IMPROVED SEPARATORS FOR SILVER OXIDE-ZINC AND SILVER OXIDE-CADMIUM CELLS FOR SPACECRAFT APPLICATION

By

Helmuth L. Pfluger
and
Howard E. Hoyt

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The Borden Chemical Company
Central Research Laboratory
Philadelphia, Penna. 19124

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PROJECT PERSONNEL

In carrying out the experimental work herein reported, the writers were assisted at The Borden Chemical Company by Assistants Ronald G. Burton and Charles J. Guinosso. At Burgess Battery Company, the sub-contract tests were under the supervision of Mr. Frederick A. Poss and Mr. J. R. Beckman.

SUMMARY

Modifications of C3-type film (methyl cellulose formulations with polyacids) have been prepared which have flexibility and electrolytic conductivity both ten times as great as the original C3. This has been achieved by incorporation of water-soluble amines and appropriate downward adjustment of the polyacid fraction.

Various amines have been studied as modifiers. Several increase conductivity without impairing flexibility. At equivalent levels of polyacid component, 10% hydroxypropylamine increased electrolytic conductivity of film in 45% potassium hydroxide one hundredfold and also doubled flexibility as measured by M.I.T. flex test.

Stability of amine-modified films in air, in electrolyte and in electrolyte with silver oxide was found to be of same order as for C3. Several examples have therefore been selected for further testing as separators in cells.

The possibility of developing membranes specifically adapted to use in KOH concentrations below 30% is being explored.

I. INTRODUCTION

In the Second Quarterly Report experiments were aimed at improving the conductivity of methyl cellulose/polyacid films to operate in KOH concentrations above 30%. The brittleness attendant upon increase in the proportion of the more conductive polyacid component promoted an investigation of suitable plasticizers in order to retain flexibility in the film. This is especially important during the operation of wrapping the electrodes. Such plasticizers had to meet the requirement of being compatible with the methyl cellulose/polyacid solution from which they were cast. These included the water-soluble low molecular weight polyethylene oxides as well as their solid, high molecular weight counterparts, the polyethylene oxides (Polyox). Other water-soluble polymeric plasticizers included polyvinyl alcohols and hydroxyethyl cellulose. Several of the three component polymer compositions gave films of attractive properties in screening tests and were prepared in sufficient quantity for construction of cells for life cycle tests.

In the work of the present period a more substantial improvement in flexibility was sought as well as stability towards silver oxide oxidation, inasmuch as past work has shown that both polyvinyl alcohol and hydroxyethyl cellulose, the flexibilizing components, were somewhat vulnerable to oxidation. The new approach of the present report was based on the principle of adding plasticizing amines to the methyl cellulose/polyacid system. The amines exerted a secondary effect of equal or greater importance; the electrical resistance of the films was drastically reduced. This led to several film formulations exhibiting both improved flexibility and lowered resistance.

In addition to the development of films to perform in electrolyte of higher concentrations the possibility of developing films to perform in KOH concentrations below 30% was explored in a preliminary way.

A. Modification of Methyl Cellulose/Polyacid Films with Amines

As in all previous work completely unsupported homogeneous films were the objective and for this reason only completely water-soluble amines whose solutions in addition were compatible with the other constituents were considered as potential plasticizers. Some of these, although water soluble, proved to be incompatible with the polymers, forming two phase solutions; such preparations were discarded. This was not an entirely arbitrary decision in that oxidation tests on films of visible two phase structure have shown a tendency to disintegrate under oxidation by silver oxide.

For purposes of comparison the initial investigation was on the effect of amines on the properties of C3 films. This work is summarized in Table I.

