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Westinghouse Research Report 67-9B6-BSEPA-R1

SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

A. Langer
R. G. Charles
C. R. Ruffing

March 31, 1967

Contract No. 951525

"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100."

Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

Third Quarterly Report

Period: January 1, 1967 to March 31, 1967

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HEAT STERILIZABLE BATTERY SEPARATORS

Third Quarterly Report

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1. Introduction

This is the third quarterly report on JPL Contract No. 951525, "Separator Development for a Heat Sterilizable Battery", covering the period January 1, 1967, to March 31, 1967. The major part of the work during this period was devoted to further investigation of the effects of preparation variables on the properties of composite separator membranes composed of materials capable of withstanding sterilization heat treatment in concentrated potassium hydroxide. A relatively minor effort was devoted to fabrication and testing of membranes having an epoxy resin filler material with chelating functional groups bonded to the resin.

The previous quarterly reports listed the functions and other desirable properties of separators for silver-zinc batteries that must be subjected to sterilization heat treatment, gave the results of screening tests on a large number of candidate materials for composite separators, described a number of membrane fabrication techniques that have been tried, and gave the results of tests on many types of experimental separators. The present report, as outlined in detail in the Table of Contents, gives the results of continuing systematic investigation of fabrication and composition variables. The most significant new result is the recognition of the effect of compression of the composite structures on electrical resistance. This factor had caused a previously unexplained variability in resistance measurements on the experimental separators.

2. Effects of Pressure on Experimental Separators

The resistance of composite films, composed of an inorganic filler and organic binder and processed by water extraction of the solvent, can be greatly and permanently reduced if these films are subjected to pressure. This fact has added another unexpected variable in the preparation of these membranes. In order to gain some information of the relationship between pressure and resistance of films for their evaluation as battery separators, the following experiments were performed.

2.1. Methods of Pressure Application

Several ways of applying the compression are possible:

The film can be compressed between flat plates. These plates can be rigid metallic plates; they can be semi-hard, as for example Lucite or other plastic; or they can be soft, as for example sheets of rubber. Soft plates should more evenly distribute the pressure, and the results should not be so sensitive to unevenness as if the plates were rigid. The pressure can be conveniently applied by a hydraulic press.

Pressing between thick, flat Lucite plates was mainly attempted. The pressure was applied after the films had been soaked in 40% KOH for at least 24 hrs. The films were pressed without wiping off the excess of the solution. Since these films after compression were thinner, the actual wet thickness of these films was measured after the compression, and this value was used in computing the resistivity in ohm-cm. The films were tested as taken from the press without further soaking in the electrolyte.

For the tests reported, an overnight ball-milled blend of 10 g filler, 15 g polysulfone, and 100 ml dimethylacetamide (DMAC) was used. Films were produced with several Gardner blade settings of the applicator. Usually 12, 10, 8, 6 and 4 mils were attempted, although not always. The films were precipitated by immersion in water and thoroughly washed in frequently changed water for several hours. The films were dried and then soaked in 40% KOH for at least 24 hrs. The pressure indicated by the

pressure gauge on the press is pounds load on a 1-1/4" dia. ram. The size of the film pressed between the Lucite plates was very close to 2" x 4" and kept the same for all films. The first value readable on the pressure indicator, 200 lb, dropped the resistance by a factor of 10. The same film was compressed further with 5×10^3 lb and 10×10^3 lb. Since in some cases the films were damaged and torn at a load of 10×10^3 lb, it was decided that a load of 5×10^3 lb should be sufficient for further evaluation.

Pressing the films between two sheets of neoprene rubber was not too successful, since the films became crinkled and otherwise deformed if higher pressures were applied. However, they were not torn. The same effect on resistance was observed as when the films were pressed between Lucite plates.

2.2. Relation between Pressure and Thickness of Films

The relation between applied pressure and thickness of wet films is shown in Fig. 1. The filler used was 10 g Zeolon H. For each of the different blade settings the change in thickness at the higher pressures is not pronounced. The main compression occurs at lower pressures.

The relation between the thickness of the films and the applied pressure for the films containing 10 g or 20 g of zirconium oxide are shown in Figs. 2 and 3. It can be seen that films with low Gardner blade setting, say 4 mils, cannot be compressed as much as films prepared with larger blade settings. It can also be seen that the main compression occurred again at relatively low loads of 200 lb, whereas doubling the load from 5,000 lb to 10,000 lb had only a relatively minor influence on thickness.

2.3. Effect of Pressure on Resistivity of Films

The effect of pressure on the resistivity of films with 10 g Zeolon H filler is shown in Fig. 4. In all three films produced by different blade settings, it can be noticed that the resistance sharply drops from a

high value for the unpressed films to a fairly low value, even if only moderate pressures are applied. The resistivity from 200 lb to 10 x 10^3 lb stayed relatively constant.

In the case of zirconium oxide the behavior was somewhat different. The electrical resistivity of hydrated ZrO_2-loaded (10 g and 20 g) films is plotted in Fig. 5 and Fig. 6 as a function of applied pressure for various film thicknesses, as determined by the Gardner blade settings. It can be seen that the resistivity decreases with pressure, but this decrease is more gradual with 10 g filler. Quite an improvement can still be achieved in going from 5 x 10^3 to 10 x 10^3 lb load on the ram (Fig. 5). This gradual decrease in resistivity is less pronounced with the 20 g filler composition (Fig. 6), where the behavior resembles more nearly that of the Zeolon H, in that a large drop in resistivity does occur at low pressures. The resistivity was calculated taking into consideration the thickness of the wet films. With both amounts of filler, the thicker films showed a more uniform decrease in resistivity than the thinner one.

The pressure had another beneficial influence, namely the resistance measured on different locations on the film showed considerably less scatter, so that more uniform values are obtained on pressed films than on unpressed ones.

2.4. Permanency of Pressure Effect

In order to determine if the pressure effect on resistance is permanent, a pressed film was washed slightly and dried. The film was activated once more by soaking in KOH. Again, a low resistance was measured. This would indicate that films of permanently low resistance can be obtained by the application of sufficient pressure to the KOH soaked films.

2.5. Continuous Pressing of Films by Rollers

Another approach is to press the membrane between two roller bars, rigid or soft, or by compacting the film by gliding the roller under a given pressure over a flat plate on which the membrane is located. Pressing between rollers would lend itself best to large scale production of films having considerable size.

Experiments were performed which utilized precision metal rollers with an adjustable gap. Two methods were possible: to spring load one of the rollers so that the film would be compressed while passing through under a constant pressure or to roll the film to a predetermined gap size. The latter method was used for the experiment. The size of the gap was chosen as the thickness of the film resulting when the films were compressed between flat plates.

The films, either unsupported or supported on Webril mesh and containing zirconium oxide or Zeolon H as filler, were soaked in 40% KOH for two days and then squeezed through the rollers at a predetermined gap. In all cases it was noticed that, when a film was obtained which had the same thickness as measured when pressed between plates, the resistance of the films was also comparable. Only a limited number of tests were made.

The observation was made that when the whitish colored film was pressed through a roller many times, and the rollers were spring loaded, the film became more and more translucent, first in certain areas and then all over. This probably indicates that the white color of the films is created by entrapped gas, possibly air, which is being squeezed out and replaced by the electrolyte. The resistivity of the film was only slightly lower when the film was rolled several times.

2.6. Effect of Pressure on Films with Varying Amounts of Filler

Since each of the different candidate filler materials has not only a different composition and different density, but also different absorptive and ion exchange properties, different behavior can be expected

from film to film even when these are prepared with the same weight ratio of filler to binder. Not only will the actual volume per gram of the different materials be different, but also the purely physical properties such as particle size vary to such an extent that the results measured on one compound cannot be directly transferred to another. These are the main reasons why it was deemed necessary to repeat the same investigation with each possible filler candidate, or at least each class of filler. The behavior of Zeolon H and hydrous zirconium oxide is reported. Zirconium oxide is a most promising candidate for separator application because of its low solubility in KOH.

The procedure for preparing these films was the same as previously described. The filler was first dried at 110°C and the indicated amount was ball milled overnight with a solution of 15 g of polysulfone dissolved in 100 ml of dimethylacetamide (DMAC). The ball milling might produce much finer particles than originally used, but the relations between ball milling time and resistivity of the film will be reported later.

As the first filler tested, Zeolon H was used, because of its small particle size and true zeolitic nature. The amount of filler was varied and the obtained results are shown in Figs. 7 to 10 for 7.5, 10, 15 and 20 g of filler with 15 g binder. Each filler content was cast in several film thicknesses, and each film was subjected to measurement of the unpressed film and the pressed film at 200 lb and 5000 lb. The same table of symbols is used throughout the report.

With 7.5 g Zeolon to 15 g polysulfone (Fig. 7), the resistivity of the unpressed films stayed high, far out of the range for battery application. The spread of the points was also large, but, upon pressing, much lower values were obtained. However, only the thinnest one fell within the limit of 150 Ω cm. The thicker ones were outside this range.

Films with 10 g Zeolon to 15 g polysulfone had a lower value of resistivity. Whereas all of the unpressed ones fell outside 150 Ω cm, a load of 5000 lb produced films well in the acceptable range. The results obtained with this mixture and loads up to 10×10^3 lb are also indicates on the graph of Fig. 8.

Still lower values were obtained with 15 g Zeolon as shown on Fig. 9. The average value for a load of 5×10^3 lb is indicated by the arrow.

Films with 20 g filler had lower average resistances after pressing than any of the previous ones (Fig. 10). All the films with higher filler content have resistivity well below the limit for battery application and also the values taken at different locations showed much less scatter.

The dashed lines on these plots represent the average of the individual slopes of the lines passing through the origin and the mean value for each group of points of the same thickness at a given compression. These dashed lines would indicate the probable behavior of such films assuming a complete reproducible casting and extraction process and that a strict linear relationship exists between film thickness and resistance.

In order to evaluate the effect of filler, the average resistance-thickness value as described was established for each film composition and the resistance extrapolated to a film thickness of 5 mils. This value was now put into relation with the amount of filler introduced into each membrane. The result is shown in Fig. 11. It clearly indicates that with less and less filler the resistance sharply rises to very high values. On the other hand, with the increase of the filler, the resistivity seems to level off. From these values it can be seen that in order to stay in the prescribed limit of resistivity the ratio of filler to binder should be at least 2/3 or even higher for the Zeolon-polysulfone composition, on a weight basis.

The same procedure as with Zeolon H was repeated with hydrated zirconium oxide.

In Figs. 12-16 the film resistance is plotted as a function of film thickness for various filler contents. For the film without filler, average resistance values lie above the 150 ohm-cm limit (Fig. 12). The results of five measurements at each thickness are shown for 10 g, 15 g, 20 g, and 30 g of zirconium oxide. With 10 g filler the average value for a film compressed by 5×10^3 lb is above the value 150 Ω cm, as indicated by the dashed line in Fig. 13.

With 15 g zirconium oxide the average line is below the 150 Ω cm limit (Fig. 14). The same holds for the 20 and 30 g composition (Figs. 15-16). If now the resistivity of this average film at 5 mil thickness is plotted against the amount of filler present we obtain the curve shown in Fig. 17. It can again be seen that the resistivity changes rapidly with the amount of filler incorporated at low filler-loadings but becomes relatively insensitive to filler content at high loadings. The filler loadings above about 10 g ZrO_2 fall below the resistivity limit of 150 Ω cm. Thirty grams of ZrO_2 could be a suitable content for a separator which gives a filler-binder ratio of 2:1. The increase in filler of course weakens the film, but this is not of great importance if the membrane is supported (as, for example, on Webril mesh).

2.7. Effects of Pressure on Films Developed by Acetic Acid

The observation was made that if, during the film preparation, the solvent (DMAC) was extracted with acetic acid-water mixtures (rather than with water alone), the resistivity of the films was somewhat changed relative to those extracted with water. In order to substantiate this observation and to put it on a quantitative basis, films containing 10 g or 20 g of zirconium oxide were cast with a constant blade setting of 8 mils and the films were developed in acetic acid-water mixtures of different concentration. After coagulation of the binder, the films were soaked in water in order to extract the remainder of the solvent and acetic acid.

Fig. 18 indicates the result with 10 g of filler. Again it can be seen that the pressure had an effect on the resistance although not as pronounced as when the extraction of solvent was made with water. It also can be seen that there is a tendency for the resistance to increase if the extraction is made with more concentrated acetic acid. Of course, the scatter of the points is quite large so that no definite relation can be stated. Most of the films fall above the 150 Ω cm limit. This plot can be made, since the films developed with different acid concentration had all very close the same thickness as shown in Fig. 19.

A similar observation was made with films containing 20 g of zirconium oxide, Fig. 20. Again it was found that the pressure decreased the resistance but that, on the average, the resistance was higher in more concentrated acetic acid. This increase was not so pronounced as with the lower filler content. There seems to be no drastic change of film appearance when extracted with acetic acid mixture as compared with those extracted with water alone. It is possible, however, that pore size or pore size distribution is affected by the use of acetic acid. This possibility needs further investigation.

3. Control of Solvent Extraction by Solvent-Water Mixtures

When the solvent in the cast films is extracted with water, one obtains structures of a variable spongy nature, depending on the amount of solvent present. One would therefore expect the porosity of the binder to be affected by the solvent extraction process. Fast extraction could produce larger pores than slow extraction. During the extraction with acetic acid mixtures some influences of acetic acid concentration on the resistance of the obtained film was noted.

Another possible way to slow down the solvent extraction process would be to extract the cast film with mixtures of water and DMAC instead of pure water. A 50:50 (by volume) mixture of water and DMAC was therefore tried.

For these experiments, a mixture of 20 g MgO, 15 g of polysulfone and 100 ml DMAC was used after thorough ball milling for several hours. MgO was chosen because it should not possess any structural porosity of its own, so that the resulting porosity would be caused by the porosity of the binder alone. The Gardner blade was set to 8 mils for all the films reported. The films were cast on glass, and the solvent was extracted by immersion into the water-DMAC mixture for different lengths of time. Immersion times of 1, 10 and 1000 min were investigated. In all cases a film was precipitated; however, if these films were put on paper or hung up for drying they completely disintegrated. Another procedure was therefore adopted to stabilize the structure. After immersion in the water-DMAC mixture as specified they were further extracted by immersion in water. In this way the rest of the DMAC was extracted, and stable films were obtained. The resulting films were hung up vertically in clips and dried either slowly for several days in air or dried in a shorter length of time in an oven heated to 120°C.

The result of these experiments is summarized in Table 3-1. The resistance value is an average of 5 measurements at random places; so are also the thickness values.

The result indicated certain trends. Shorter extraction times in the water-DMAC mixture seem to result in films with lower resistance. The resistance of films given 1000 min extraction time was about 3 times that of films with extraction of 1 min duration. Another trend seems to be noticeable; namely the oven dried films have considerably larger resistance (up to a factor of 5) than air dried ones. Since the thickness of these films when soaked in KOH is the same, this finding could indicate that oven-dried films have fewer or much smaller pores. One would expect, of course, that the pores shrink in the heat treatment when oven-dried.

TABLE 3-1

Effects of Extraction by Water-DMAC Mixtures

Time of Extraction (min)	How Dried	Unpressed Wet Thickness (mils)	Unpressed Resistance (ohms)	Pressed* Wet Thickness (mils)	Pressed* Resistance (ohms)
1	air	3.7	1.78	3.5	.65
1	oven	3.8	over 100	3.6	1.60
10	air	3.6	22.4	35	1.08
10	oven	4.3	over 100	315	4.57
1000	air	3.6	53.9	2.8	1.82
1000	oven	3.2	71.0	2.8	8.96

*Pressed with 5000 lb load on ram.

4. Additional Factors Influencing Film Resistance

4.1. Effects of Different Fillers

For testing different filler membranes in the silver-zinc battery, especially as to dendritic penetration and overall performance, films were prepared containing titanium oxide, magnesium oxide, tin oxide and strontium stannate in a weight ratio of 20 g filler: 15 g polysulfone: 100 ml DMAC. The mixtures were ball milled overnight, spread on a glass plate with a blade setting of 6 mils, and developed by extraction of the solvent with water. The films soaked in 40% KOH were subjected to a pressure of 5000 lb on the 1-1/2 ram and the resistance measured 5 times at random spots. The measured values are indicated on Fig. 21. Only one blade setting was used (6 mils) which resulted in a set film thickness somewhat over 2 mils. It was observed that all these compounds developed quite uniform films, with resistance values all falling in the acceptable limit of battery separators when pressed.

Tin oxide, ball milled for only 20 min, gave a higher resistance than when ball milled for 16 hr. The same trend, but not so pronounced, was observed with strontium stannate. Titanium oxide gave a film of very low resistance, and also the film produced with magnesium oxide was rather low. An interesting fact is that the magnesium oxide film was relatively thicker than the other films produced at the same blade setting.

These results would indicate that any suitable finely powdered substance can be incorporated into these films. In appearance they resemble any other pigmented barrier of composite nature.

4.2. Effects of Ball Milling of Filler Suspension

There are two kinds of voids intrinsic to the structure of the film. First, there are those due to the filler material, because of its internal structure, as in the zeolites, or resulting from the large amount

of water of hydration in gel-forming filler substances. Second, there must be porosity in the binder, resulting in part from fast extraction of solvent and in part from places where the filler and binder don't completely fill the space. The porosity resulting from each of these contributions can have a different size and size distribution, so that the resistivity could be affected by any one of a number of parameters.

One question to be answered by experiment was the effect on resistivity of ball milling, since it can be assumed that ball milling affects the particle size of the filler.

To test this influence, hydrated zirconium oxide of 200 mesh (Biorad) was used. The mixture consisted of 20 g zirconium oxide, 15 g polysulfone and 100 ml DMAC. Films of different blade setting (6, 8, 10, 12 mil) were cast on glass and water extracted. These films were made after the mixture was ball milled for 20, 60 and 1000 minutes. The resulting films were washed in water overnight and dried. For resistivity measurements, the films were soaked in 40% KOH for 24 hr. and the resistivity determined both as-obtained and after being pressed between Lucite plates at a load of 5×10^3 lb on the ram. Five determinations were taken, and the average resistance determined. From these averages, the 5 mil extrapolated resistance was obtained. An average film behavior was constructed as indicated by the dashed lines in Figs. 22, 23 and 24.

The extrapolated value for 5 mil thickness on the average film behavior was correlated against ball milling time. Fig. 25 shows that longer ball milling gave a slightly lower resistance, but this difference is not large enough to be considered. One can conclude that the ball milling time, resulting probably in different particle size, does not have too large an influence on resistance, an influence one would expect. The fact that prolonged ball milling produces very uniform films is sufficient justification for this practice.

One could argue that, with larger particles, more electrolyte could be retained in the volume of the structure. Also, since small particles expose a much larger surface, which could be sealed by the binder, one would expect the porosity to diminish with decreasing particle size. That this is not observed suggests that it is the high porosity of the binder that contributes substantially to the porosity of the entire structure.

4.3. Air-Dried vs. Water-Extracted Films

Water extraction of the solvent gives films which are quite uniform in appearance and relatively low in resistance when soaked with the electrolyte. The effect of compression of the films results not only in a thickness decrease, but also in a considerable decrease in electrolytic resistance. It was of interest to determine whether films prepared by oven drying and possessing considerable amounts of filler would also show this effect. Films were made from a composition of 30 g Zeolon, 15 g polysulfone and 100 ml DMAC, ball milled overnight. The blade settings in mils were 4, 6 and 8. The films were oven-dried at 120°C for at least 16 hr, and the resistivity was determined after soaking in KOH.

It was observed that dry films of this type are very brittle, cracking with the slightest bend, and therefore are hard to handle. After soaking in the electrolyte they were more pliable, but still could not be bent sharply. These films do have a rather low resistance. The resistances taken at different places were all very similar. There was practically no change in resistance after pressing between Lucite plates at a pressure of 5×10^3 lb on the ram. See Fig. 26. The resistance changes as to location on the film and compression are so small, that they are not visible on the graph.

