrane compartments are juxtaposed with only a 1/32 inch layer of tygon separating them.

A bed of Rexyn 201 resin beads in the hydroxyl form is used to absorb the CO<sub>2</sub> from the stream of air passing over the reference membrane. Ion exchange resin was used to avoid migration of ions into the membrane chamber. This particular resin was chosen because of its long-term stability in the hydroxyl form. The resin is converted to the proper form by batch washings first in 0.2 molar Na<sub>2</sub>CO<sub>3</sub> then in 1 molar NaOH. The dummy bed of styrene beads in the test gas stream is for thermal similitude in case a temperature gradient exists in the cell.

Contact to the membranes is made via platinized platinum screens placed along parallel edges of the membrane compartments.

## System Testing

The component parts, other than membranes, were subject to failure testing. A criterion of 500 tests or, equivalently, 24 hours of continuous operation was selected as a reasonable goal for components. A dual membrane cell using one membrane as a reference was used to determine the failure point of each of the components.

Component life in each case depends on the quantity of reactant present so it can be extended substantially at the cost of increased cell size and weight. A gas sample volume of 18 ml per membrane per test was felt to be adequate to bring the membrane very close to equilibrium. From the sample size and the number of tests, the quantity of components and the sampling system were sized.

## Acid-Gas Guard

The function of the acid gas guard is to trap the minute quantities of acid gases other than  $\text{CO}_2$  which may be present in the sampled gas, such as  $\text{HCl}$  or  $\text{H}_2\text{S}$ . These are undesirable since their effect on the membrane's resistance is highly irreversible and cumulative. The acid gas guard chamber is about  $1 \text{ cm}^3$  in volume. The chamber contains one gram of pelletized  $\text{Ag}_2\text{CO}_3$  (8-16 mesh).

For the test, flow paths were cut so that gas to the test membrane was channeled through the guard chamber while gas to a reference membrane was not. Humidified air was bubbled through 18 percent hydrochloric acid thus producing a partial pressure of  $\text{HCl}$  in air of 1,940 ppm. Before failure of the test membrane (i.e., a rapid drop in resistance) the silver carbonate guard was able to scrub 5 liters of test gas. Although this represents only 5.7 percent of the stoichiometric capacity it is much more than adequate in terms of the present test requirements particularly considering the fact that the partial pressure of  $\text{HCl}$  used in the test was 200 times greater than the M.A.C.

Inspection of the silver carbonate pellets at the conclusion of the test revealed that they were completely covered with a thin skin of silver chloride. The bulk of the material was still  $\text{Ag}_2\text{CO}_3$ . The capacity of this component can be improved, if need be, by increasing the surface area.

## Humidifier

The humidifier consisted of a piece of felt  $2 \times 5 \times .007 \text{ cm}$  which was folded and inserted into a chamber  $1 \times 2 \times 0.9 \text{ cm}$ . The felt was saturated with 1.03 grams  $\text{H}_2\text{O}$  (acidified to pH 5 with  $\text{H}_2\text{SO}_4$ ). The flow paths in the test cell were designed such that the air to the test membrane was channeled through the humidifier compartment while the air to the reference membrane was not. Scrubbed air ( $\text{CO}_2$ -free) was bubbled through a saturated solution of  $\text{Ca}(\text{NO}_3)_2$  at  $25^\circ \text{C}$  thus maintaining a constant 50 percent relative humidity in the air test stream.

When the test gas was passed over the reference membrane the resistance went up almost immediately. After 12 liters of 50% R.H. air had been passed through the humidifier compartment at a flow rate of about 6 ml/min no change in resistance was observed in the test membrane. The test was stopped at this point because the humidifier was considered to be adequate in terms of the initial test requirements (24 hours continuous operation at about 6 ml/min = 8.6 liters of air).



The function of this component is to scrub carbon dioxide out of the reference membrane flow stream. This component was tested by filling a compartment 2 x 4 x 0.9 cm with strong base ion exchange resin and passing humidified air containing 4% CO<sub>2</sub> through both the test and reference compartments. The resin was converted to the OH<sup>-</sup> form by repeated washing in strong caustic solution. After 16 liters of 4% CO<sub>2</sub> air had passed through the cell there was no appreciable change in the resistance of the test membrane. The resistance of the reference membrane dropped to a lower value within minutes. After 16 liters of 4% CO<sub>2</sub> air the gas stream was changed to 0% CO<sub>2</sub> and the reference membrane reverted back to its original steady state value. The absorber compartment with its present loading of resin is thus adequate for almost twice the design goal of treatment of 8 liters of air.