Table I. - Amine-Containing C3 Films

Reference	Composition	pH	Film Properties @ 50% R.H. MIT Flex 200 g. tension mils	cycles	Tensile psi	Elec.Res. 45% KOH milliohms-in.^{2}
Avg. C3	PVMMA 30/MC 70, Reference	2.2	1.5	756	10,000	357
485-120 B	C3 + 10% 3-hydroxypropylamine	6.9	1.5	1476	6,100	15
485-120 A	C3 + 30% "	9.2	1.5	1400	--	9
499-36 A	C3 + 5% propylamine	3.9	1.5	325	12,200	6
499-36 B	C3 + 10% "	4.3	1.6	14	5,970	3
499-36 C	C3 + 20% "	7.8	1.7	1	4,650	31
499-35 A	C3 + 5% butylamine	3.6	1.5	514	13,100	185
-35 B	C3 + 10% "	4.2	1.6	275	10,600	9
-35 C	C3 + 20% "	6.8	1.6	163	6,680	0
482-68	C3 + 10% 3-methoxypropylamine	5.5	1.5	180	8,520	16
482-69	C3 + 20% "	-	1.6	1406	3,980	50
482-81 A	C3 + 5%(ethoxy)3-propylamine	3.3	1.5	590	12,900	360
-81 B	C3 + 10% "	3.9	1.4	414	12,400	200
-81 C	C3 + 20% "	4.2	1.5	943	6,460	22
-81 D	C3 + 40% "	6.2	two phase soln.			
482-83 A	C3 + 5% 1,6-hexadiamine	3.8	1.4	957	10,300	217
-83 B	C3 + 10% "		two phase soln.			
499-34 A	C3 + 5% morpholine	3.6	1.4	658	13,400	3
-34 B	C3 + 10% "	4.1	1.5	75	7,810	6
-34 C	C3 + 20% "	6.4	1.6	217	5,500	9
482-70	C3 + 10% choline	-	1.6	148	10,100	16
482-71	C3 + 12.5% "	-	1.7	14	8,600	13
482-82 A	C3 + 5% $(CH_3)_4NOH$	3.8	1.4	617	11,400	88
-82 B	C3 + 10% "	4.3	1.4	46	8,560	3
-82 C	C3 + 20% "	6.6	1.4	3622	2,750	3
504-140	C3 + 5% $BzMe_3NOH$	-	1.6	4024	9,140	7260
504-139	C3 + 10% $BzMe_3NOH$	-	1.5	4745	7,820	1520
499-144 A	C3 + 25" "	-	1.9	3177	--	0
499-145 A	C3 + 5% propanediamine	--	two phase soln.			1180
499-145 B	C3 + 10% "	--	two phase, film too soft			
499-146 A	C3 + 5% aminopropylmorpholine	--	1.5	-	-	1205
499-146 B	C3 + 10% "	-	two phase soln.			-
499-146 C	C3 + 20% "		"			-
482-80 A	C3 + 5% triethanolamine	3.1	1.5	662	12,900	220
-80 B	C3 + 10% "	3.9	1.5	381	11,600	66
-80 C	C3 + 20% "	4.7	1.6	3843	4,730	3
483-58-1	C3 + polyethylenimine	Precipitate, insoluble hot and cold				

From the results of Table I, 3-hydroxypropylamine appeared to be the most effective plasticizer for the C3 composition (3PVMMA/7MC) at levels below 10% plasticizer on the polymers. Some of these amines, it will be noted, had a negative effect, embrittling the film. This was especially true with propyl and butylamines. The diamines, propane diamine and hexane diamine, gave two phase solutions, possibly by a cross-linking effect. This occurred also with some of the higher molecular weight amines. Polyethylenimine gave a solid precipitate.

It can be seen that a remarkable incidental effect occurred: the resistance of the compositions was lowered in all cases by the addition of amine. This suggested that formulations, intrinsically less brittle by virtue of containing less polyacid, could be brought into the desired conductivity range by the addition of amines. In Table II C1 and C2 and B2 compositions were formulated with 3-hydroxypropylamine at various levels. From this exploration a number of film preparations emerged which had both better flexibility and conductivity than C3.

From the results of Tables I and II a number of film compositions were selected for further testing for stability to oxidation in potassium hydroxide solutions, saturated continuously with silver oxide according to procedures earlier described (1). The stability is estimated by the tensile strength of the oxidized film compared to the strength of the film exposed to the electrolyte only, expressed as the quotient. Measurements were made on the electrolyte-saturated film. In Table III films were tested in silver oxide-saturated 30% KOH at room temperature for 3 days, at 50° C. for three days and in 45% KOH at room temperature for three days.