This finding indicates that such films, if they could be made more flexible or supported on Webril, might offer an additional technique alternative to coagulation by water. In appearance these new films are quite

superior to the first films prepared by oven drying as reported in some of our early reports. However, further experiments gave the following results.

A quantity of polysulfone/DMAC/Zeolon (weight ratio 15/100/40) was ball milled 16 hr. A constant blade setting of 6 mil was chosen. The variables were: (1) whether air-dried before curing, (2) initial oven temperature, and (3) oven time till final temperature. Although a great many films were prepared, most of them contained voids and were powdery and very brittle. The shrinkage of the polymer in curing seems to create a dual problem of getting void-free films and removal of the cured film from the casting surface. The few void-free films obtained have not been further evaluated because of their extreme brittle character. It is doubtful if this technique would warrant further investigation.

4.4. Incorporation of Charcoal

A limited number of films were cast which contained 5 g of charcoal in 15 g of binder. These were made in different thicknesses as indicated in Fig. 27. The resistance was quite high before pressure was applied but decreased with increased pressure. The film had a blue-black appearance and was relatively brittle in handling. After compression to 5×10^3 lb all of the films fell below the 150 Ω cm limit. The thin films are very hard to handle without damage, and would therefore be impractical for battery application.

5. Continuous Coating of Films on "Webril" Support

Until the necessary strength needed for the films used as separators is achieved, it would seem necessary to support the film by a polypropylene web. If such a support is coated on the glass support by an applicator, only one side is actually covered since the Webril rests on the glass. Also, during coagulation of the filler-binder mixture, only one side contacts the water and therefore this side seems to have different properties from the other. This can also be seen on microscopic cross section examinations. In order to coat the 1.5 mil Webril on both sides the equipment shown in Fig. 28 and in the schematic sketch in Fig. 29 was used. In the arrangement first tried the Webril was drawn between two glass tubes with only a narrow gap between. The glass tubes were later replaced by steel shimstock knife blades as shown in Fig. 29. These blades seem to give a more uniform coating. For the 1.5 mil Webril the blade opening was about 3 mils. The resulting thickness of film was about 2.5 mils when developed and dried. In order for the Webril film to be centered between the blades it was rolled over 1/2 in. diameter Teflon guide rods in the form of a roller, the lower one being immersed in a tank of water. The finished product could be put on a take-up roll after passing through the wash water. This take-up roll was slowly driven by a motor. The pay-off roll, on which the Webril was wound, had a friction brake so that the Webril was always stretched. The speed of travel was about 1 ft/min. The coated Webril was later soaked in water for 16 hrs to extract all of the solvent and dried in air. The coating mixture was supplied to both sides of the film from a funnel. Ball-milled mixtures containing 10, 12, 15, 20, 30, 40, 50, 60 and 70 g of Zr oxide in 15 g polysulfone and 100 ml DMAC were tried. The solutions containing 10, 12 and 15 g of filler showed poor wetting of the Webril support and, as a result, produced coatings of uneven thickness. Coating mixtures which contained 50 g hydrated zirconium oxide gave the best results in terms of the continuous coating technique. Films which contained more than 50 g of zirconium oxide tended to have powdery surfaces. Films prepared by the technique just described are being tested further in terms of the parameters necessary for battery separator application.

6. Membrane Sterilization Tests

Sample membranes were exposed for 60 hours in 40% KOH at 135°C in sealed Teflon cells holding about 40 ml of electrolyte, but also containing about 2 g of filler in a Webril package held together with platinum wires. The electrolyte was first saturated with the filler, by heating for 16 hr at 135°C without the membrane, and then heated under the same conditions for 60 hr with the membrane. Films containing Zr hydroxide, Zeolon H, Linde sieves and titanium oxide were used. One series of membranes containing Zr hydroxide was also exposed to sterilizing conditions with the cell containing 2 g of Ag_2O in addition to the 2 g of $Zr(OH)_4$. The result of these measurements is summarized in Table 6-1, where the results are compared to exposure of the same films in hot KOH not containing any of the excess amount of filler.

In the case of zirconium hydroxide and titanium oxide, the loss of filler is greatly reduced with the presaturated electrolyte. Zirconium oxide showed only a minor loss of 3.5% total weight of the film, whereas titanium oxide had a gain of over 6% increase in weight.

For Zeolon and for Linde sieves, the loss in weight even with excess dissolved filler was still quite large, probably too large to be acceptable for separator use. The difference between cycling in a straight and filler-containing electrolyte was the greatest in Linde 3A, about ten percent.

In cases where silver oxide was also present, there was a weight variation between the different samples, which appears to be from uneven deposition of metallic silver on the membrane. Some films had only dark spots, whereas others had a metallic appearance all over. The amount of silver deposited on these films varied from +4% determined analytically as Ag to as high as +22%, taking into account the original weight of the sample. The deposited silver did not change the mechanical properties of the films. The membrane thickness was not measurably affected, the physical strength seemed not to be altered, and the flexibility was not impaired.

The membranes could be folded and unrolled around a sharp edge in the same way as the untreated films. This indicates that the presence of silver oxide does not destroy the films. Moreover, since the battery will be sterilized apparently in the discharged state, with only metallic silver present, no severe deterioration of the membrane is expected.

From these data we have concluded that hydrated zirconium oxide and titanium hydroxide appear to be the most resistant to extraction of the filler under sterilizing conditions. The Zeolon and Linde sieves show considerable solubility even with the filler-containing solutions.

TABLE 6-1

Results of Sterilization Cycle Tests on Composite Membranes*

Test No.	Filler Loading (g filler/ 15 g polysulfone)	Cycled without excess filler	Cycled with 2 g excess filler	Wgt. % change
1	5 $Zr(OH)_4$	2 cycles	--	-25.6
2	15 $Zr(OH)_4$	--	1 cycle	-3.5
3	5 $Zr(OH)_4$	--	1 cycle + 2 g Ag_2O	+27.4 (+ 22% Ag)
4	10 $Zr(OH)_4$	--	1 cycle + 2 g Ag_2O	+0.4 (+ 4% Ag)
5	20 $Zr(OH)_4$	--	1 cycle + 2 g Ag_2O	-2.2 (+ 4% Ag)
6	5 Zeolon H	1 cycle	--	-25
7	5 Zeolon H	--	1 cycle 1 cycle 1 cycle	-19.4 -19.5 -18.6
8	5 Linde 10 X	1 cycle 2 cycles	-- --	-24.9 -27.4

(Continued)

TABLE 6-1 (Continued)

Test No.	Filler Loading (g filler/ 15 g polysulfone)	Cycled without excess filler	Cycled with 2 g excess filler	Wgt. % change
9	5 Linde 10 X	--	1 cycle	-13.8
			1 cycle	-13.8
			1 cycle	-13.8
10	5 Linde 3 A	1 cycle	--	-23.2
		Fired % remaining 0.4%		-22.8
		0.5%		-22.5
11	5 Linde 3 A	--	1 cycle	-19.2
			1 cycle	-18.7
			1 cycle	-18.8
12	5 Linde 13 X	1 cycle	--	-25.6
		Fired % remaining 0.1%		-26.0
		1.2%		-24.2
13	5 Linde 13 X	--	1 cycle	-19.1
			1 cycle	-18.4
			1 cycle	-17.0
14	5 Titanium oxide	1 cycle	--	-21.6
15	5 Titanium oxide	--	1 cycle	+ 6.1
			1 cycle	+ 6.1
			1 cycle	+ 6.8

*Each cycle 60 hr at 135°C in 40% KOH.

7. Characterization of Membranes

7.1. Tensile Strength of Films

Selected unsupported films and also coated Webril membranes were tested for tensile strength. Tables 7-1, 7-2, and 7-3 report these data. There is a decrease in both tensile strength and elongation in all samples after one exposure period in 40% KOH containing excess $Zr(OH)_4$ and Ag_2O. The exposure was 60 hours at 135°C.

There does not appear to be any great changes in strength in the unsupported film whether tested wet (water) or dry.

7.2. Microscopic Observation of Membranes

It was desired to obtain some insight into the structure of these heterogeneous films which seem to acquire a spongy-like structure by water extraction of the solvent. Membranes were cut by a microtome, and the cross section was examined under the microscope. Photomicrographs are shown in Figs. 30 and 31. These indicate that the side of the film next to the glass plate is more uniform than the edge exposed to the water. Detailed interpretation of the photographs is not easy because some waviness might be introduced by the cutting process. Since the white spots are present also in unfilled membranes, of which Fig. 31 is typical, they cannot represent the distribution of the filler. Further information could be gained by observation of thin sections in transmitted light. For this reason microtome slices 7 μ thick were made from unsupported cast film with and without filler (Zr oxide). Figs. 32 and 33 show the film at two different magnifications, 100 X and 500 X.

The open areas in film shown are holes, which could be present in the film but could also be formed during the mounting and cutting process. The difference between the two pictures is not too pronounced, so that it is almost impossible to express any opinion as to the particle size of the

zirconium oxide. If the films have large voids, then it would be these openings which would collapse during pressure on the film, thus rendering the film more conductive. More information would be needed to interpret the pictures.

7.3. Silver Diffusion Tests

7.3.1 Polarographic Silver Determination

In a previous report it was noted that the polarographic determination of silver with a rotating platinum disc electrode did not give reproducible results. The polarograms obtained in this way varied considerably from run to run. Despite many attempts, this approach to silver concentration determination was abandoned.

However, the determination of diffusion coefficients of silver through membranes by polarographic means has some advantages over other methods, in that the diffusion current is strictly proportional to concentration. The same instrument as described in previous reports for the zinc determination could be used.

There are some few indications in the literature that silver can be determined polarographically using a dropping mercury electrode and DC polarography, although some difficulties can be expected. This approach to silver concentration determination was therefore further investigated. Polarography in concentrated KOH (40%) is virtually unknown, since for most polarography 0.1 M, or at most 1.0 M, solutions are used. The high concentration of KOH causes an increase in the background current.

A Sargent DC polarograph was used for this study. The dropping time of the mercury was 4 sec. The potential was applied against a large external Hg, HgO electrode, with the same concentration of KOH as in the main solution. Oxygen was expelled from the solution by prolonged bubbling of purified nitrogen through the supporting electrolyte. Polyethylene bottles were used throughout the experiment. A sensitivity of 0.01 was chosen and

maximum damping was employed. The sensitivity is expressed in μA/mm chart length. In this way individual drop oscillations reflected in the current intensity were smoothed out.

Monovalent silver dissolves in KOH to some extent. The complex formed is not known, but a dihydroxy or trihydroxy complex [for example, $(Ag(OH)_2)^-$] might be present. In some previous work on silver determination, it has been noticed that the silver does not produce a normal polarographic wave, which would have its start from the background current of the supporting electrolyte. Actually, already at zero potential, the current starts below the zero line of the background current. This behavior has been attributed to the strong amalgamation tendency of silver and mercury. It was therefore of some interest to investigate the behavior in 40% KOH.

Curve (a) in Fig. 34 represents the background current. Because of a large tank circuit in the (RC) line, the individual oscillations are smoothed out. Curve (b) represents the same 40% KOH to which a drop of silver nitrate was added. After shaking for some time the filtered clear solution was used. The diffusion current is represented by i_d sat. when the solution was saturated with silver salt. Curves (c) and (d) were obtained by properly diluting the saturated solution with 40% KOH. Because the obtained curves are parallel in nature, they can be used for evaluation of the diffusion current by simply subtracting the background current, as indicated by the arrows on the graph. The point on the voltage scale where the evaluation is made is not critical because the diffusion current has a prolonged plateau.

Fig. 35 was obtained by plotting the diffusion current against the different concentrations obtained by dilution of the saturated solution. The result is a straight line going through the origin, indicating that this method of obtaining diffusion current values is acceptable. This linear relation between silver ions in solution and measured diffusion current can therefore be used for determination of silver diffusion through

membranes. The same instruments as described for the zinc diffusion were used with only minor changes. Because considerable improvement in the homogeneity of films has been achieved, it was decided to enlarge the diffusion area (A) from about 0.33 cm^2 to exactly 1.00 cm^2 by precision milling. This speeds up the determination considerably. Also the volume of liquid was reduced to 50 ml for the same reason. Another precaution was taken. During prolonged runs, mercury from the dropping electrode normally falls into the main diffusion compartment and accumulates. Since silver is reduced on the mercury surface close to zero potential, it is possible for spontaneous amalgamation of the silver ions to occur. The vessel was so arranged that the mercury was collected on the bottom of the polarographic cell and from there flowed into a separate compartment. In this way the collected mercury was only in slight contact with the electrolyte both in terms of surface and time. This precaution was taken despite the lack of any indication that plating out of silver on mercury actually did occur.

As the silver ion supply, a saturated solution of silver oxide was used, freshly prepared by adding a drop of concentrated silver nitrate to the 40% KOH. Although the solution was not clear because of suspended silver oxide, it is believed that this arrangement will not influence the diffusion of the silver ion through the membrane. One can therefore assume the concentration on the silver side as constant, namely that of saturation at solubility of the silver oxide in 40% KOH at the given temperature. Fig. 36 shows some preliminary results with a cellophane membrane. The supporting solution was freed of oxygen by flushing with purified nitrogen and the polarogram taken. After an interval of two hours, part of solution was sucked into the polarographic vessel and the polarogram run under identical conditions. This was repeated twice more after intervals of an hour each. Also the final solution concentration the system should reach was taken. Not enough data were obtained for a full evaluation but the method seems to be promising. Upon disassembling, it was noticed that the membrane had a dark appearance. Whether this would change diffusion of the

silver ion during the diffusion process cannot be stated. The silver should approach the limiting value asymptotically. Fig. 37 represents the relation between diffusion time and silver concentration in arbitrary units.

7.3.2 Silver Diffusion through Composite Membranes

Silver diffusion through composite membranes (20 g filler, 15 g polysulfone in 100 ml DMAC) was investigated with Zeolon H and hydrated zirconium oxide as fillers. The films were water-coagulated and pressed under 5×10^3 lb pressure. The membranes were soaked in KOH for 12 hours before use.

The rate of silver diffusion through the membranes was much smaller than observed with cellophane, by a considerable factor. The experiment had to run overnight (about 16 hr) in order to see any marked influence of silver on the diffusion current. Even so, the diffusion current was only 2.2% of the diffusion current obtained with a silver-oxide-saturated solution. If we take the solubility of silver oxide in 40% KOH at room temperature as being close to 40 mg Ag/l, we can easily calculate, since only 50 ml of electrolyte was used, that 0.044 mg of silver penetrated the 1 cm^2 membrane in 16 hr. This gives a diffusion rate of only 2.8×10^{-6} g Ag/cm^2 hr. This value represents a rather small amount of silver to be transported. Both membranes gave such small values.

7.4. Pore Size and Pore Size Distribution Measurements by Dye Diffusion

One unsolved problem of composite films is the porosity of the structure. There seems to be no simple direct method for pore size distribution measurements. Even the methods for average pore size determination are based on simplifying assumptions which might not be

realized in practical separators. The water or electrolyte permeability method as described by Cooke and Lander* and by Salkind and Kelley* have equations from which the average pore size can be ascertained.

For battery application the pore size distribution seems to be of importance. A method which probably could be developed is pore size determination by dye diffusion. Since dyes are available in a variety of molecular weights and the concentration can be easily measured by colorimetry, the diffusion of a given dye through a membrane should be a measure of pore size and distribution. Of course, dyes which do not increase in size either by polymerization or hydration should be selected. Hemoglobin, for example, has a diameter about 30 Å and is spherical in nature. If none penetrates, one can ascertain that the pore size is below this value. The transmission of different dye molecules could be a measure of size distribution if properly evaluated.

A dye diffusion experiment was carried out using a zirconium oxide filled membrane as the test membrane. Several dyes were used and their concentrations measured by a spectrophotometer, using the most absorptive wavelength for the particular species. For diffusion, the same vessels were used as for the study of diffusion of Zn and Ag, with stirring.

An intensely colored solution containing several milligrams of dye in 50 ml solution was placed on one side, the other side containing water. It was observed that dye penetration is relatively slow but that the concentration increases with time (taking several hours for detectable amounts to diffuse. Different dyes seem to behave differently (e.g. Ponceau R, Methylene Blue, Wool Violet). Further use of the method requires calibration on films of known porosity. However, these results do indicate that the membranes that were tested in this manner do not have extremely large pore sizes.

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*J. E. Cooper and A. Fleischer, editors. (Air Force Aero Propulsion Labs., 1965). page 31 and 43.

7.5. Testing Silver Zinc Cells with Composite Separators

Many tests can be devised which can aid in evaluating the suitability of a separator for use in a silver-zinc battery. These include electrical resistivity when soaked in the electrolyte, the rate of diffusion of silver and zinc complexes through the separator, the diffusion of the OH^- ions or the dendrite growth through separators. No such tests, however, can be a substitute for a direct evaluation of battery behavior. Most such tests are made in specially constructed cells which deviate appreciably from the conditions actually prevailing in the silver zinc cell. It is debateable to what extent results of this type can be correlated with practical battery behavior. It was therefore decided to make actual tests with some of the separators we have developed, utilizing simple two plate batteries.

The zinc-silver cell is assembled in the discharged stage. The zinc electrode used is unusual in that it consists of a thin metal foil, made out of Cu or Ag, usually perforated, which is surrounded by a layer of slightly pressed zinc oxide powder. In order to keep this powder in place, the electrode is wrapped (for example) in a thin sheet of non-woven polyethylene mat. The silver electrode is separated by the main separator. As electrolyte, 40% KOH is used, saturated or only partly saturated with zinc oxide.

In the charging process it is believed that the zinc is plated from the zincate complex present in the electrolyte, but the direct reduction of the zinc oxide in contact with the electrode cannot be excluded. Since zinc oxide is present close to the zinc electrode, the zinc does not have to diffuse through the membrane boundary to replenish the plate and the tendency to develop dendrites could therefore be greatly diminished. This might be the reason why batteries on shallow discharges can be cycled a considerably larger number of times than batteries under deep discharge.

In the actual construction as shown in Fig. 38, a single membrane was stretched and pressed between two rubber gaskets confining the zinc and

silver electrode compartments. The end plate was made out of Lucite and the thickness of the gasket were so chosen that the cell was under slight compression. Both sides were vented and filled with 40% KOH saturated with zinc oxide. Since both electrodes were almost the size of the compartment one can assume that the cells were operating under no excess of electrolyte. The silver electrodes were cut from commercial silver zinc batteries.

The cells were identical except for different separators, as listed below.

1. Consisted of a film 3.6 mil thick having 117 Ω cm resistance, composition was 20 g $Zr(OH)_4$, 15 g polysulfone.
2. Had a film 4.6 mil thick, 89 Ω cm. Composition, 20 g Zeolon H, 15 g polysulfone.
3. Had a PUDO 193 cellophane separator.

The amount of silver used in the electrodes represents about 0.8 A-hr theoretical, based on sintered silver without grid. The battery was charged at the 10 hr rate to 150% theoretical capacity and then discharged through a 10 Ω resistance until about 0.8 V, representing the sharp decline in potential. The whole discharge curve was monitored on a recording potentiometer and the number of ampere hours recovered was determined by graphical integration of the charts. This process was repeated 5 times for each film. The result is shown in Fig. 38. The ratio between actual output and theoretical capacity expressed in % will be designated as efficiency of the cell (Ef).

With ziconium hydroxide as filler the efficiency was high, 95%, but decreased during successive charge until after 5 cycles it was only 25%.

For Zeolon H the efficiency started much lower, around 60%, and decreased only to about 35%.

The cellophane had an efficiency of close to 100% and stayed high during several charges.