## SECTION IV

### READOUT SYSTEM DESIGN

For the purpose of discussion it is convenient to divide the CO<sub>2</sub> detection unit into two systems. The "sensor" consists of membranes, housing, humidifier, gas propulsion device and other apparatus necessary to the process of bringing a sample of test gas into intimate contact with the sensor membrane. The "readout" comprises all components necessary to detect the resistance of the sensor membrane and to convert this measurement into a reading of CO<sub>2</sub> concentration.

The only relevant design objective was that the total power consumption should be below  $\frac{1}{2}$  watt. Since no power is used in the sensor unit, this is all available for the readout system. No weight requirement was placed on the readout.

Negotiations with the contract monitors produced the further limitation that, since the prime objective of the program was the development of membrane sensing elements, only a small portion of the funding should go into electrical or electronic development. Consequently, the readout system was, from its inception, the simplest and most inexpensive system which would demonstrate the properties of the sensor.

The readout system was designed to keep the power consumption below  $\frac{1}{2}$  watt. It was assumed that the power for the sensor would be 110V, 400 cycles. This voltage is used directly as a signal voltage, which eliminates the need for an oscillator. Since 400 cycles is in the middle of the audio range, a pair of earphones can be used to detect the signal.

The readout schematic is shown in Figure 12. Values are based on a sensor membrane with a resistance of 200K ohms in air and above 100K ohms in 4% CO<sub>2</sub>.