Table II. - Modification of Various Film Compositions With 3-Hydroxypropylamine

Reference	Composition	pH	Film Properties 50% R.H. MIT Flex 3 200 g. tension mils	cycles	Tensile Strength psi	Elec. Res. in 45% KOH milliohms-in.^{2}
485-76	B5* + 5% KOH to -	3.5	1.5	217	-	22
485-127 A	B5 + 5% 3-hydroxypropylamine	3.5	1.5	446	-	16
485-127 B	B5 + 10% "	3.8	1.4	1080	9,340	3
485-127 C	B5 + 30% "	5.4	1.7	3582	1,730	-
499-140	B2# + 3.2% KOH to -	3.8				1855
482-98 D	B2 + 3% 3-hydroxypropylamine	4.55	1.4	4101	-	398
-98 C	B2 + 6% "	4.95	1.5	3687	-	90
-98 B	B2 + 10% "	6.45	1.4	11,425	-	31
-98 A	B2 + 20% "	10.8	1.4	569	-	138
504-16	B3.3^z + 3.4% KOH to -	4.0	1.6	1688	11,800	200
504-19	B3.3 + 5.3% 3-hydroxypropylamine	4.0	1.4	1682	10,300	3
504-23	B3.3 + 7.5% "	4.4	1.4	2757	8,520	28
504-24	B3.3 + 14.4% "	5.0	1.6	4958	4,770	63
504-25	B3.3 + 25% "	6.15	1.8	1311	2,360	0
499-71	C2 (2PVMMA/8MC)	2.2	1.5	1546	12,600	1546
499-75 G	C2 + 3% 3-hydroxypropylamine	3.5	1.5	1119	11,900	360
-75 F	C2 + 6% "	4.1	1.5	1212	8,310	50
-75 E	C2 + 10% "	6.0	1.5	7196	5,620	31
-75 D	C2 + 20% "	8.5	1.7	4639	4,560	35
499-70	C1(1PVMMA/9MC)		1.5	3427	11,700	3130
499-74 C	C1 + 3% 3-hydroxypropylamine	4.5	1.5	3231	9,600	1290
-74 B	C1 + 6% "	8.5	1.5	6879	7,960	452
-74 A	C1 + 10% "	10.1	1.5	4523	6,790	324
483-90	C2 + 10% "	6.0	1.2^x	8501^x	7,050	44

Notes to Table II:

* 5PAA/5MC homogenized to clear solution by adding KOH to pH 3.5. The remainder of the B5 group were homogenized to clear solutions by addition of the amine.

2PAA/8MC homogenized to clear solution by adding KOH to pH 3.8. The remainder of this B2 group was prepared by addition of the amine to the KOH-adjusted B2.

z 3.3 PAA/6.7 MC homogenized to clear solution by adding KOH to pH 4. The remainder of this B3.3 group was homogenized by addition of the amine only.

Table III. - Oxidation of Films in KOH Saturated with Ag_2O.

Type	C3	Cello-phane	C3 + 10% HAP	C2 + 10% HAP	B5 + 10% HAP	B2 + 10% HAP	B3 + 10% HAP
References	504-37 485-104		485-120B 499-30	504-6	485-127B	482-98B	504-24
			30% KOH-Ag_2O 72 hours, 23° C.				
(A) KOH only, psi	2510	3130	1700	-	725	-	-
(B) KOH-Ag_2O, psi	2160	457	1590	-	759	-	-
B/A	.86	.15	.94	-	1.04	-	-
			45% KOH-Ag_2O 72 hours, 23° C.				
(A) KOH only, psi	3190	4710	2290	-	1250	-	-
(B) KOH-Ag_2O, psi	3290	3920	2040	-	1200	-	-
B/A	1.03	.83	.89	-	.96	-	-
			30% KOH-Ag_2O 72 hours, 50° C.				
(A) KOH only 23°C, psi	2090	3130	1380	2630	-	1550	1036
(B) KOH-Ag_2O 50° C, psi	2290	0	1310	2560	-	1810	1002
B/A	1.09	0	.95	.98	-	1.17	.97

Notes: C films are methyl cellulose-PVMMA films.

B films are methyl cellulose-polyacrylic acid films

HAP is 3-hydroxypropylamine. Percents are parts per 100 parts of polymers in film.

It can be seen from Table III that the films of the new formulations held up very well in tensile strength under silver oxide oxidation. A more significant measurement might be in the determination of permeability before and after exposure to the oxidizing condition. Future experiments are planned for this. A measurement even more directly pertinent might be in changes of conductivity induced by oxidation. Because of limitations in present equipment conductivity changes were confined to measurements in 45% KOH as given in Table IV.