After 5 deep discharge cycles the battery was taken apart and the membrane inspected visually and under the microscope. The findings were as given in the following paragraphs.

7.5.1 Zirconium Hydroxide

The film was heavily colored on the side which pressed against the silver electrode. Some parts were a much darker brown, especially at the top of the cell. The bottom of the cell was lightly colored. A sharp demarcation line was observed between cell and gasket. The other side facing the zinc was a much lighter color and quite spotty in places. A microscopic investigation revealed that at a very few places near the bottom of the cell, zinc dendrites had penetrated through the membrane from the zinc side to the silver side forming a minute mossy structure. The film, when washed and dried, showed no electronic conductivity between electrodes pressed against both sides, although a resistance of 10 megohm would have been registered. That the coloration was due to deposited silver or silver oxide was shown by putting a drop of diluted nitric acid on the film. The dark coloration disappeared.

7.5.2 Zeolon H

This was similar in appearance to the zirconium hydroxide-filler membrane. The zinc side seemed to be a shade less colored and only a tiny dendritic penetration of zinc was observed. The film was straight and seemed not to have suffered any mechanical damage.

7.5.3 Cellophane

The film was very heavily colored on both sides, probably due to the transparency of the cellophane. The film was crinkled and upon drying started to disintegrate, having no mechanical strength.

7.5.4 Tin Compounds

Additional films made from stannic oxide and barium stannate were discouraging. The efficiency on the first cycle was low below 50%, dropped during the second cycle, and was negligible on the third cycle. Dismounting the cell revealed that no zinc penetration occurred but the films were heavily colored, with a brown powdery substance on the films on both sides. This substance could be wiped off. It could be the cause of the failure.

Since only a very limited number of trials was performed and since such experiments should be evaluated statistically on a larger number of cells, no general conclusions can be drawn. The experiments do seem to indicate, however, that composite films of the type described are able to function as battery separators although not yet approaching the behavior of the best cellophanic type. The composite films, of course, have the advantage that they are greatly superior in stability. It is possible that much better cycling performance would have been obtained with multiple layers of thin separator membranes, since dendrite penetration appeared to be limited to a very few spots.

TABLE 7-1

Membrane Tensile Strength

Cast Unsupported Polymer Film

10 g $Zr(OH)_4$/15 g Polysulfone/100 ml DMAC (40% filler)

Film Thickness 2.1-2.2 mils

Wet strength PSI		Dry strength PSI	
550		405	
527		317	
529		399	
441	Average 511 PSI	413	Average 397 PSI
504	Av. Elongation 12%	453	Av. Elongation 6%

Film Thickness 4.2-4.5 mils

Wet strength PSI		Dry strength PSI	
433		446	
462		441	
470		513	
443		464	
462	Average 454 PSI	436	Average 460 PSI
	Av. Elongation 16%		Av. Elongation 11%

TABLE 7-2

Membrane Tensile Strength

Unsupported Film, 26% by wgt. $Zr(OH)_4$ in Polysulfone

Film Thickness 3.0 mil

As cast strength PSI		Cycled strength PSI	
482		417	
468		433	
513		333	
474		414	
538	Average 502 PSI	432	Average 406 PSI
537	Av. Elongation 10%		Av. Elongation 3%

19% loss in tensile strength, one cycle

70% loss in elongation, one cycle

Coated 3 mil Webril Polypropylene, 26% by wgt. $Zr(OH)_4$ in Polysulfone

Coated Thickness 4.9-5.2 mil

As coated strength PSI		Cycled strength PSI	
6080		3490	
5830		4450	
5810		4290	
5600		4200	
6550		4770	
5580	Average 5908 PSI	3950	Average 4192 PSI
	Av. Elongation 34%		Av. Elongation 26%

29% loss in tensile strength, one cycle

24% loss in elongation, one cycle

TABLE 7-3

Membrane Tensile Strength

As Cast vs. Cycled Condition

Coated 3 mil Webril Polypropylene, 6% $Zr(OH)_4$ by wgt. in Polysulfone

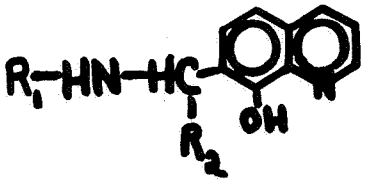
As coated strength PSI	Cycled strength PSI
5340	3450
4590	4160
6850	4170
4750	4190
6790	4010
6440	3380
Average 5793 PSI	Average 3893 PSI
Av. Elongation 38%	Av. Elongation 25%

33% loss in tensile strength, one cycle

34% loss in elongation, one cycle

8. Resins Containing Bonded Chelating Groups

Battery separator membranes have been prepared containing, as fillers, epoxy resin particles derived from the 8-hydroxyquinoline derivatives I. Ten of these cured epoxy resins, derived from I, Epon 826, and m-phenylenediamine according to procedures described in the earlier quarterly reports, have been incorporated into polysulfone films in a



I

manner similar to the preparation of the films with inorganic filler. Specifically each gram of cured resin was combined with 3 g polysulfone resin and 20 ml dimethylacetamide. The mixture was ball milled for 16 hr with a porcelain 000 mill. The film was cast on glass using a Gardner applicator to establish the wet thickness at 7 mils. The film was then extracted with water and air dried at room temperature in the usual fashion. The air-dried films were 3.0 to 4.6 mils in thickness. They have physical characteristics similar to those containing inorganic fillers.

We have measured the electrical resistivities of the films containing chelating epoxy resin fillers, using the same techniques developed for the films made from inorganic fillers. The present membranes showed the same sensitivity to applied pressure found in our previous work with inorganic fillers. In Fig. 39 is a plot, for a typical film, of electrical resistivity

vs. applied pressure.* The initially formed film has quite a high resistivity value but this falls rapidly with applied pressure and falls below the 150 ohm-cm limit at the higher pressures. The other epoxy resins give membranes which behave similarly. In general, the resistivity values obtained for a particular applied pressure seem to be insensitive to the nature of R_1 and R_2 in formula I. Table 8-1 lists the resistivity data for each of the films studied.

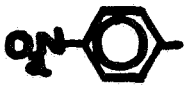
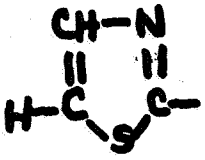
Fig. 40 shows the variation of film thickness with applied pressure for the same film referred to in Fig. 39. The changes in thickness are relatively small and are insufficient to account for the large changes in resistivity.

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*As before, the pressure was applied and then released before the resistivity measurement was made.

TABLE 8-1

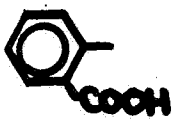
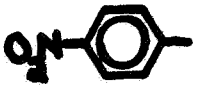
Electrical Resistivities of Polysulfone Films Containing Chelating Epoxy Resins as Fillers

R_1	R_2	Applied Pressure (lbs/in^2)	Average* Resistivity (ohm-cm)
		0	high
		200	281
		5000	2.9
		0	801
		200	63.1
		5000	55.7
		0	1157
		200	179
		5000	147
		10000	140
		0	528
		200	47.0
		5000	40.7
		0	1102
		200	34.6
		5000	33.5
		0	high
		200	92.6
		5000	95.9

*Average of five values

(Continued)

TABLE 8-1 (Continued)

R_1	R_2	Applied Pressure (lbs/in^2)	Average* Resistivity (ohm-cm)
		0	1570
		200	54.5
		5000	49.3
		0	high
		200	38.2
		0	high
		200	68.6
		5000	54.7
		0	high
		200	43.9
		5000	38.9
		0	510
		200	43.8
		5000	32.3

*Average of five values

9. Summary and Conclusions

The work on inorganic-filled composite separators so far shows considerable promise for the development of satisfactory heat-sterilizable separators for silver-zinc batteries. The most satisfactory separator of this type appears to be a polypropylene-reinforced, water-extracted, compressed film of polysulfone with hydrated zirconium oxide or titanium oxide filler material at a loading of about 30 g filler per 15 g polysulfone. This structure and composition of membrane appears at this time to be suitable not only as to required properties but also for development of fabrication procedures of large areas of uniform material. Further work is needed to confirm this expectation. Especially needed is preparation of larger quantities for complete evaluation of product properties resulting from larger scale production and the process variables affecting them.