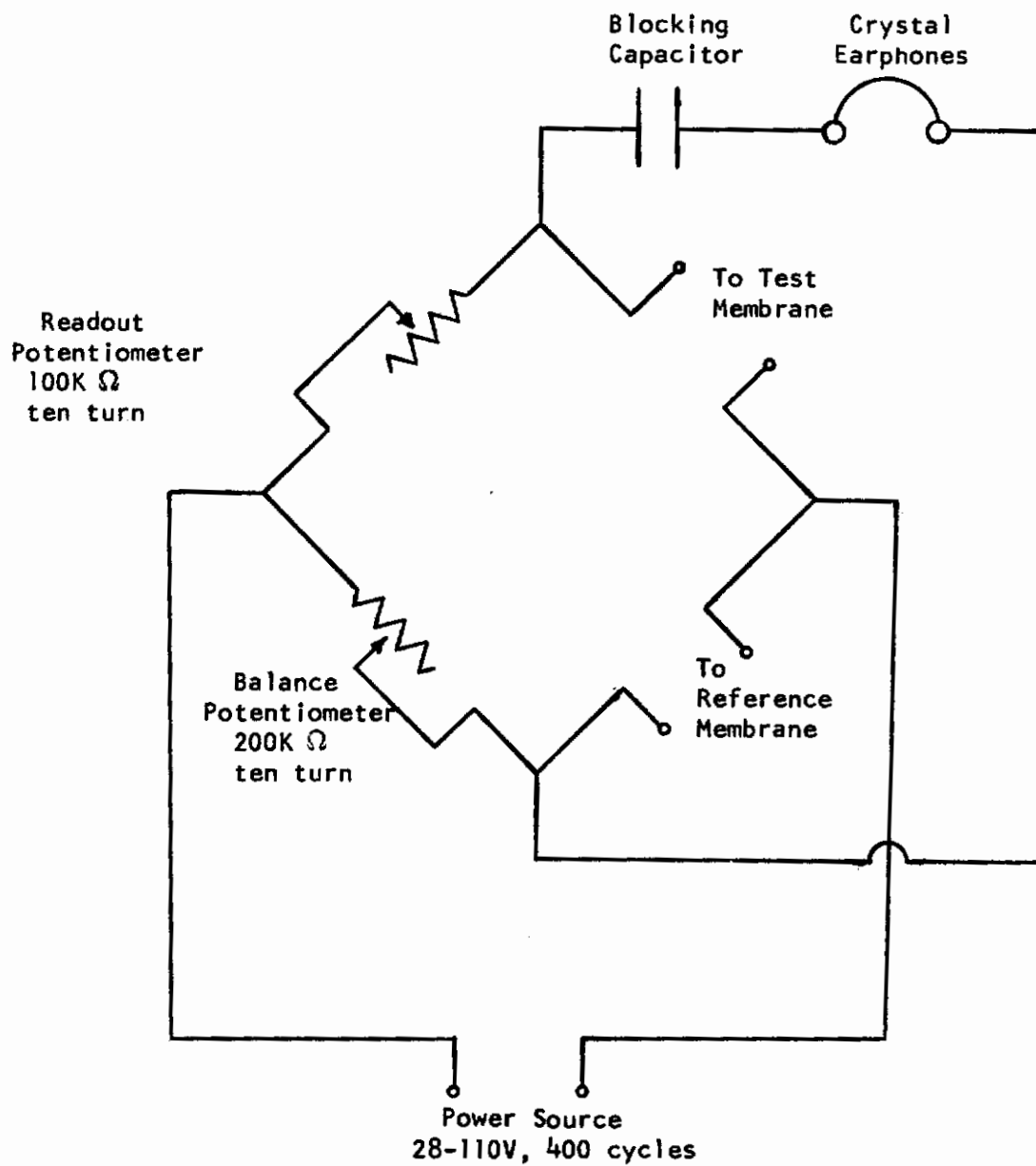


Figure 12. Electrical Circuit Diagram

The initial step in the operation of the unit is to obtain a null point by adjusting one of the potentiometers to the point of minimum sound in the earphones. The bridge is balanced by drawing in a sample of CO<sub>2</sub>-free air and adjusting the 200KΩ balance potentiometer to the null point. This reference sample may be obtained by passing air containing some CO<sub>2</sub> through the cartridge containing base-form resin supplied with the unit. The balance potentiometer setting is then locked. A test sample is drawn into the cell and a null point is obtained using the 100KΩ readout potentiometer. A null value is read from the readout dial on the potentiometer.

The partial pressure is calculated from the equation:

$$pCO_2 = k(NV)$$

where pCO<sub>2</sub> is the CO<sub>2</sub> partial pressure in atmospheres, NV is the null value from the readout potentiometer and k is the operating constant. The precise value of k is determined by calibrating the unit with a gas of known concentration.

## SECTION V

### RECOMMENDATIONS FOR FUTURE WORK

With the feasibility of using an anion membrane as a carbon dioxide sensor element well demonstrated, a number of avenues toward future improvements are opened. These encompass a wide variety of aspects of the sensor and the sensor element.

**Membrane thickness** - The most likely method of reducing response time is to make the active part of the element thinner. The present membrane is almost as thin as a stable self-supporting piece of polymer could be made. Further reduction in thickness would require the polymer to be cast on an inert support of some convenient geometry. For this, the present polymer formulation is usable.

**Sensitivity to Humidity** - A considerable increase in operational simplicity could be obtained if the membrane resistance were not strongly influenced by its water content. There are two possible routes to this end. The present polymer could be used if an ionizing solvent of considerably lower volatility could be found which was compatible with the polymer. Alternatively, a polymer with less sensitivity to water content could be developed. This might be closely related to the present polymer type, for example a similar polymer with considerably lowered water content.

**Reference Membrane** - A membrane with the same temperature coefficient of resistance but with no sensitivity to CO<sub>2</sub> would make a more convenient reference membrane. This would eliminate the need for the CO<sub>2</sub> absorber compartment which currently sets the limit on continuous operating time.

**Readout Simplification** - A readout system in which the result appeared on a panel meter instead of on a resistor dial would be more complicated electrically but more simple for the operator to use.

**Security Classification**

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<b>13. ABSTRACT</b> <p>The purpose of this program was to develop a novel carbon dioxide sensor based on obtaining changes in the electrical resistance of anion-exchange resin proportional to the ambient partial pressure of carbon dioxide. The change in resistance is due to the increased ionization of a weakly ionized base in the presence of a slightly acid gas. A laboratory program was conducted to evaluate the response of various types of weak-base ion-exchange polymers to carbon dioxide concentrations in the range of 0 to 4%. The optimum material consisted of a condensation polymer of resorcinol, formaldehyde and triethylenetetramine. A laboratory model of the CO<sub>2</sub> Sensor was fabricated using these sensing elements in the form of small, thin strips. In order to minimize the effects of humidity and temperature, the model contained two sensing elements, one being a reference. A guard chamber has been provided to absorb any strongly-acid gases. Electrical readout is made on a balancing potentiometer with an earphone detector. The Sensor is small (about 50 cubic inches), weighs less than 6 ounces, has a power requirement of less than 0.5 watts, and its operation is independent of gravity.</p>		

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## Security Classification

14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	<p>Carbon Dioxide Sensor Respiratory Instrumentation Life Support Equipment</p>						

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