Table IV. - Resistance of Films Exposed to 45% KOH-Ag_2O
(72 hours at 23° C.)

Reference 485-	Composition	Resistance in 45% KOH milliohms-in^2		
		Unstirred	Stirred 72 hrs.	Stirred with Ag_2O - 72 hrs.
-	Cellophane	19	69	22
120-B	C3 + 10% HAP	15	41	6
125-B	C5 + 10% HAP	6	100	0
127-B	B5 + 10% HAP	3	9	16

It is believed that the values shown do not represent significant changes. Further, more accurate work is planned in this area.

The 3-hydroxypropylamine has a boiling point of 188° C. and, although undoubtedly present as the amine salt of the polyacid in the film, could conceivably be lost by evaporation from the thin films on storage or long exposure to air. To test this possibility representative films were hung in a current of air at 72° C. and 50% R.H. for several weeks and then tested for flexibility. Results are given in Table V below.

Table V. - Effect of Exposure to Air of Amine-Plasticized Films

Ref.	Film Composition	10% Soln.	Thick-ness	MIT Flex (200 g Tension, 50% R.H.)		
				Orig.	Air-Exposed Film	
		pH	mils	Cycles	Days	Cycles
485-120B	C3 + 10% $HOCH_2CH_2CH_2NH_2$	4.3	1.6	1476	51	599
499-137	C2 + 10% "	6.0	1.2	8501	30	5878
482-60	Methyl cellulose + 12.5% "	12.5	1.7	3217	90	2076

Some loss in flexibility was found in all cases. Whether this would be a serious problem under less rigorous conditions, as in normal storage, remains to be determined.

It was noted that when the films were hung in unconditioned air that undue brittleness developed. This was suspected to be more the result of humidity conditions than to loss of amine and was confirmed by conditioning films and testing at two different humidities, with the results shown in Table VI.

Table VI. - Effect of Relative Humidity on Flexibility of Films

	C2 + 10% HAP 504-6	C3 MP 146-49
MIT Flex, 200 g. tension, 50% R.H., 72° F. - cycles	3789	627
MIT Flex, 200 g. tension, 40% R.H., 77° F. - cycles	1515	378
Flex of completely desiccated film	1-2 bends	1-2 bends

It was not readily feasible to test the films under controlled zero relative humidity (last line of table) but the flexibility was estimated by desiccation within a closable polyethylene bag to constant weight over calcium sulfate (Drierite). Both films fractured within the closed bags when a single bend was applied by hand. The weight loss from 50% R.H. (moisture content) was about 9% in both cases.

The action of moisture was shown to be reversible. Thus a C3 film was U wrapped around simulated electrodes and heated in an oven for five hours at 58° C. An exposed edge of the thus dried films was broken by a single bend. The assembly was reconditioned at 72° F., 50% R.H., the assembly unwrapped and test specimens cut on the straight sections and at the bend, with the following results, average of 5 specimens.

Original MIT Flex on film 50% R.H., 72" F.	754 cycles
Reconditioned film straight sections, 50% R.H., 72° F.	701 cycles
Reconditioned film at bend 50% R.H., 72° F.	632 cycles

It seems likely that the plasticizing effect of 3-hydroxypropyl amine is in lending additional hygroscopicity to the film and that the primary plasticizer is actually water. This same principle is involved in the plasticization of cellophane with glycerin and glycols.

It is known that flexibility is inversely proportioned to film thickness. Films of this study have been customarily cast to give a target thickness of 1.5 mils. Two compositions were cast over a range of thickness and the flexibility determined experimentally. As can be seen from Figure 1 the flexibility varied exponentially with thickness. On this basis one of the experimental films used in the construction of test cells was prepared at 1.2 mils thickness instead of the customary 1.5 mils. This was the formulation of the last line of table II (C2 plus 10% HAP), which film gave more than 10 times the flex cycles usually shown by C3.

Flexibility is of chief concern in wrapping electrodes by the U wrap during the final bend. All of the films of this study are extremely flexible once immersed in the electrolyte.