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Curve 581036-A

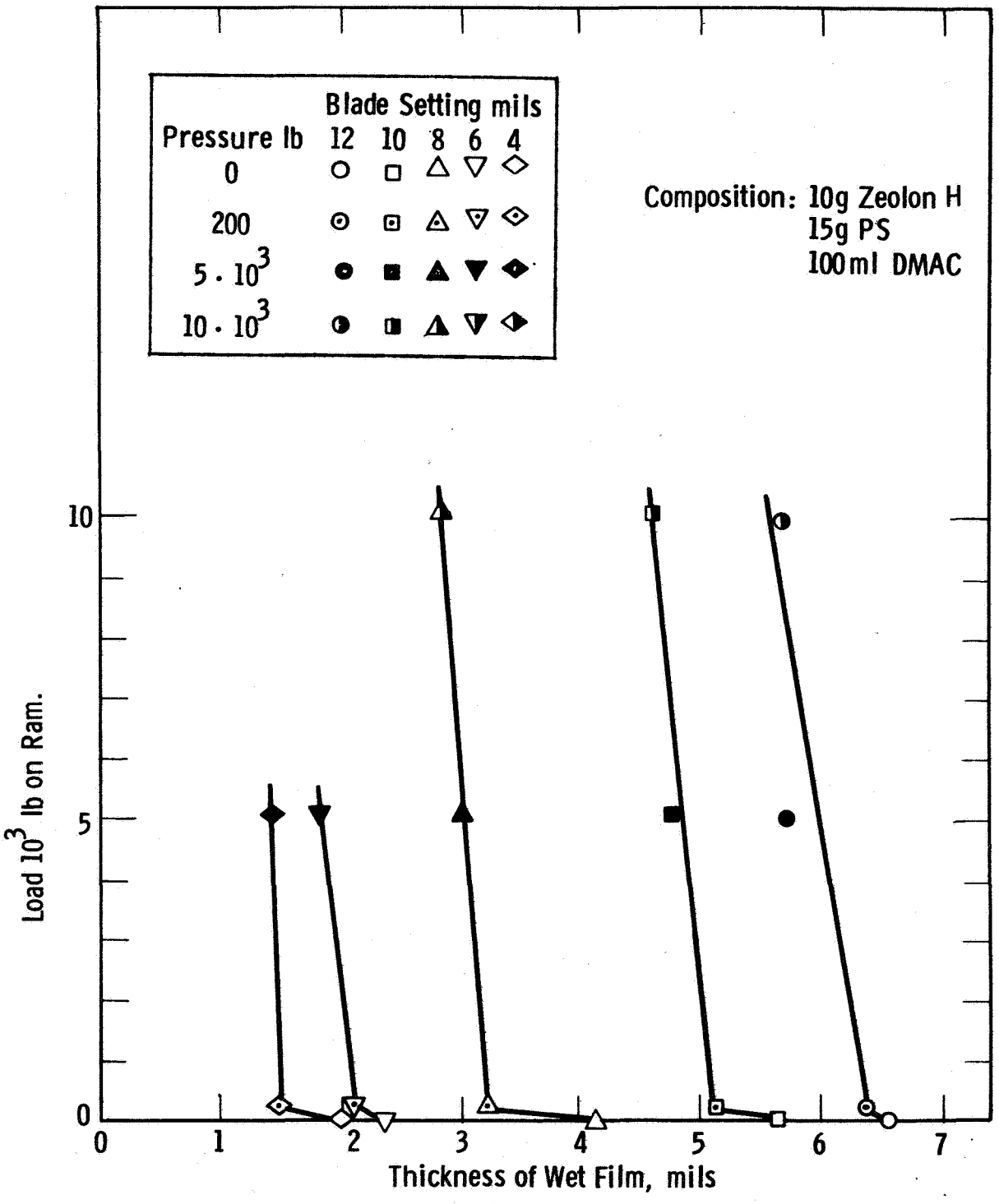


Fig. 1—Relation between applied pressure and thickness of wet films

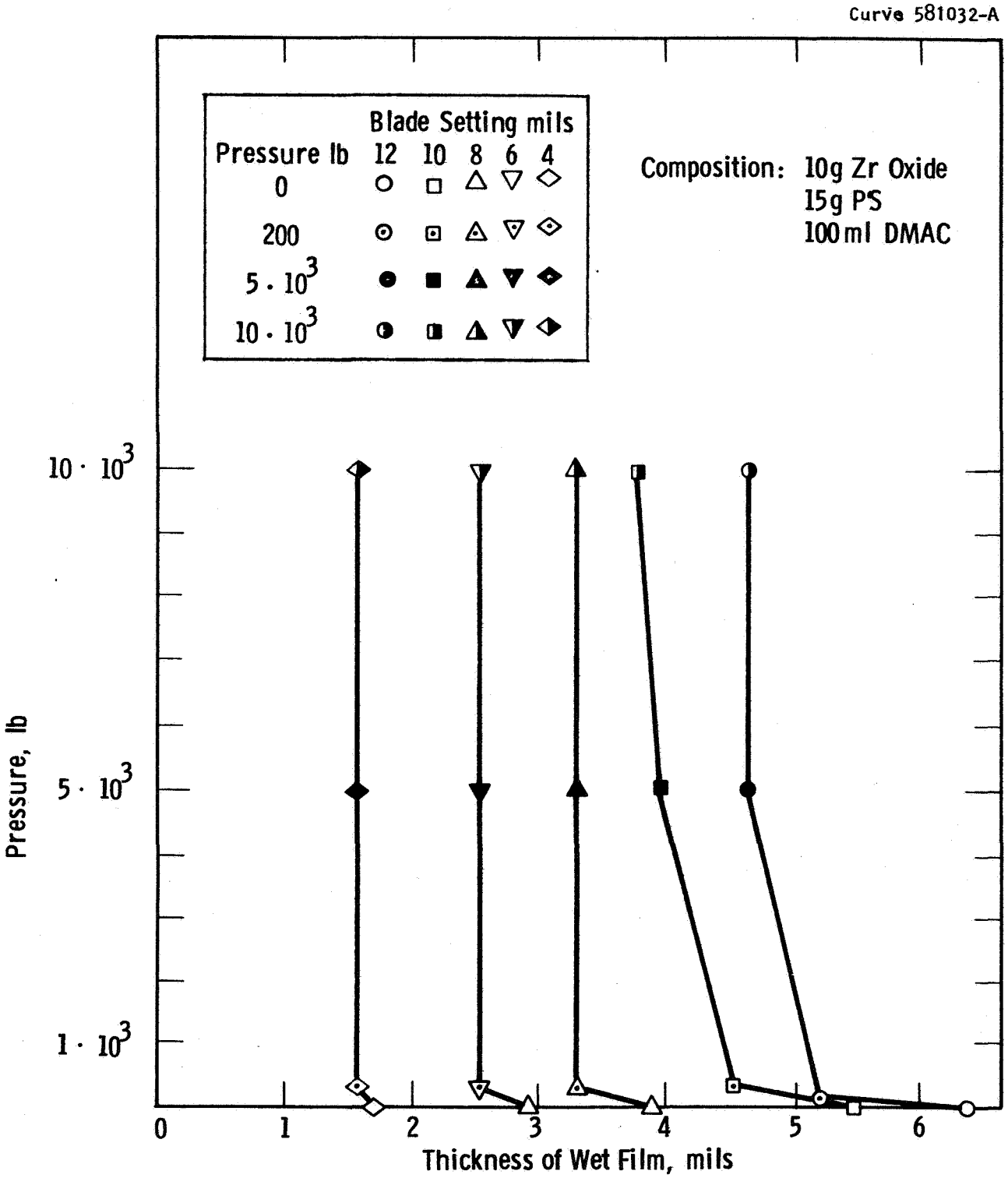


Fig. 2—Relation between applied pressure andthickness of wet films

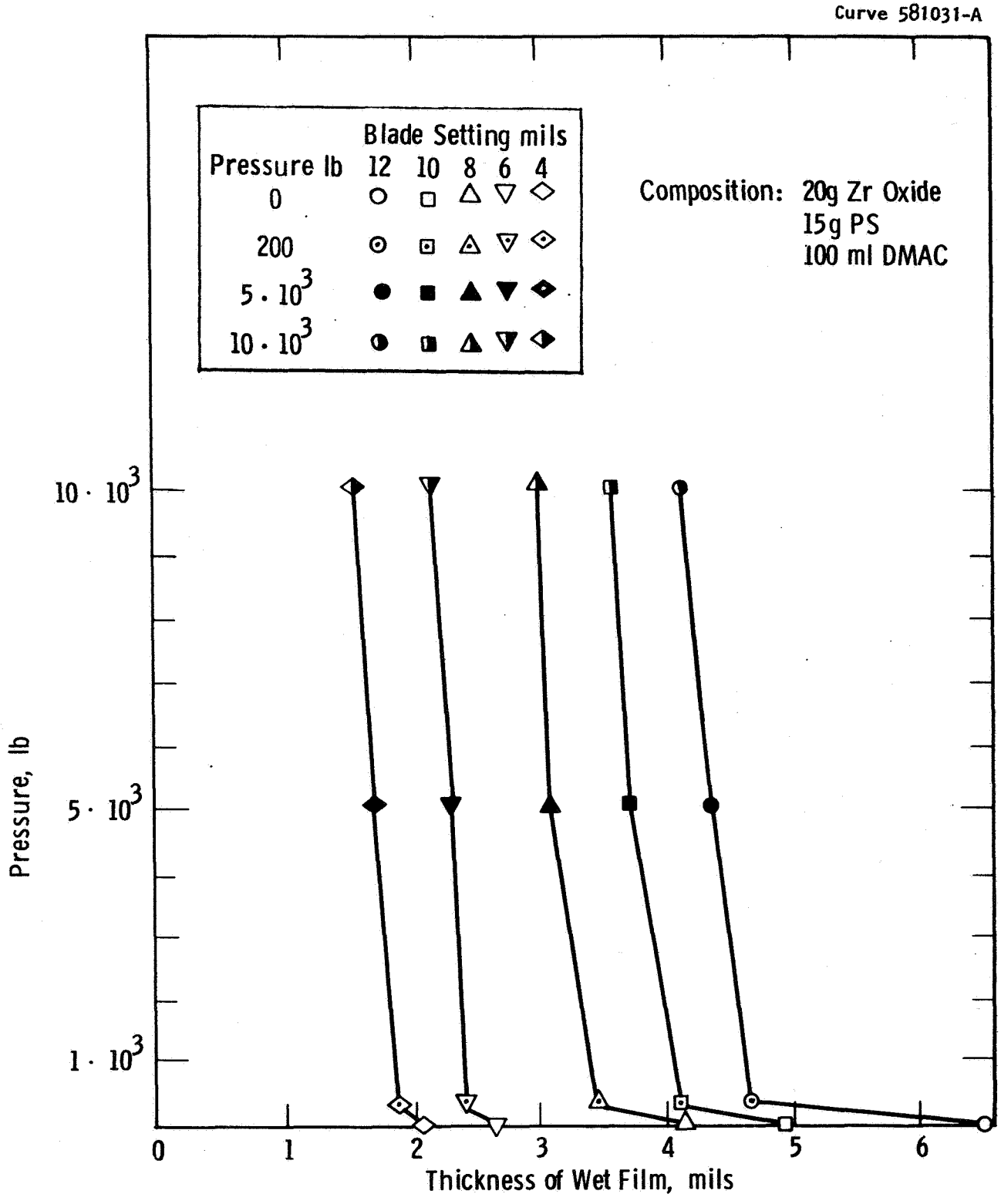


Fig. 3—Relation between applied pressure and thickness of wet films

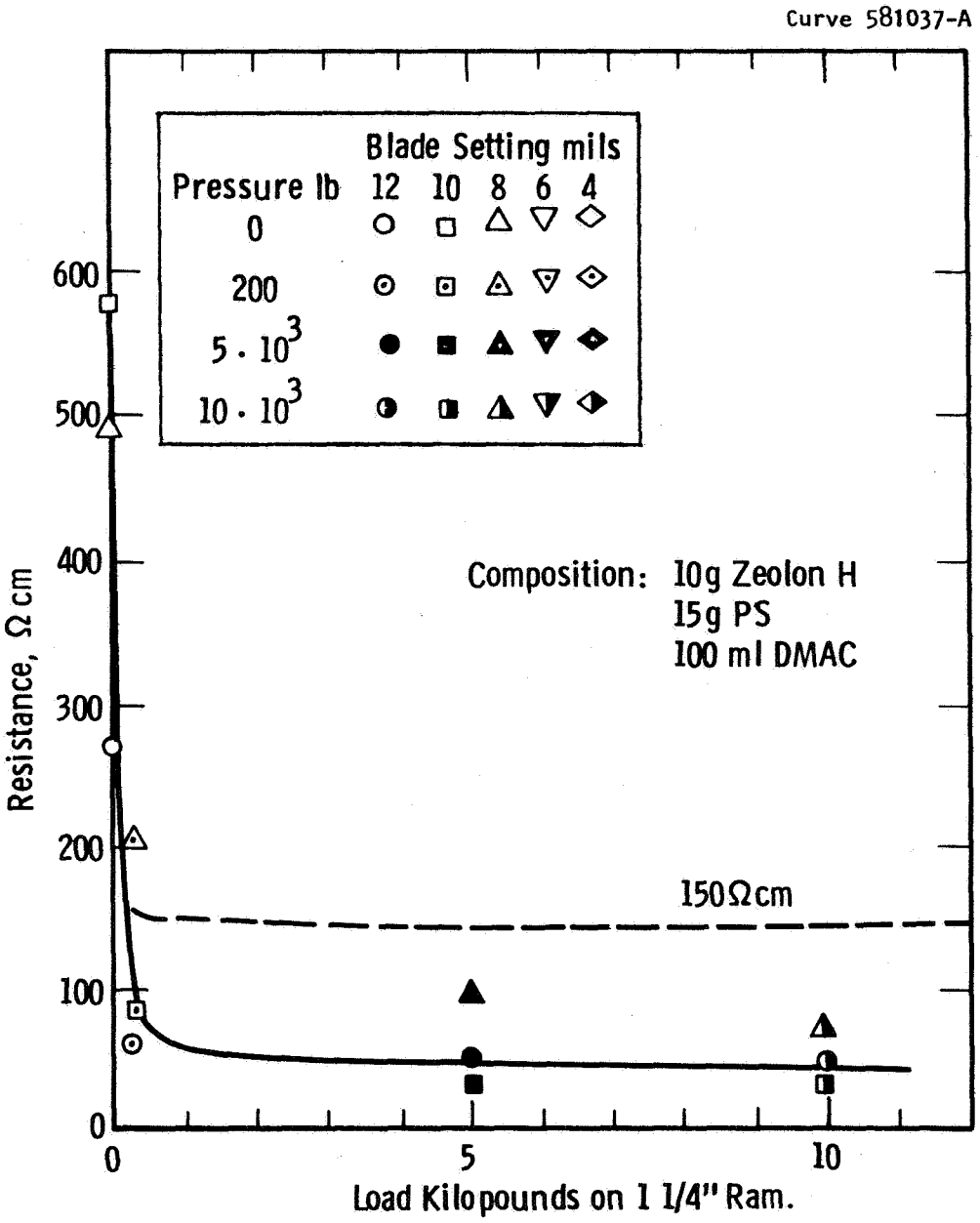


Fig. 4—Relation between compression and resistivity of films

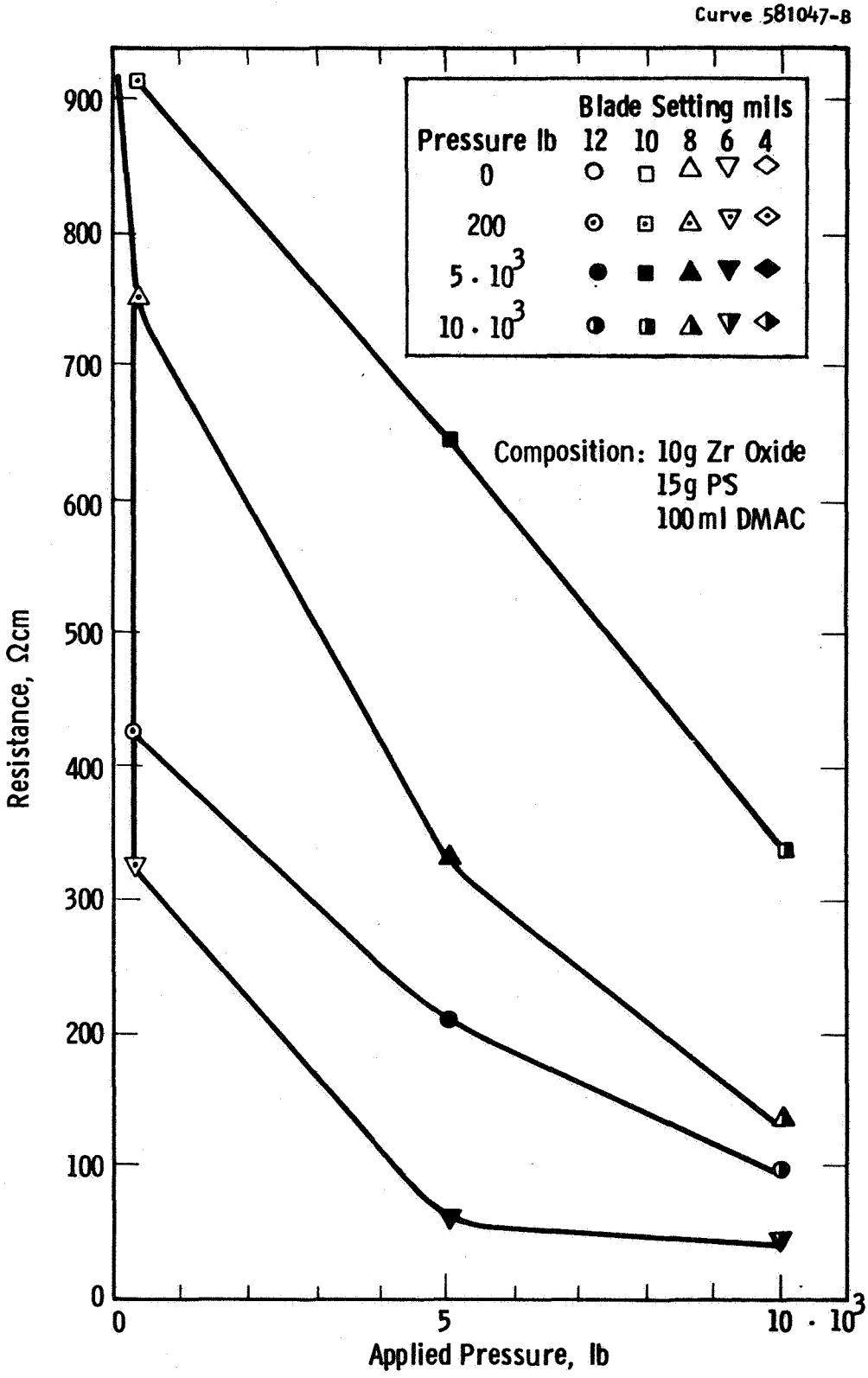


Fig. 5—Relation between compression pressure and resistivity of films

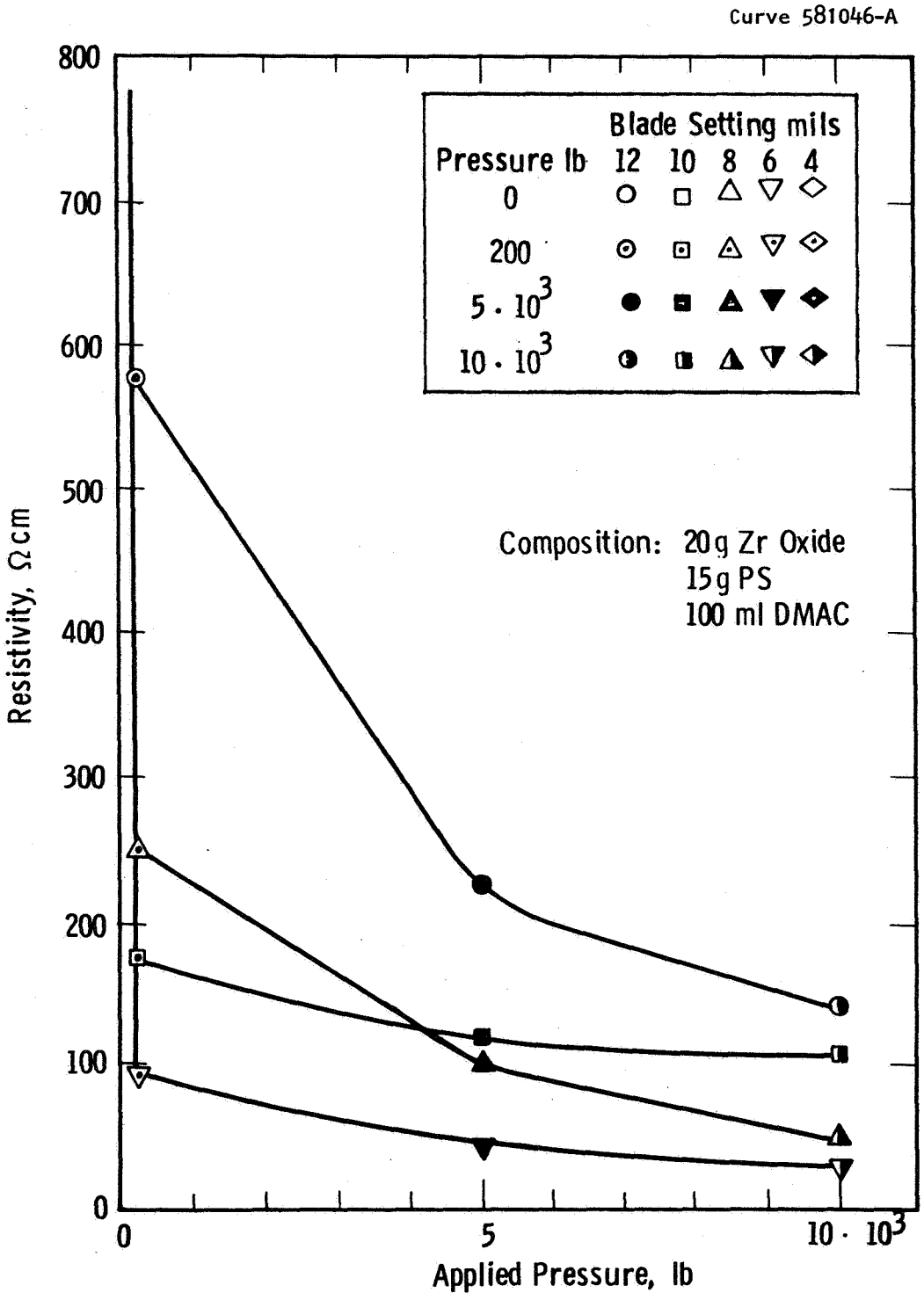


Fig. 6—Relation between compression pressure and resistivity of films

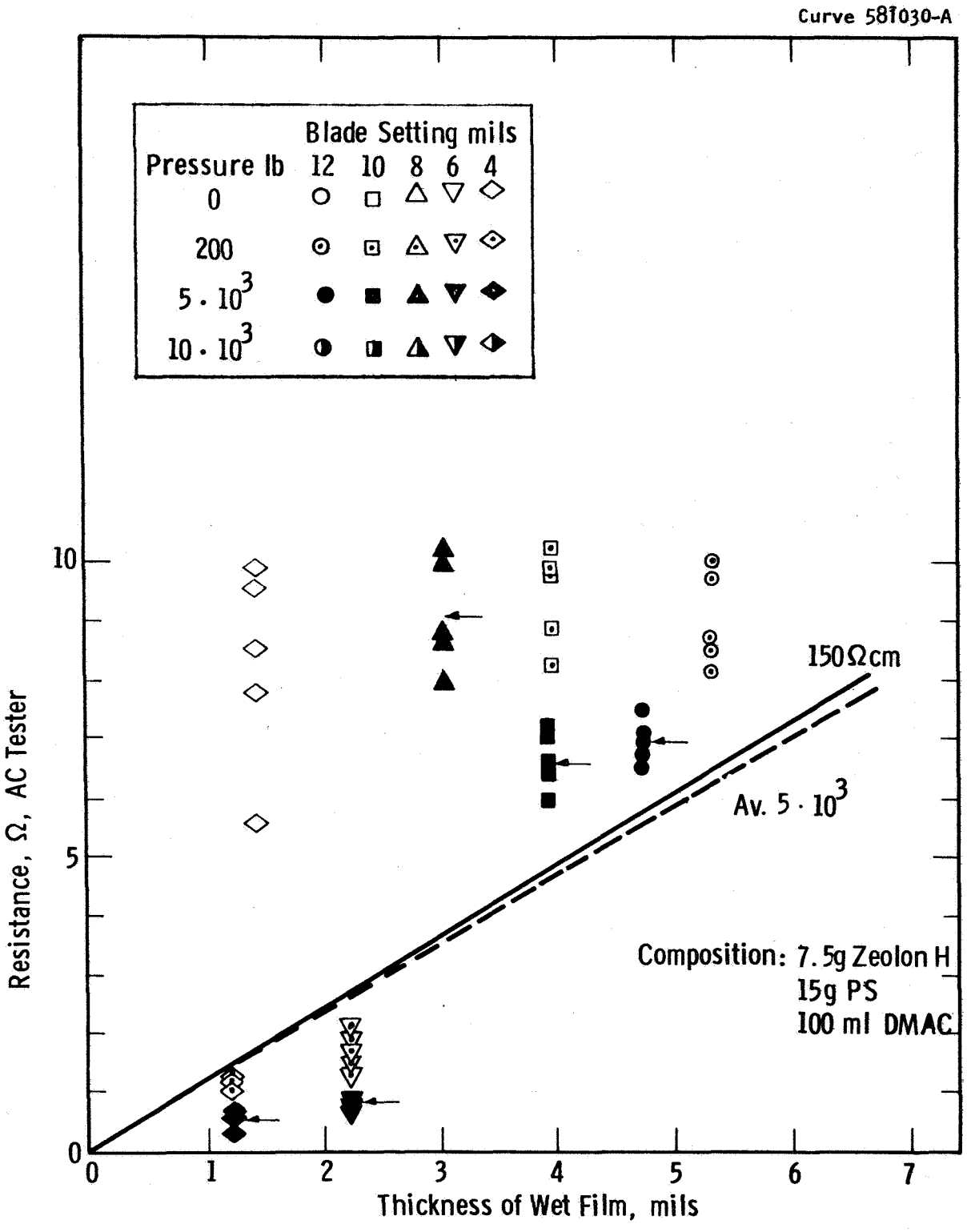


Fig. 7—Relation of thickness and resistance films, prepressed

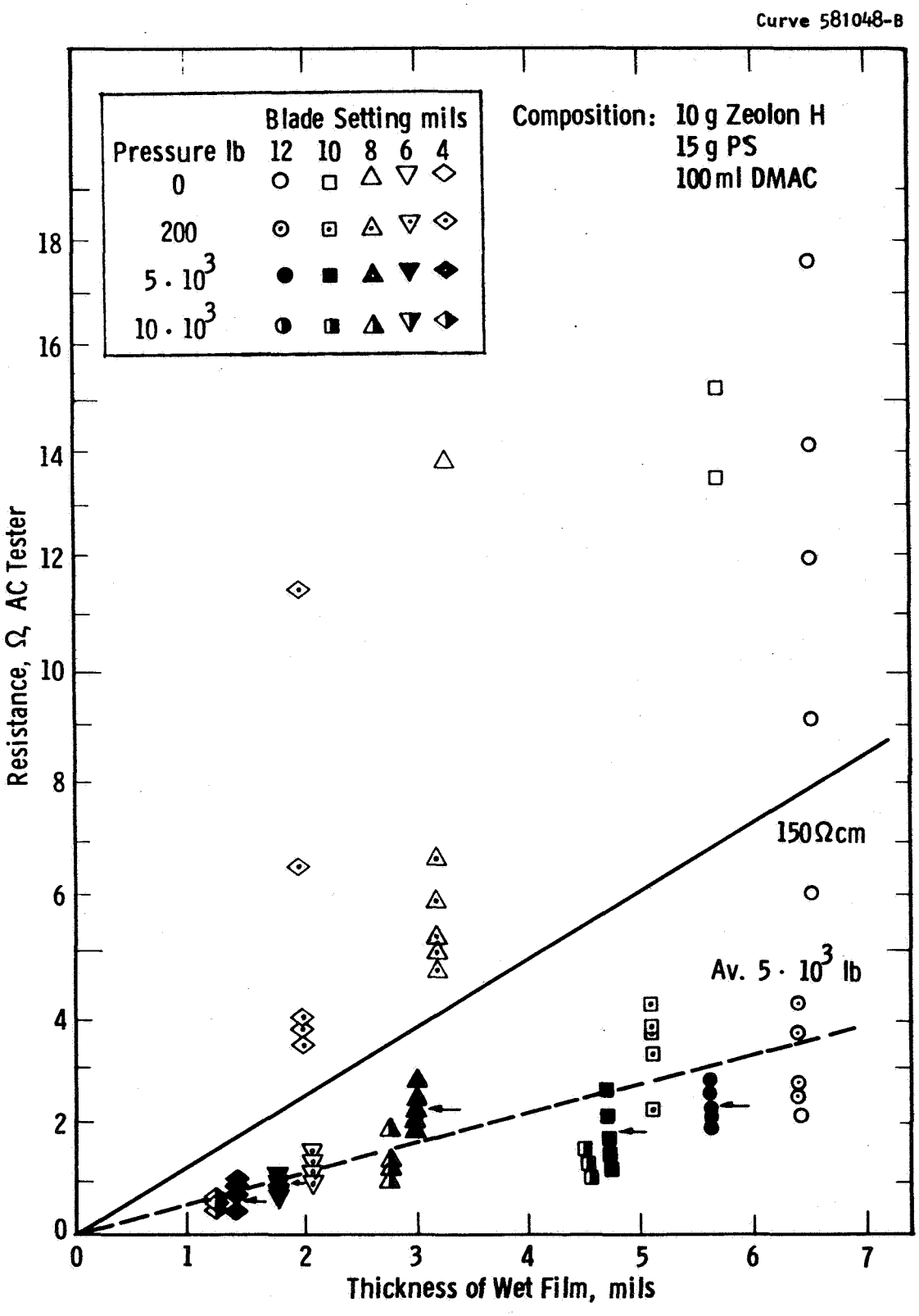


Fig. 8—Relation of thickness and resistance films, prepressed

Curve 581023-A

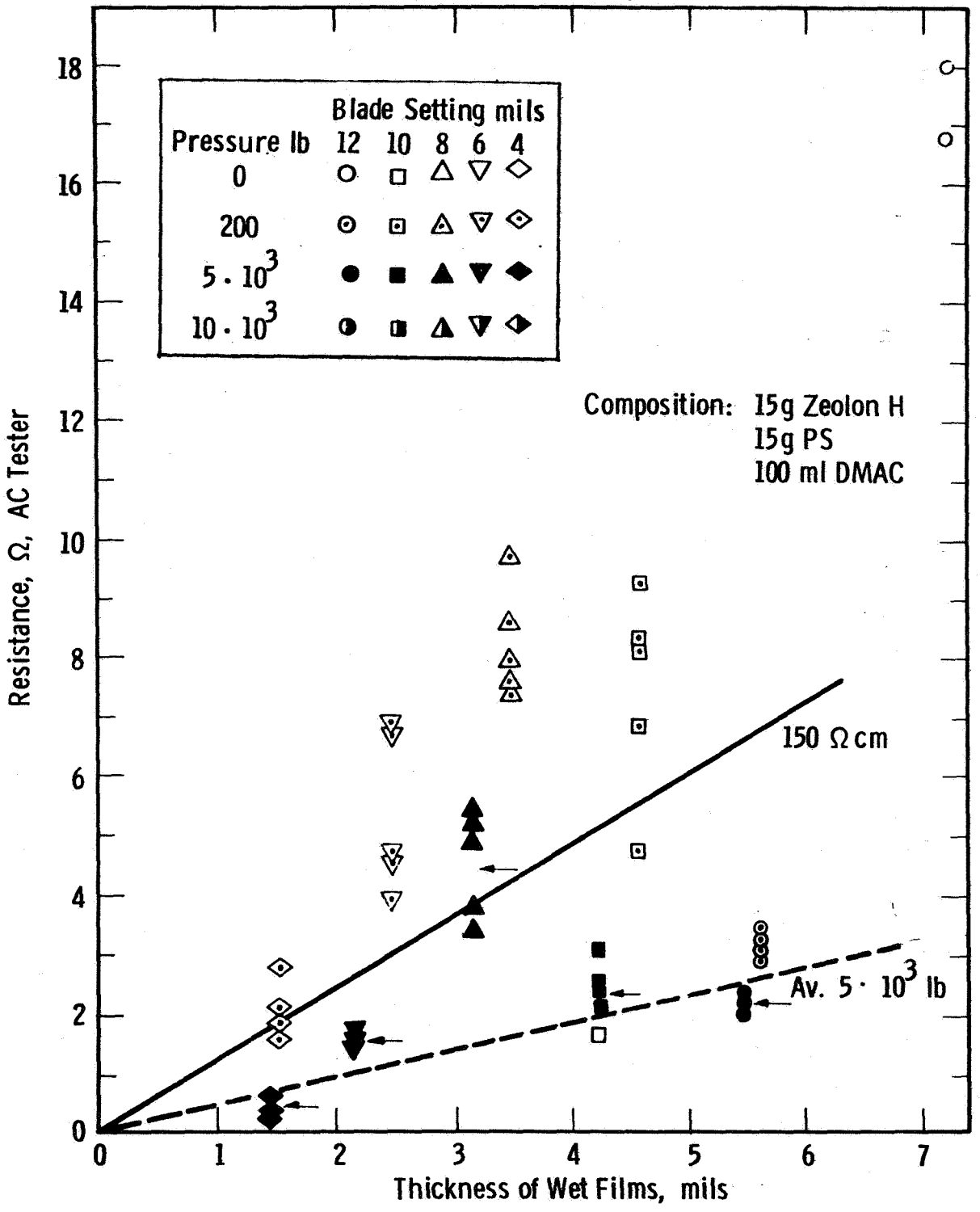


Fig. 9—Relation of resistance and thickness films, prepressed

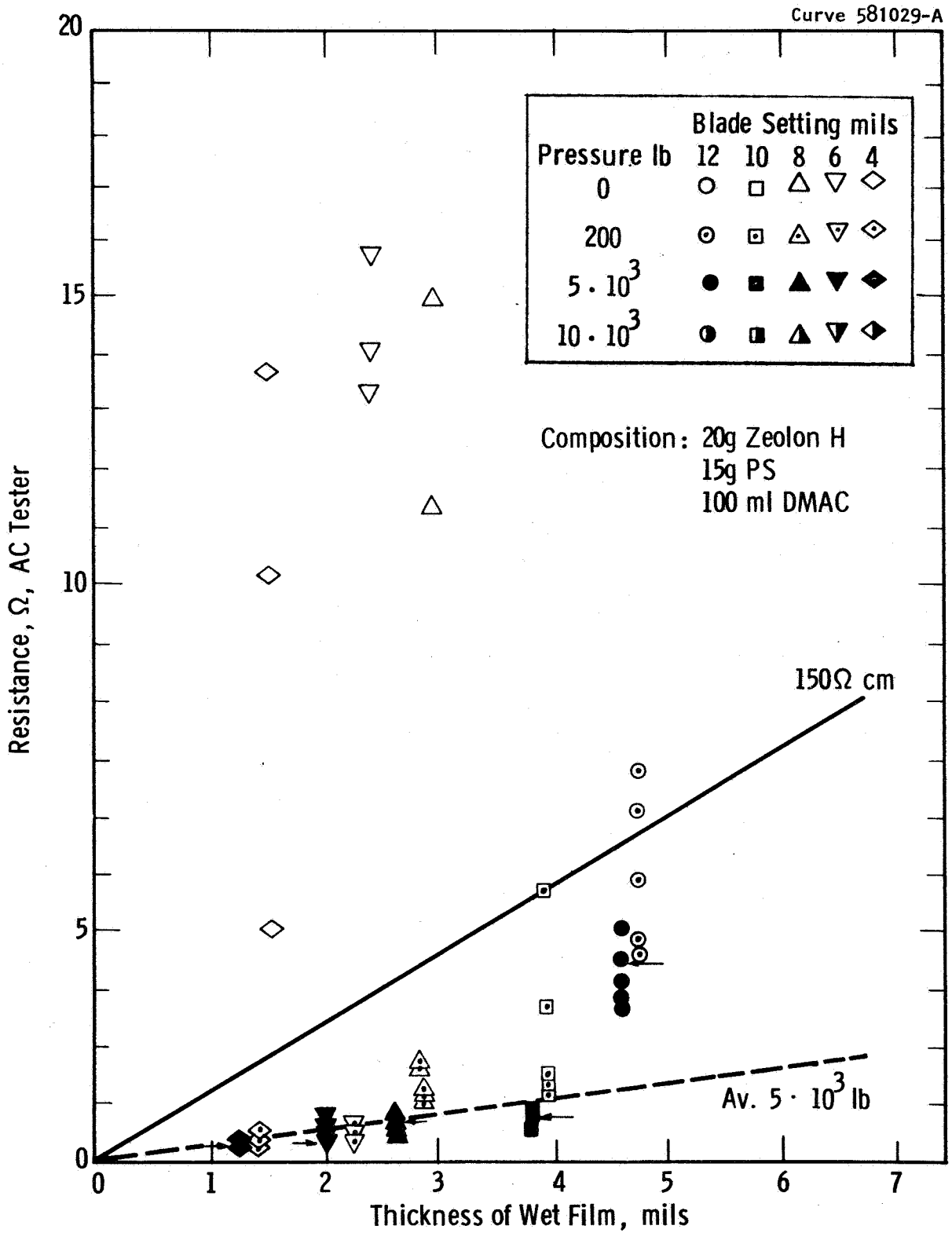


Fig. 10—Relation of resistance and thickness films, prepressed

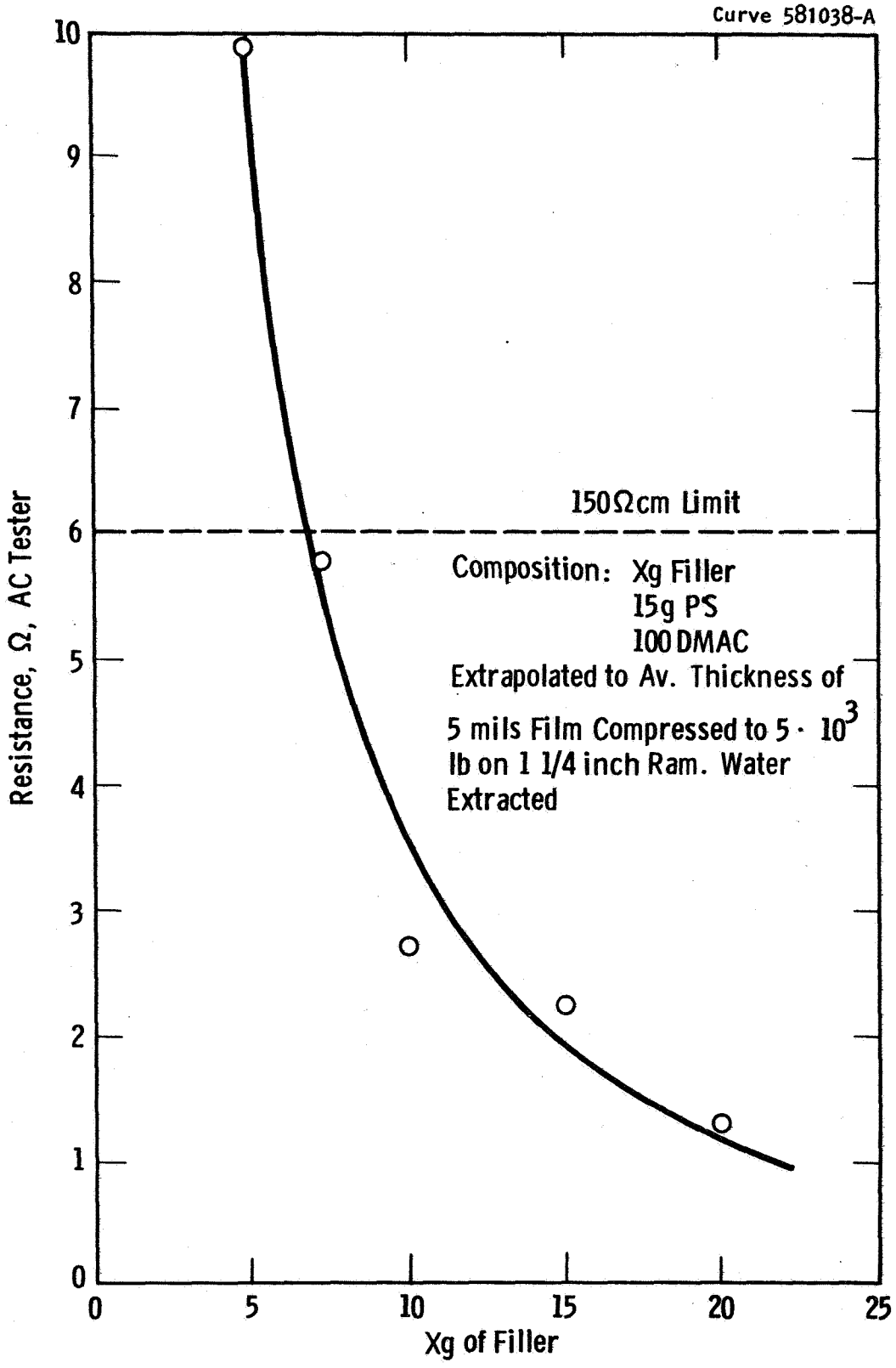


Fig. 11—Effect of filler on film resistance

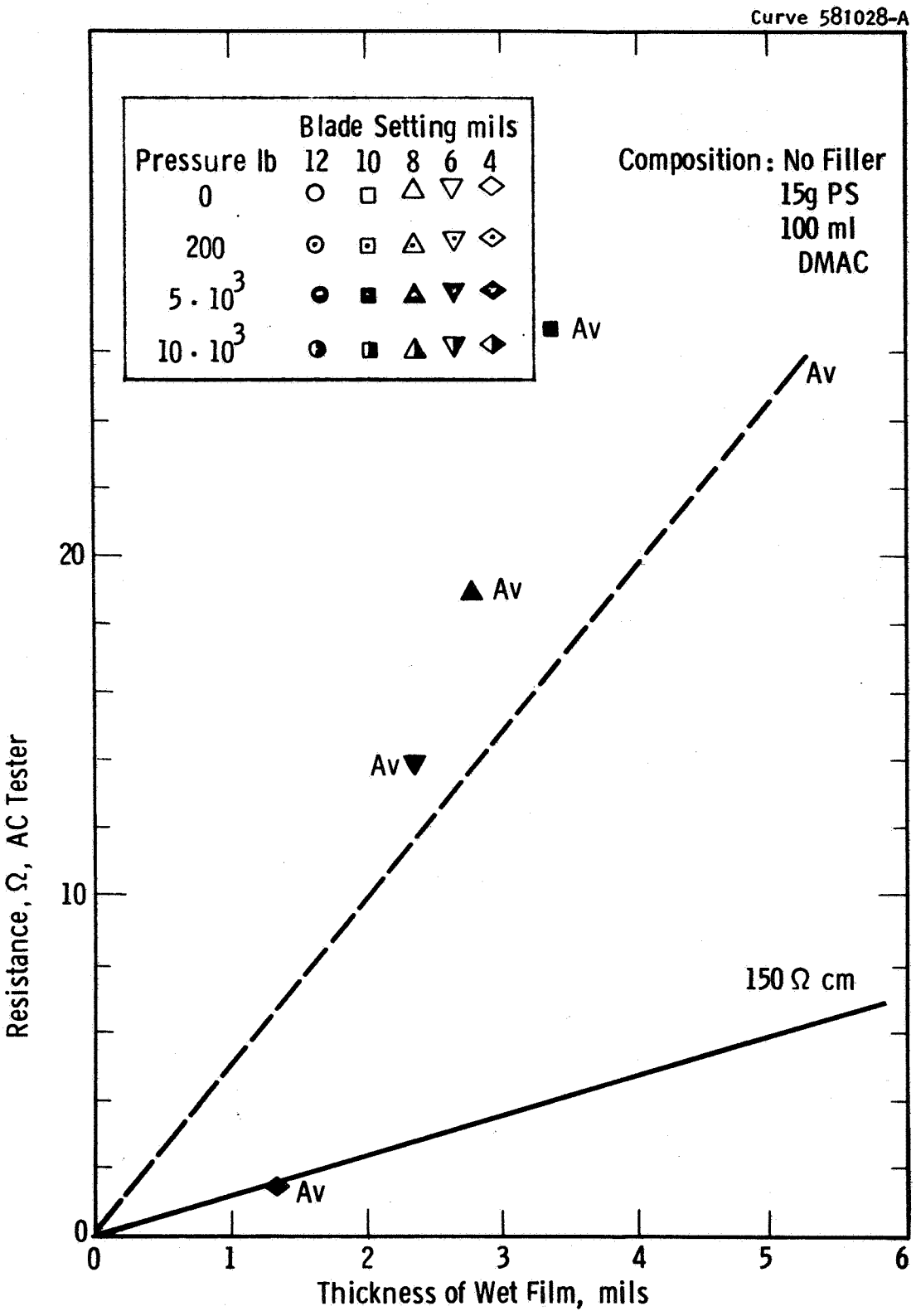


Fig. 12—Relation between resistance and thickness films, prepressed

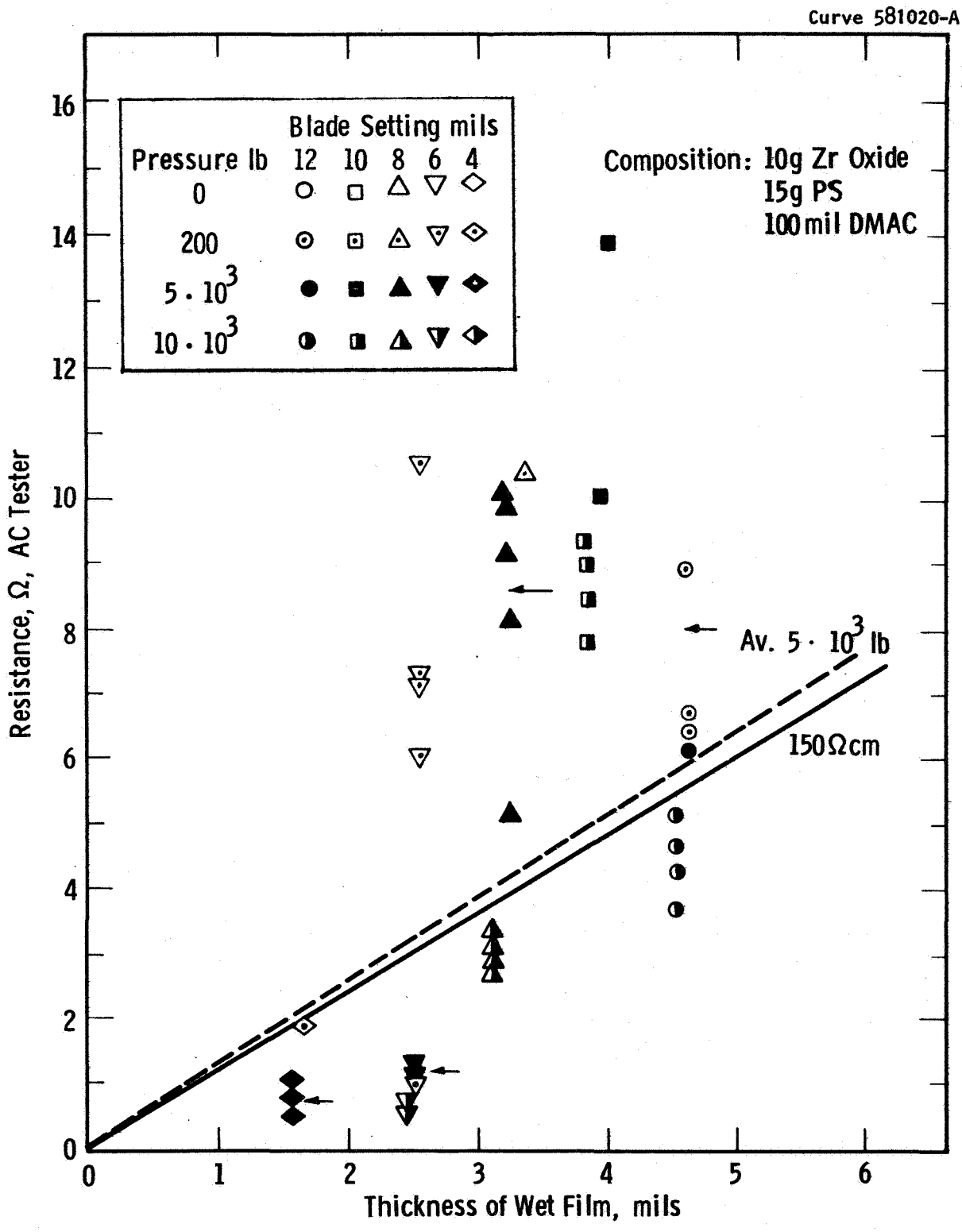