The 3-hydroxypropylamine is completely soluble in 30 to 45% KOH and there was some concern that on immersion of the film in the electrolyte loss of amine would result in increase of resistance to that of the unplasticized film. This was tested on two formulations as shown in Table VII. Resistance was measured after 1 day soaking in 45% KOH and again after several days vigorous stirring in a large excess of 45% KOH to provide maximum possible extraction of the film.

Table VII. - Effect of Exposure of Films to Extraction Condition - (Condition 12 sq.in. 1.5 mil film stirred with 400 ml 45% KOH)

Reference 499-	Film Composition	Electrical Resistance in 45% KOH milliohms-in.^{2}			
		No stirring	Stirring		
		1 day	3 days	6 days	15 days
75F	C2 + 6% $HOCH_2CH_2CH_2NH_2$	50	25	16	10
71	C2 as is (control)	1178	-	-	1010
137	C3 + 10% $HOCH_2CH_2CH_2NH_2$	15	-	-	35
9	C3 as is (control)	374	-	-	357

Within the sensitivity of our equipment no change in the resistance of the films occurred under conditions conducive to extraction. This would appear to indicate that the amine was not extracted. A more definitive investigation will be reported in the next quarterly report.

Interdependence of Film Composition and KOH Concentration

There are possible advantages to operating the silver-zinc cell at concentrations below 30%. In certain uses cells are charged to the point of gassing and it is desired to reconvert the gases to electrolyte on discharge. For such purpose low concentrations of KOH are beneficial because they redissolve the gases more easily. Secondly, since zinc oxide is less soluble in lower concentrations one might predict that this electrode might be less rapidly changed in its morphology during its life. There has been some experimental evidence for this (2).

One would expect that in going below 30% concentrations less polar compositions would be required; in the methyl cellulose/polyacid system a lower proportion of polyacid would be called for. This was explored in a preliminary way by measuring the resistance, swelling and solubility of methyl cellulose combinations in 15 to 45% KOH as shown in Table VIII.

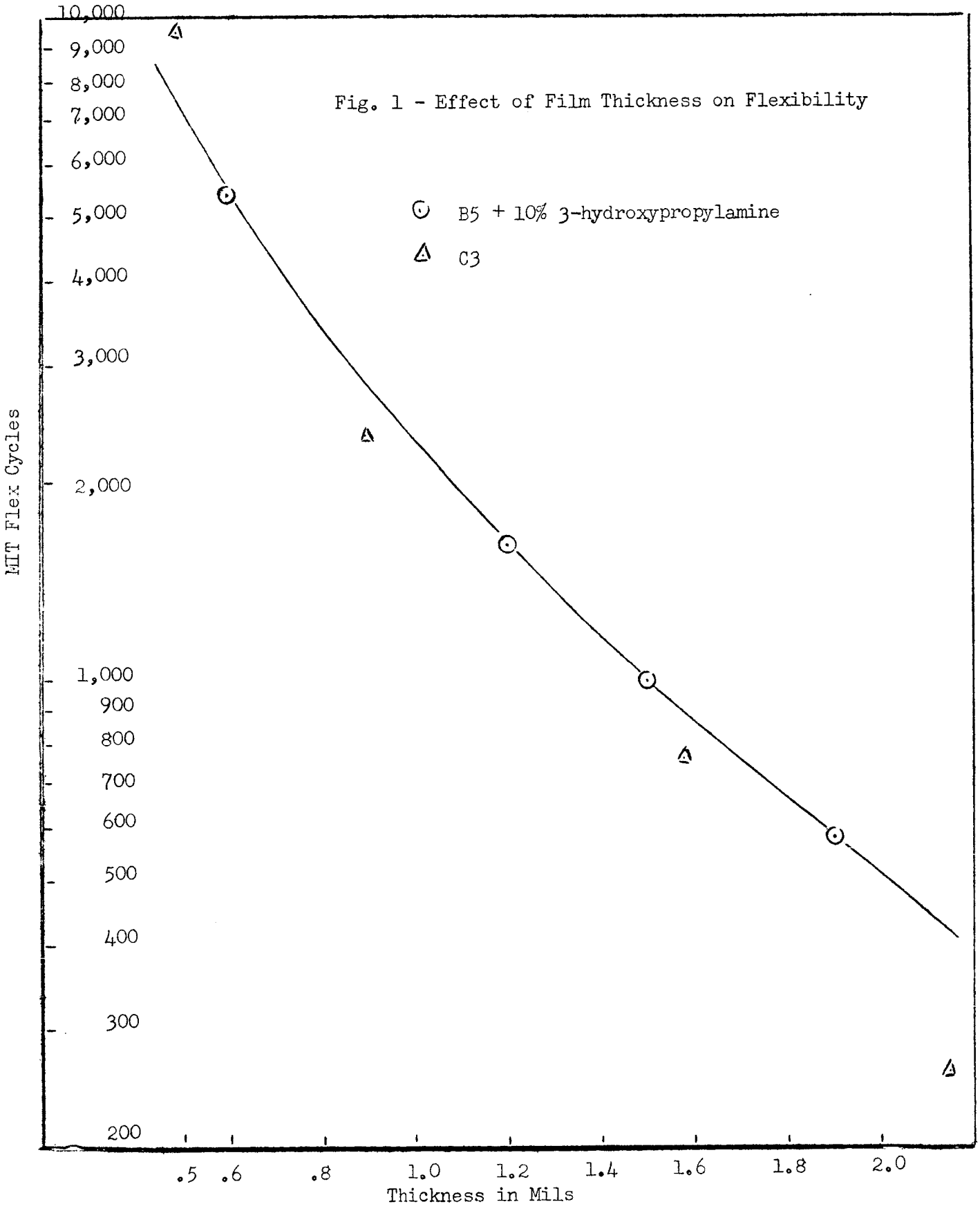
Table VIII. - Effect of KOH Concentration on Film Properties