Fig. 13—Relation between resistance and thickness films, prepressed

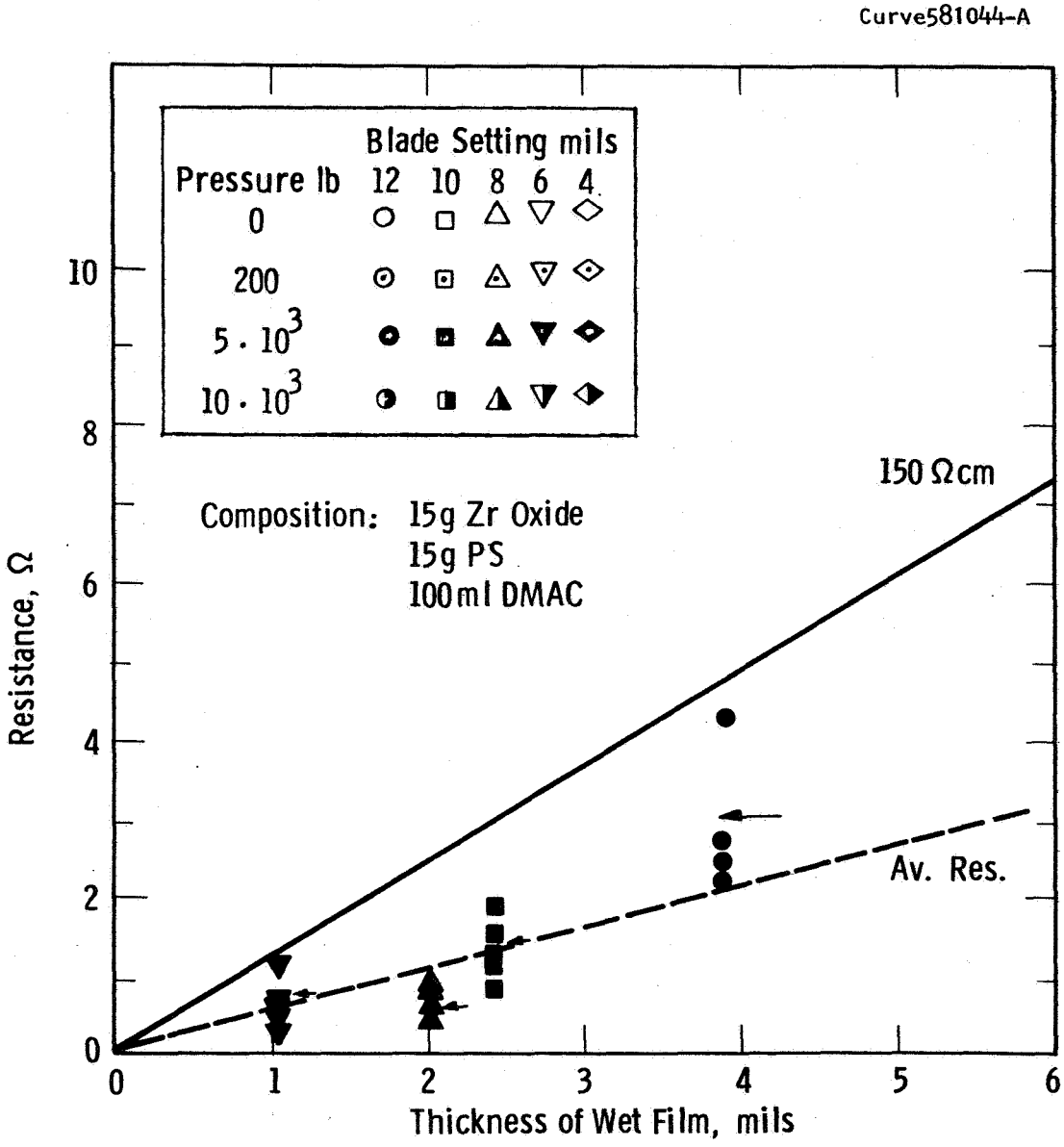


Fig. 14—Relation between resistance and thickness films, prepressed

Curve 581021-A

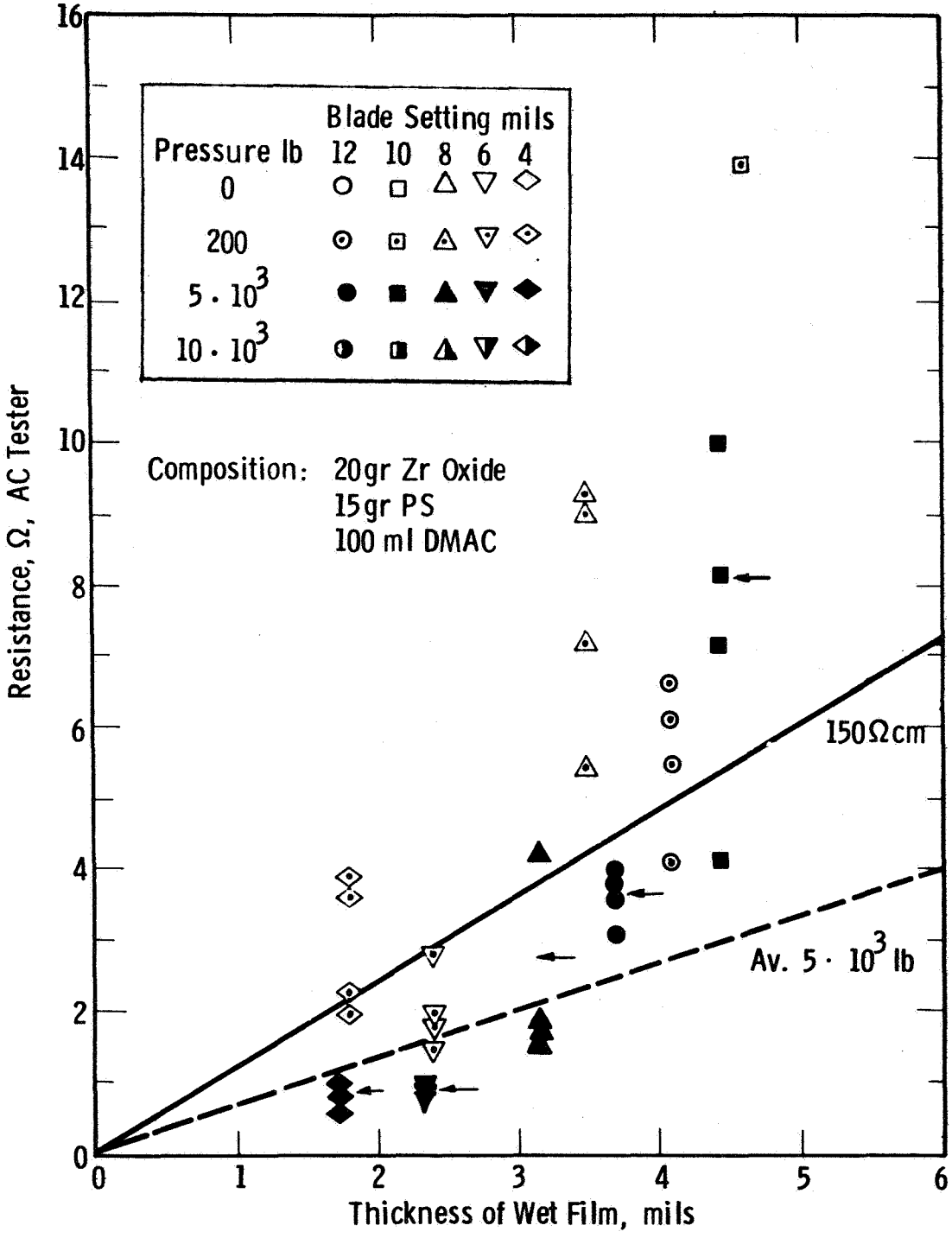


Fig. 15—Relation between resistance and thickness films, prepressed

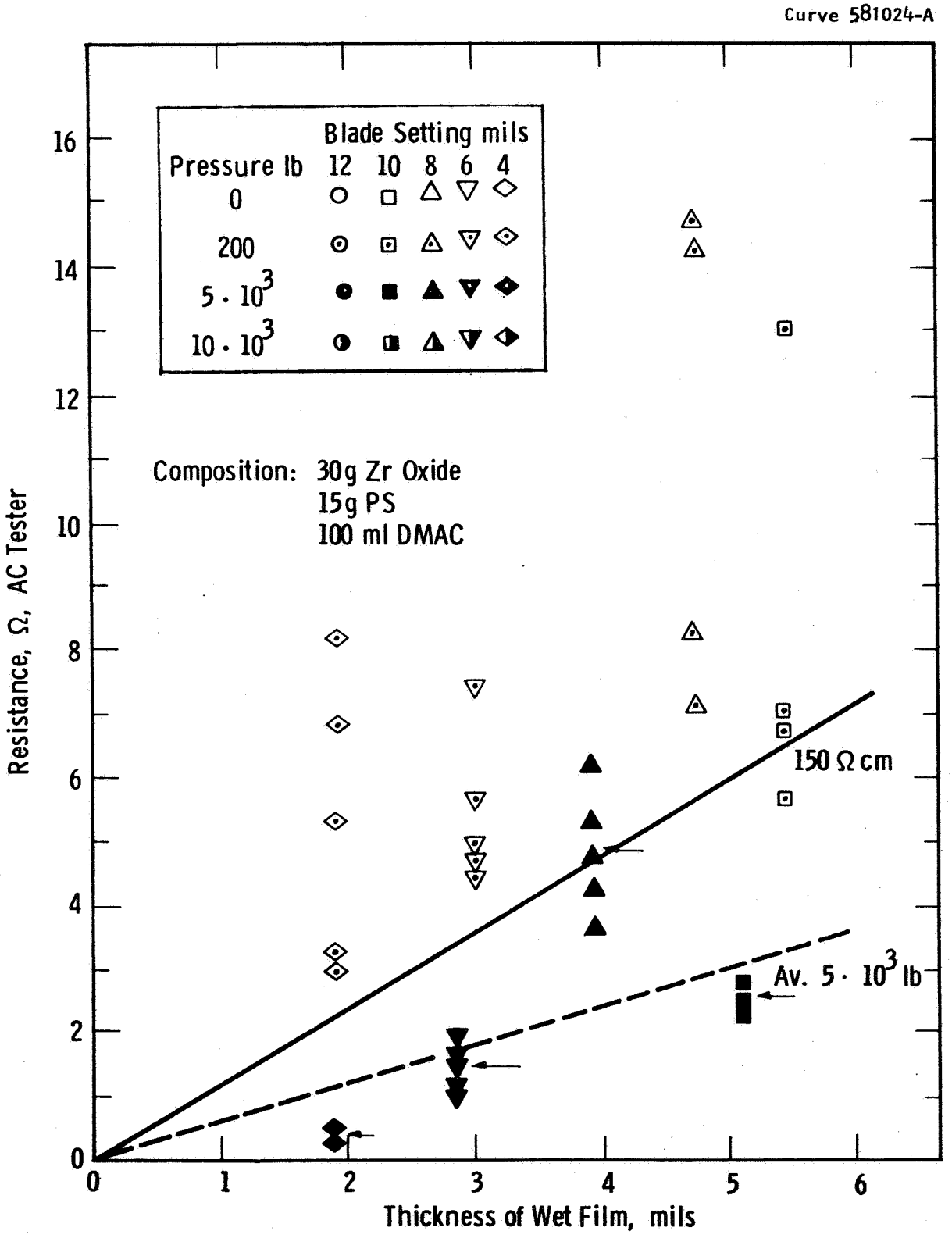


Fig. 16—Relation between resistance and thickness films, prepressed

Curve 581042-A

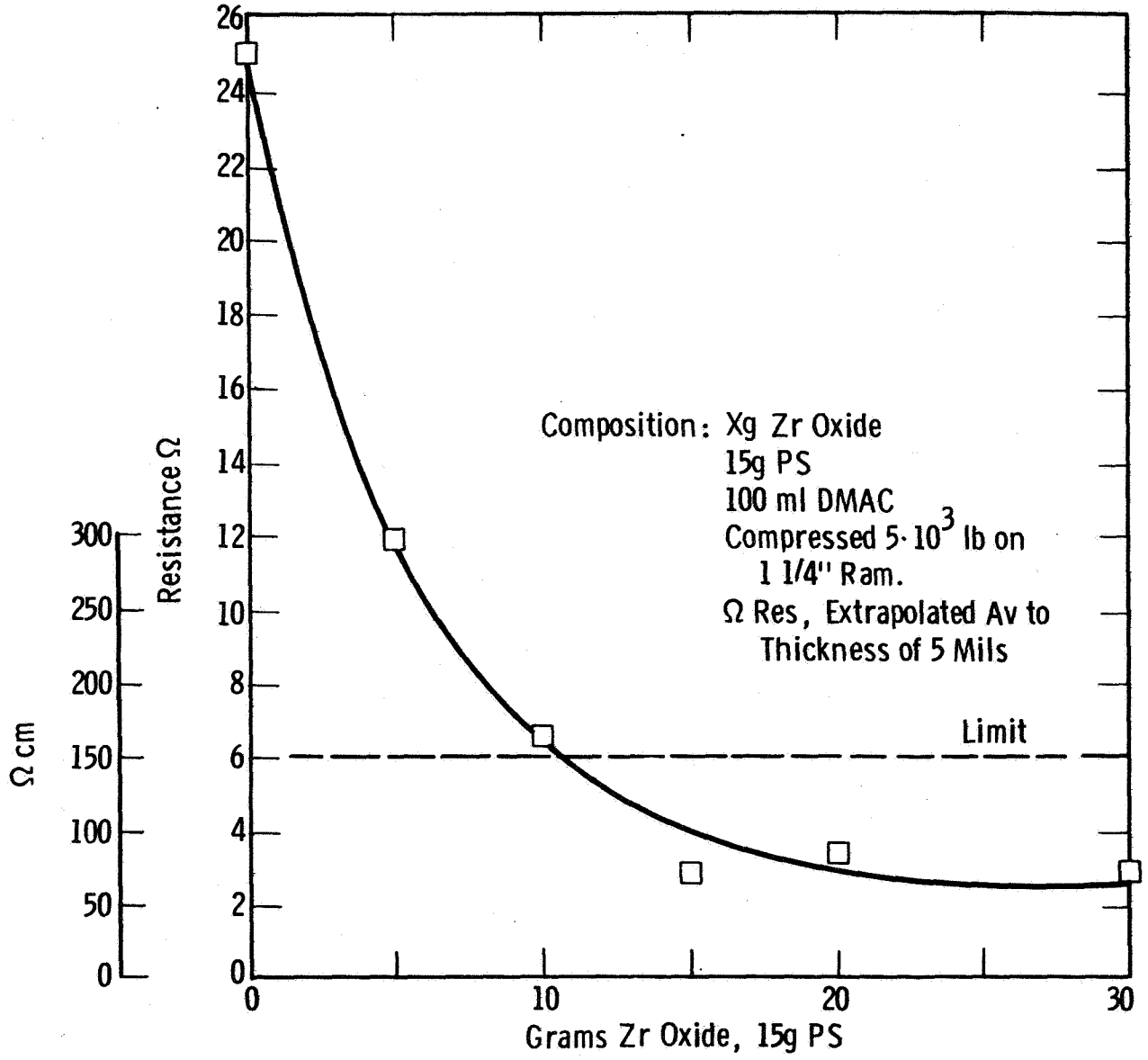


Fig. 17—Influence of amount of filler on resistance of films pressed at 5×10^3 lb

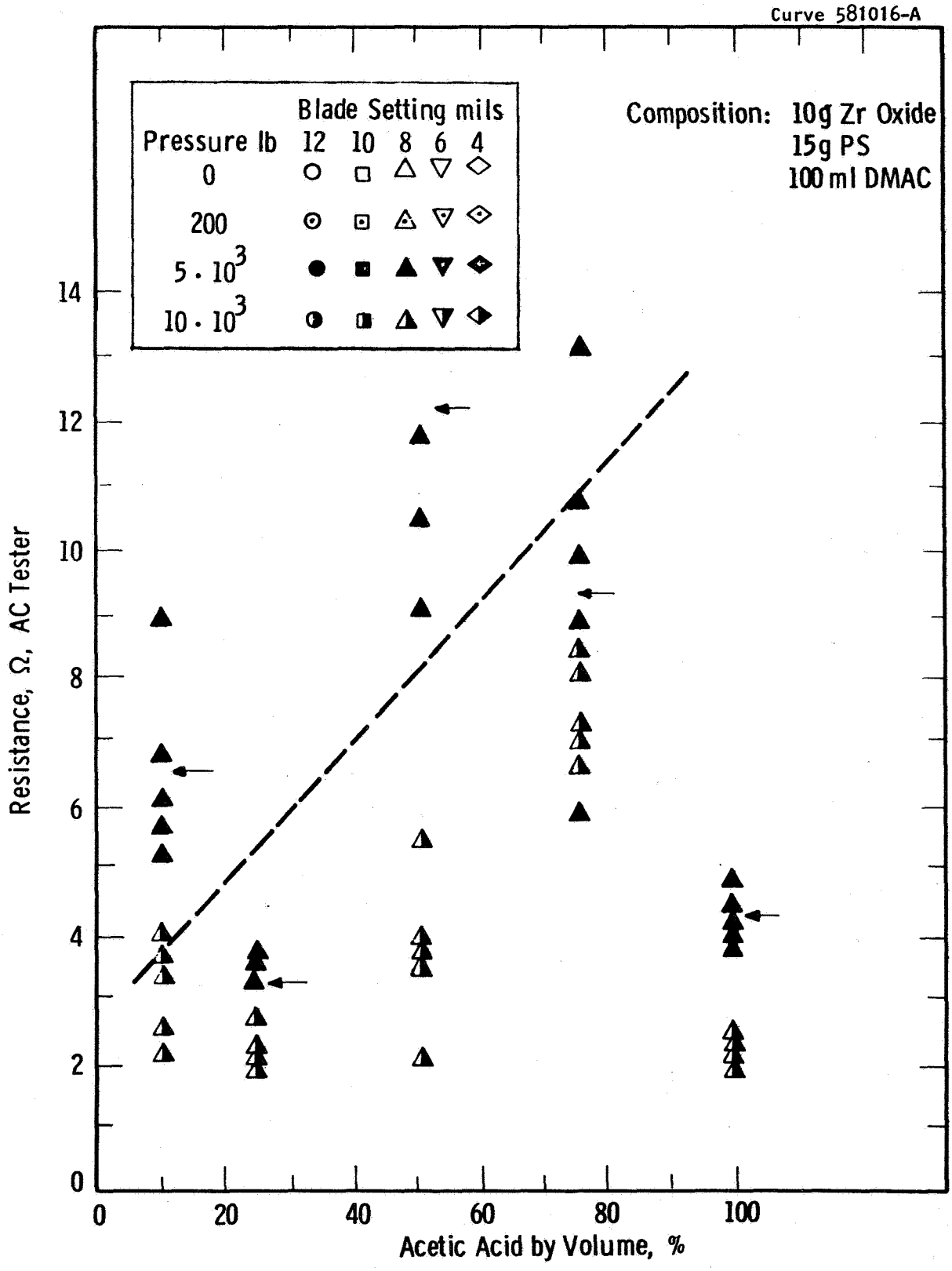


Fig. 18—Relation of resistance and acetic acid concentration used for DMAC extraction

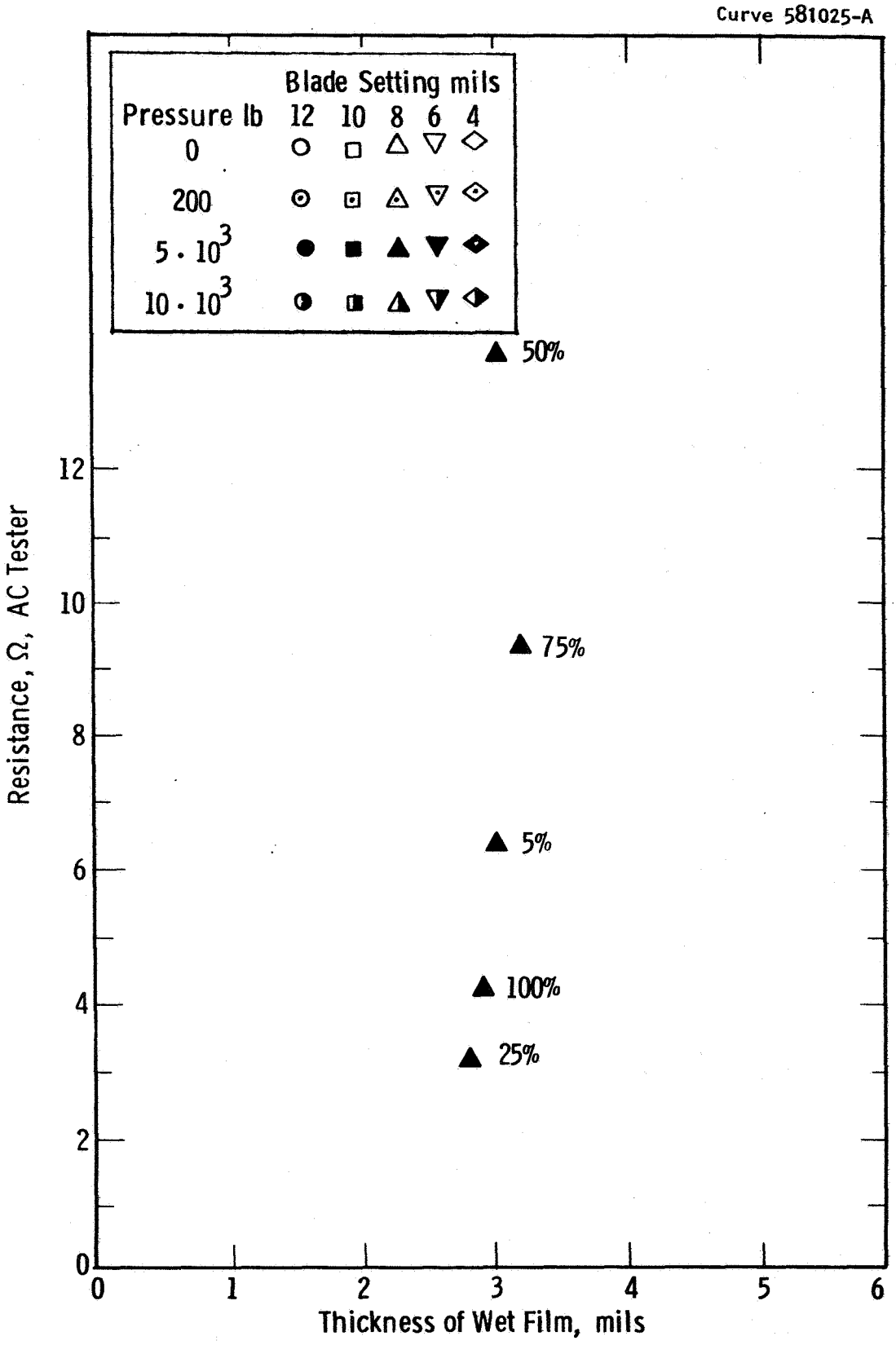


Fig. 19—Thickness-resistance relation of films precipitated with acetic acid of various concentration composition

Curve 581017-A

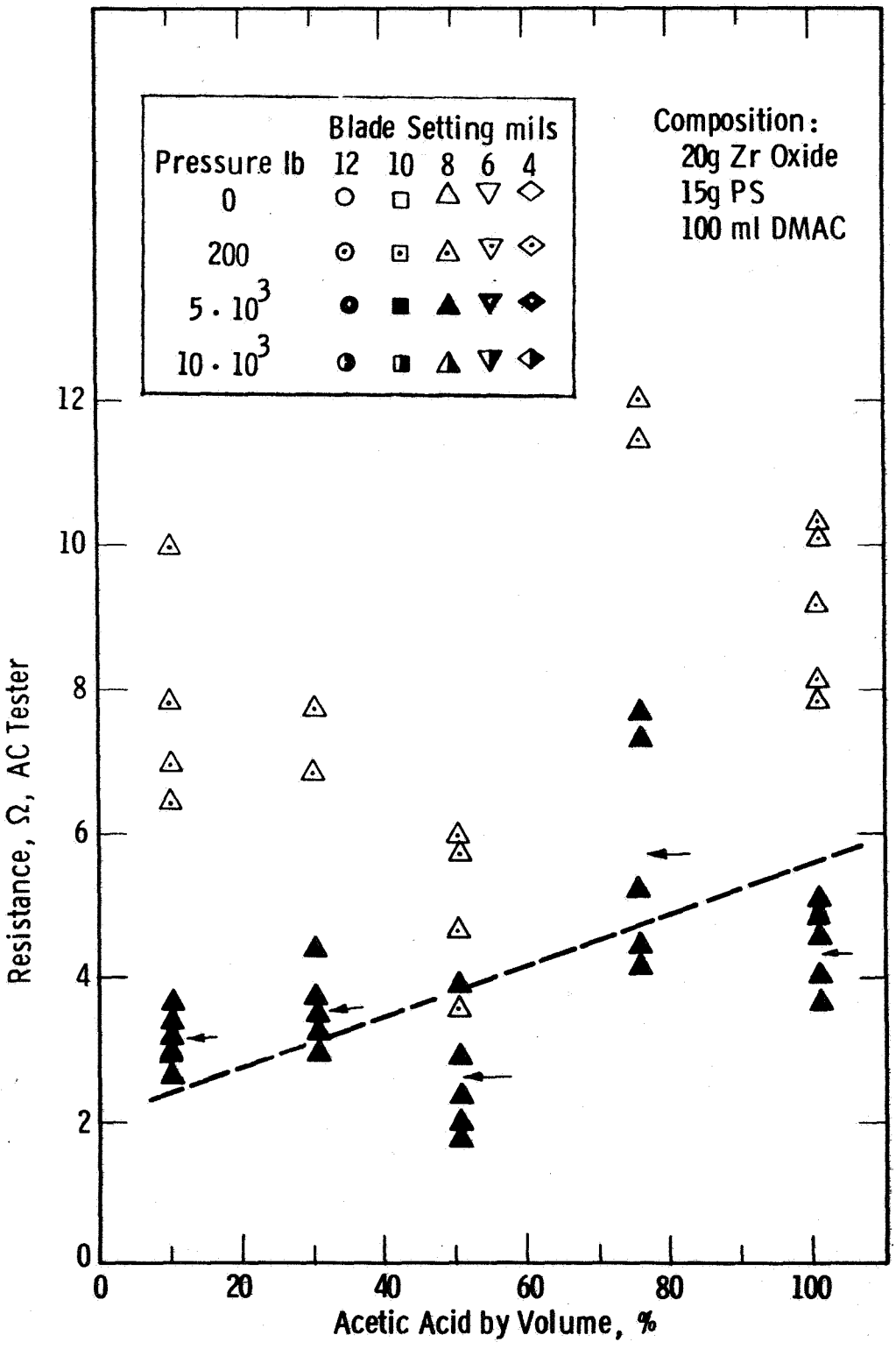


Fig. 20–Relation of resistance and acetic acid concentration used for DMAC extraction

Curve 581022-A

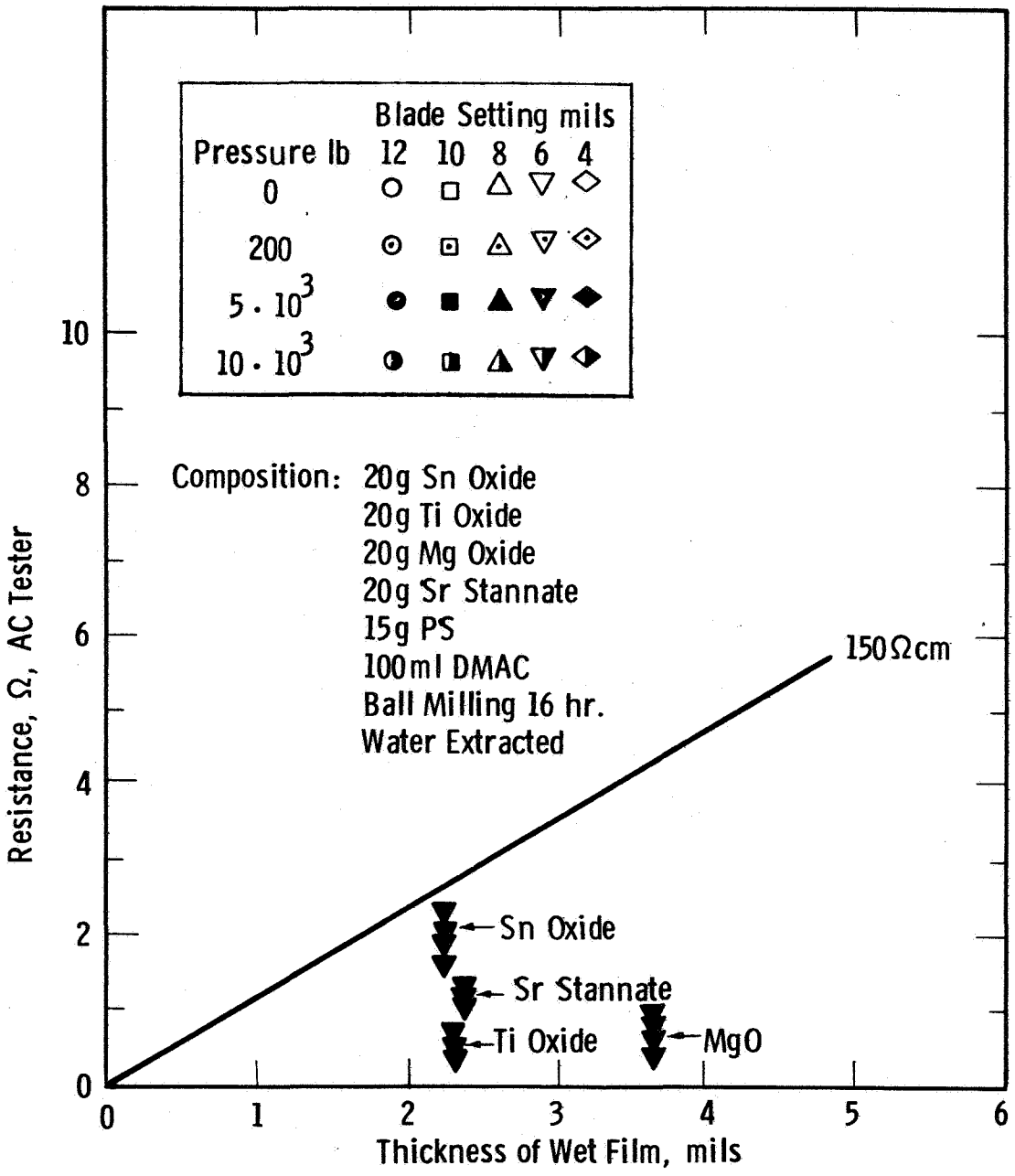


Fig. 21—Relation between film thickness and resistance

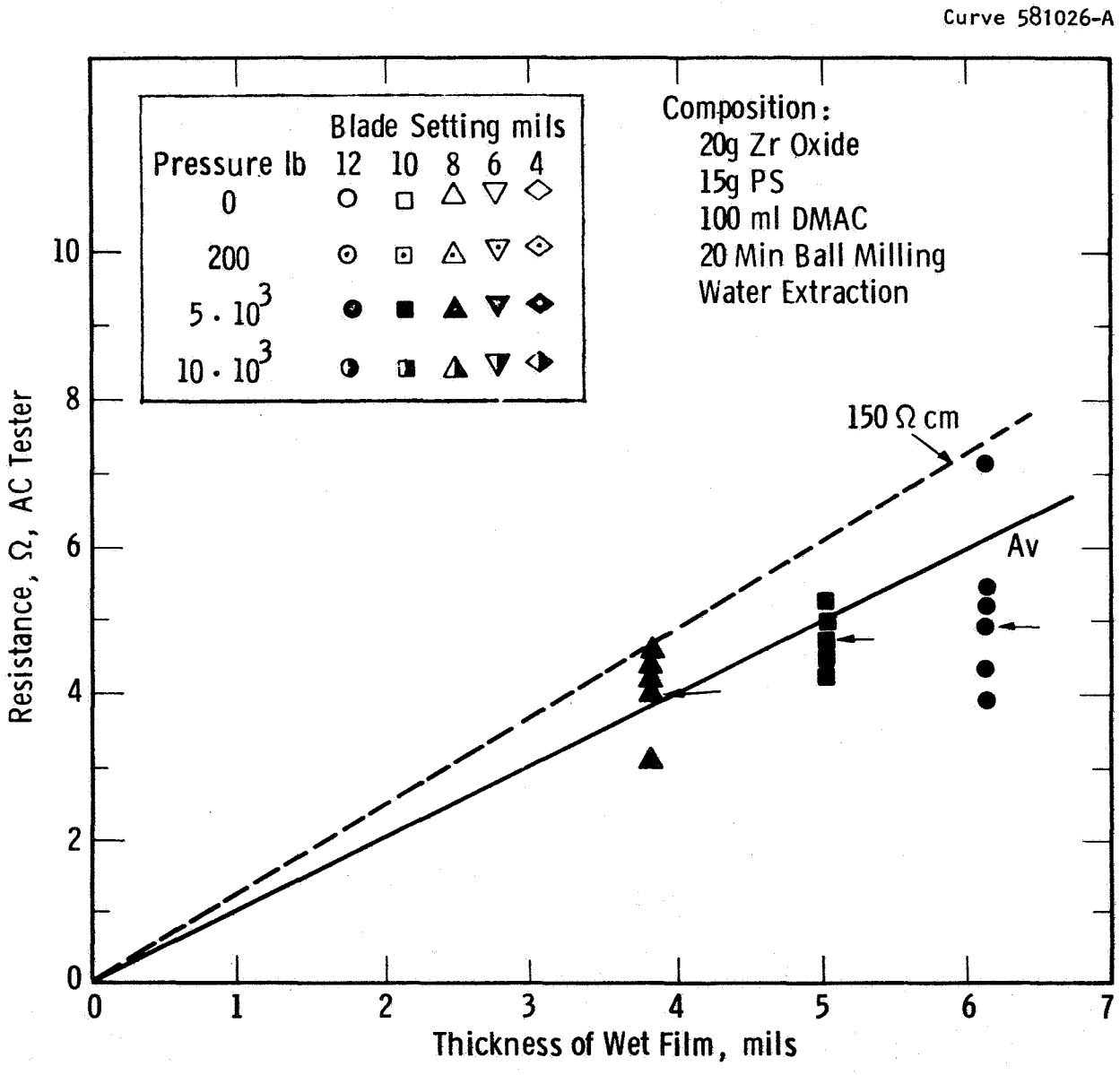


Fig. 22—Relation between resistance and film thickness. 20 min ball-milling time

Curve 581043-A

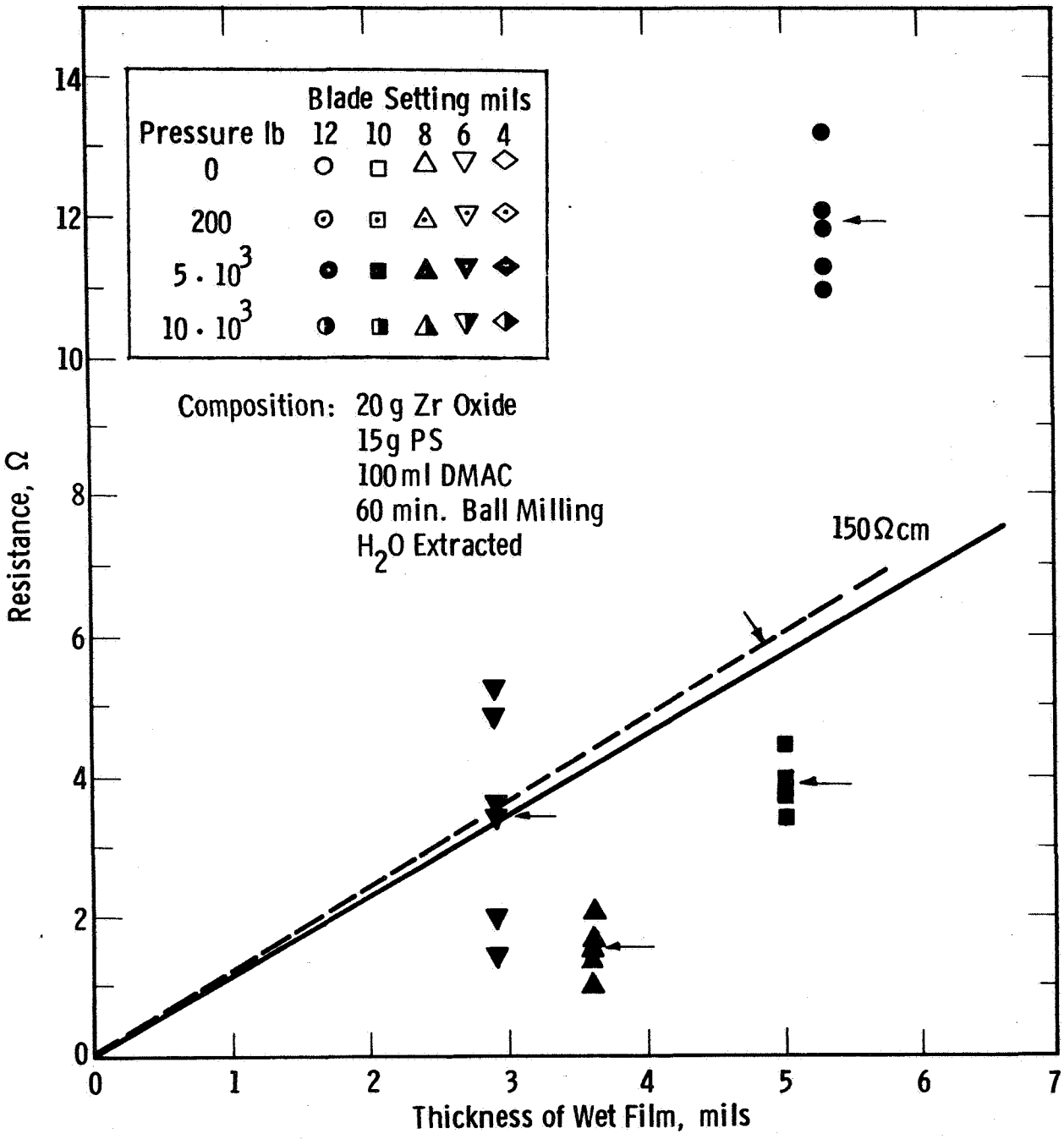


Fig. 23—Relation between resistance and thickness
60 min. ball-milling time

Curve 581027-A

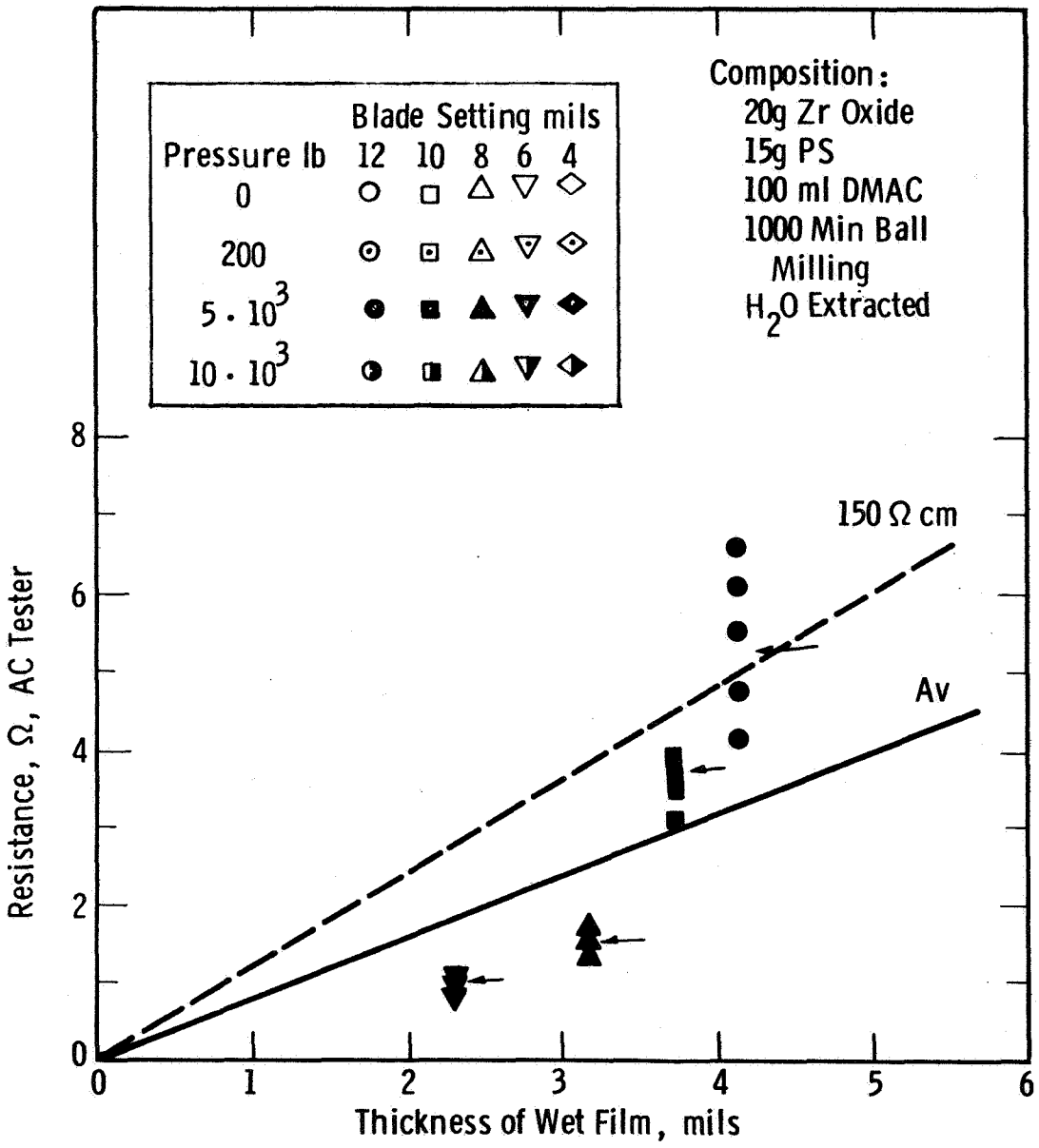


Fig. 24—Relation between resistance and film thickness. 1000 min ball-milling time