Film Property	% KOH	Methyl Cellulose	C1	C2	C3
Swelling Ratio*	15	1.71	-	2.40	2.47
	20	1.52	-	1.90	2.16
	25	1.27	1.46	1.63	1.84
	30	1.23	-	1.57	1.72
	45	1.25	1.46	1.55	1.69
Resistance (milliohms-in.^{2})	15	-	-	-	(6)
(values in parentheses are	20	(38)	-	-	(22)
approximate because of present	25	(125)	(129)	(38)	(9)
instrumental limitations at	30	(418)	-	(31)	(21)
low resistances)	45	6080	3130	1178	357
Solubility in Electrolyte	15	+	+	+	+
(indicated by Ag_2O reaction	20	+	weak	+	+
test)	25	0	0	weak	+
	30	0	0	0	0
	45	0	0	0	0

Notes: * Wt. of blotted swollen film/wt. of air dry film at 50% R.H.

From Table VIII it can be seen that as KOH concentration is lowered swelling and conductivity increase as well as the tendency for at least a portion of the film to go into solution. It seems probable, therefore, that polarity could be adjusted in this system or a related system to develop a membrane suitable for any chosen KOH concentration, which would remain intact and supply the required properties. To arrive at the formulation would, of course, require more sensitive resistance measurements and also a more quantitative measurement of dissolved material in the electrolyte.

The Ag_2O method used to detect dissolved organic matter in the KOH consisted in warming an equal volume of supernatant KOH with 30% KOH saturated with silver oxide; a brown color developed during one minute heating was taken as evidence of dissolved organic matter. The sensitivity of the method was examined briefly. The test appeared to be quite sensitive to cellulosic material, 0.01% on sodium carboxymethyl cellulose and relatively insensitive to PVMMA, 0.1%. It is planned to develop a method which will quantitatively determine any type of dissolved organic material. This would be useful in examining the electrolyte in cells, under aging or sterilization conditions.


Fig. 1 - Effect of Film Thickness on Flexibility
B5 + 10% 3-hydroxypropylamine
C3
MIT Flex Cycles
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
900
800
700
600
500
400
300
200
.5
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
Thickness in Mils

References:

(1) "Improved Separators for Silver Oxide-Zinc and Silver Oxide-Cadmium Cells for Spacecraft Application", Final Report June 28,1963 - September 27,1964. Borden Chemical Company. Prepared for Goddard Space Flight Center NAS5-3467.

(2) "Sealed Zinc-Silver Oxide Secondary Battery System" April 13, 1964-June 30, 1964. Yardney Battery Co. p. 36. Contract No. DA-36-039AMC-02238 (E).