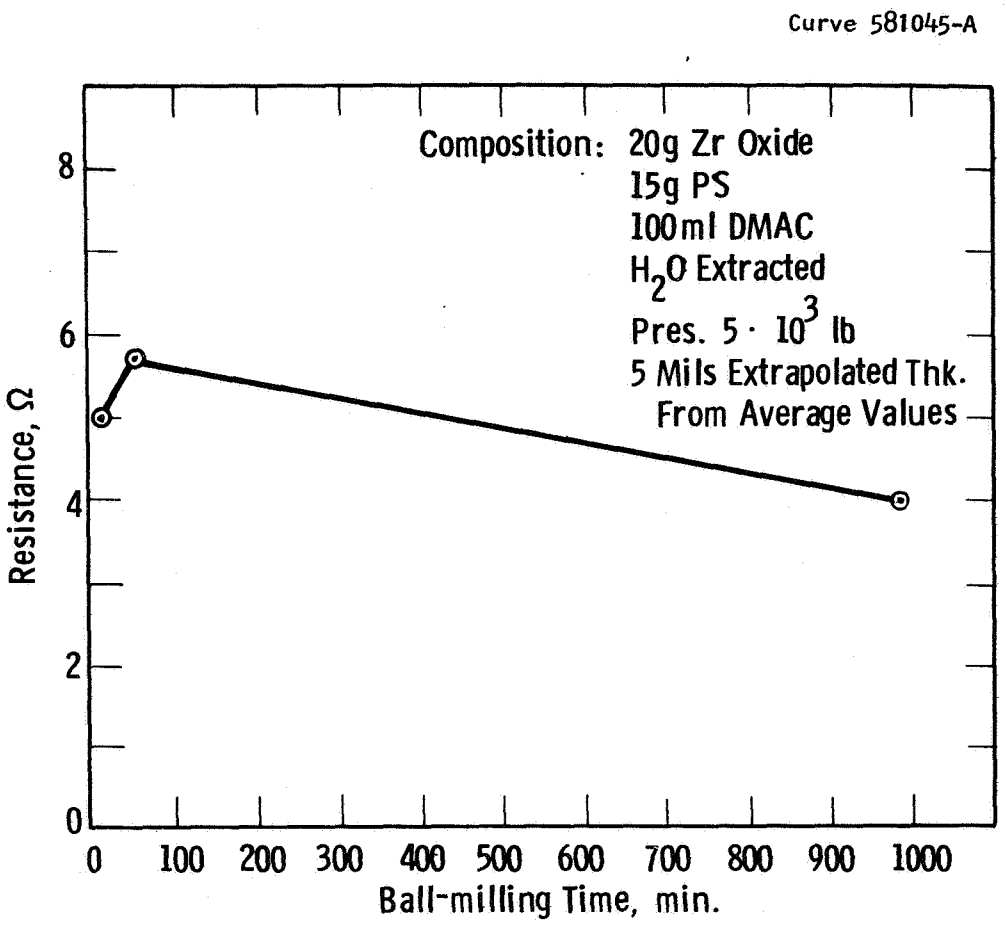


Fig. 25—Relation between ball-milling time and resistance

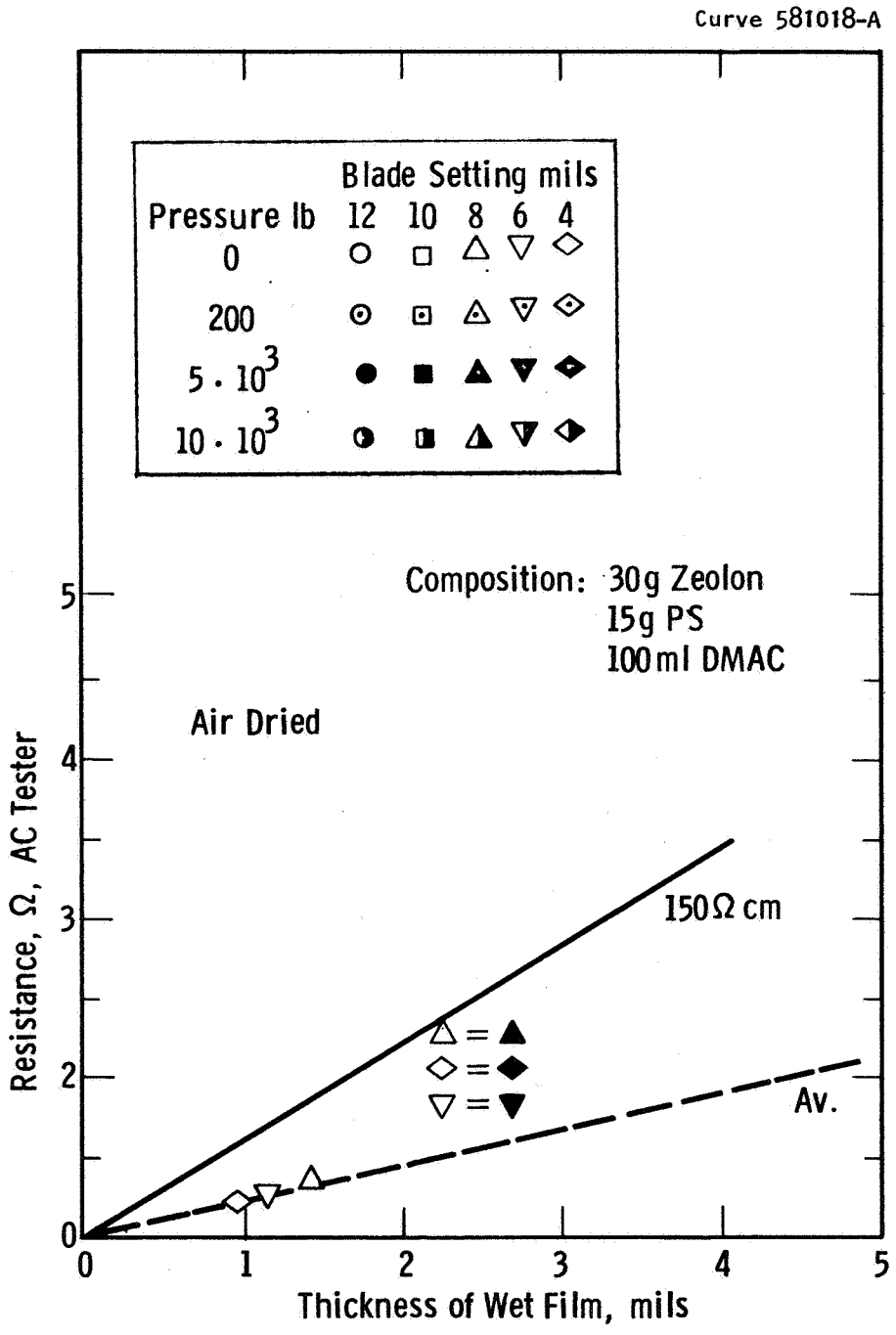


Fig. 26—Resistance versus thickness for air dried films

Curve 581019-A

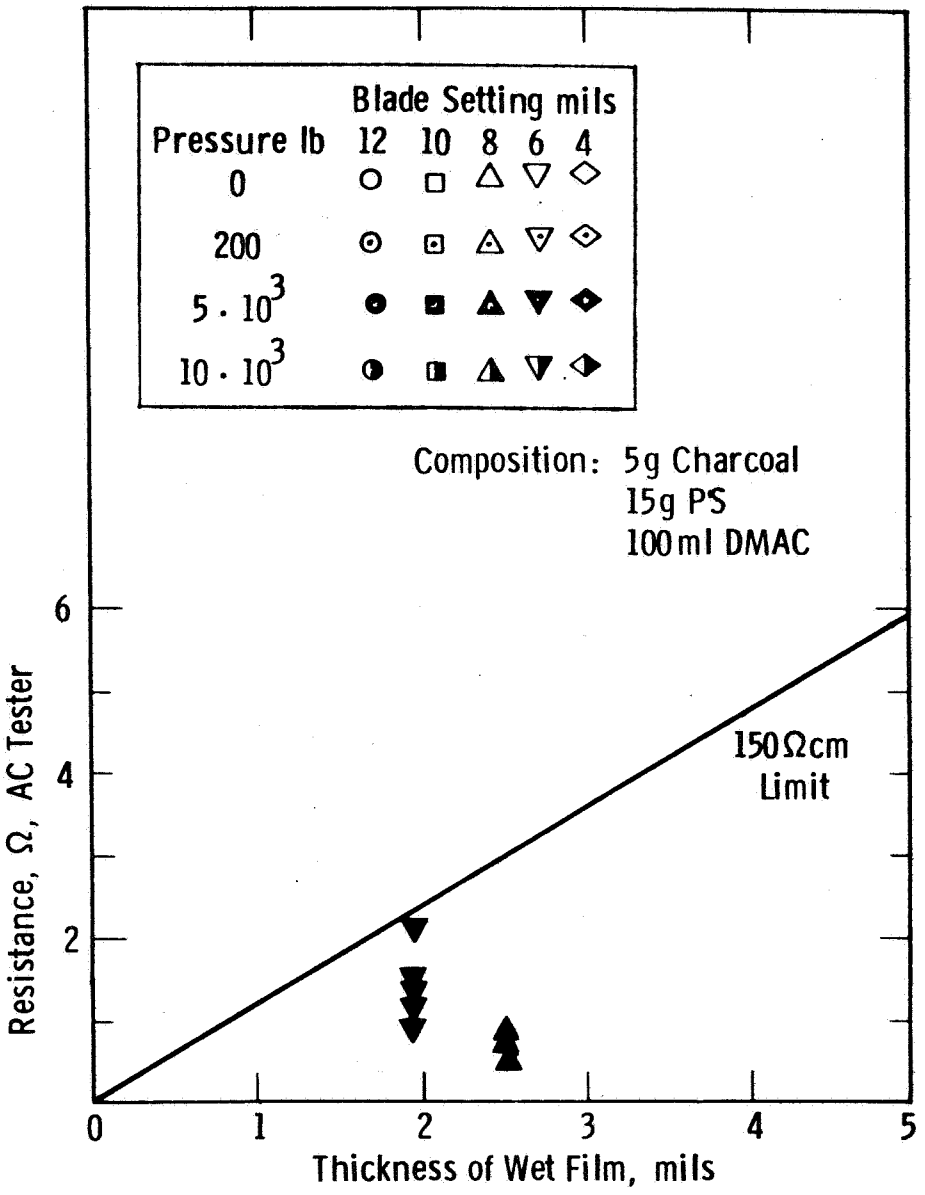
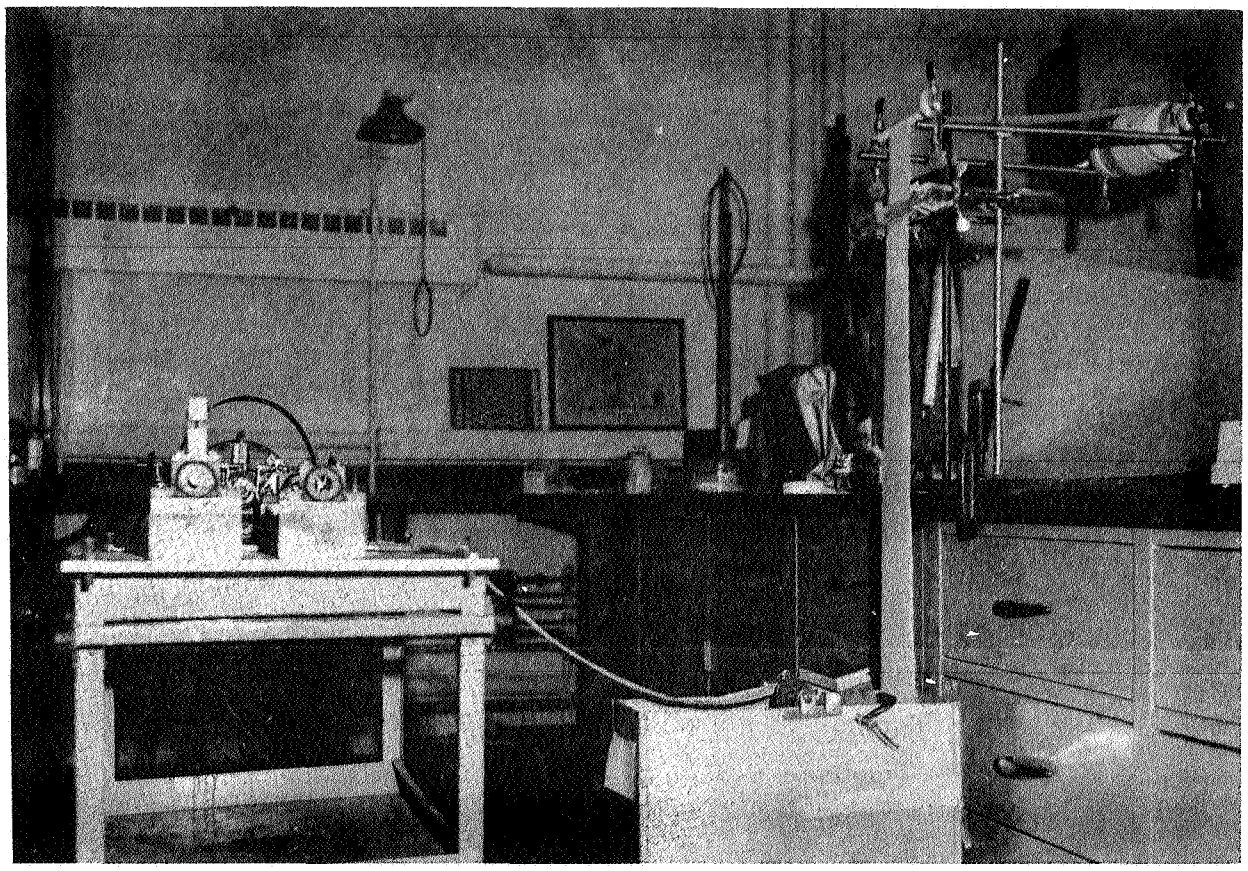


Fig. 27—Resistance-thickness relation of charcoal filled films



Continuous Coating of Polypropylene Webril
with Filled Polymer Solution

Figure 28

Dwg. 853A582

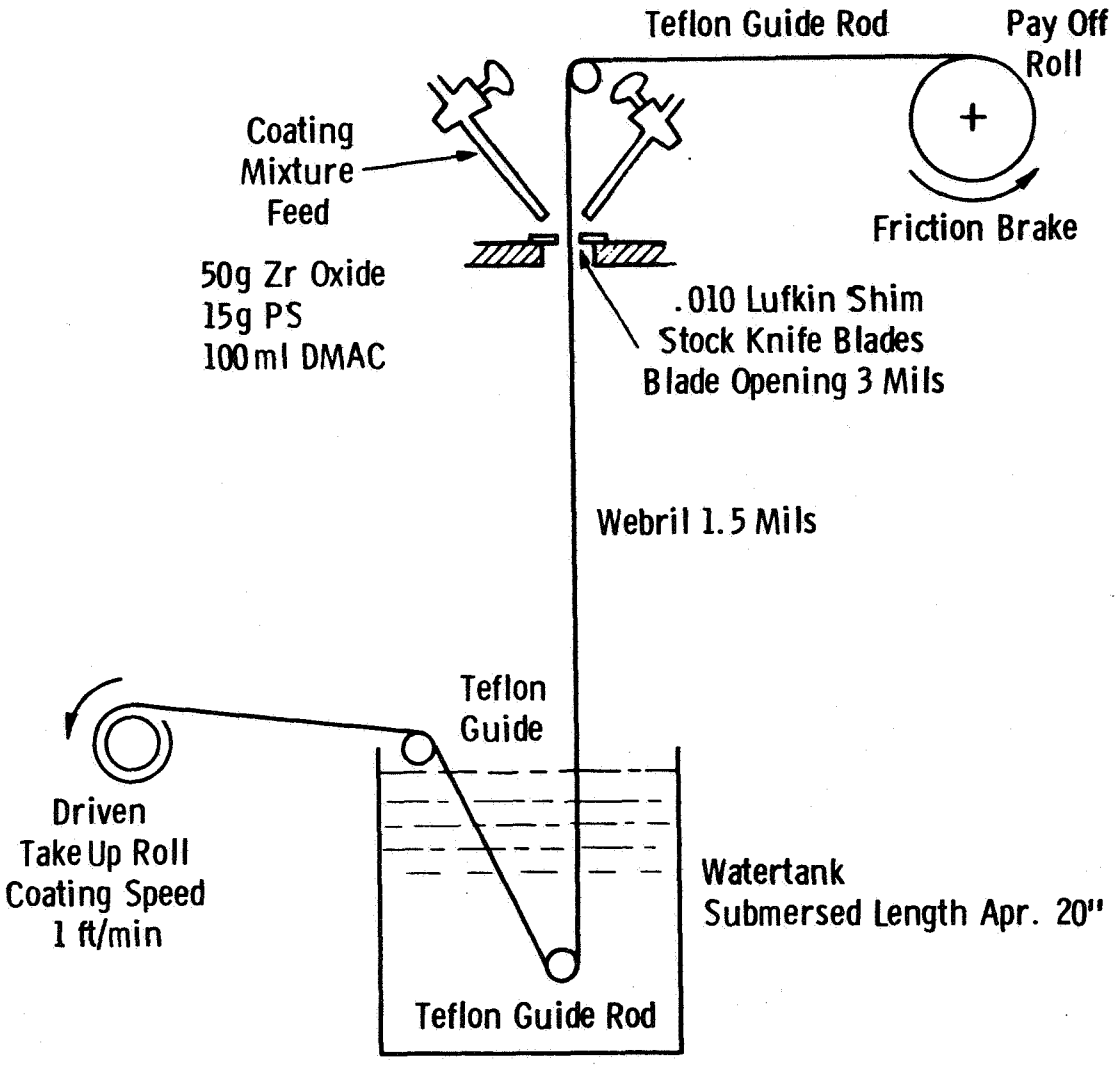
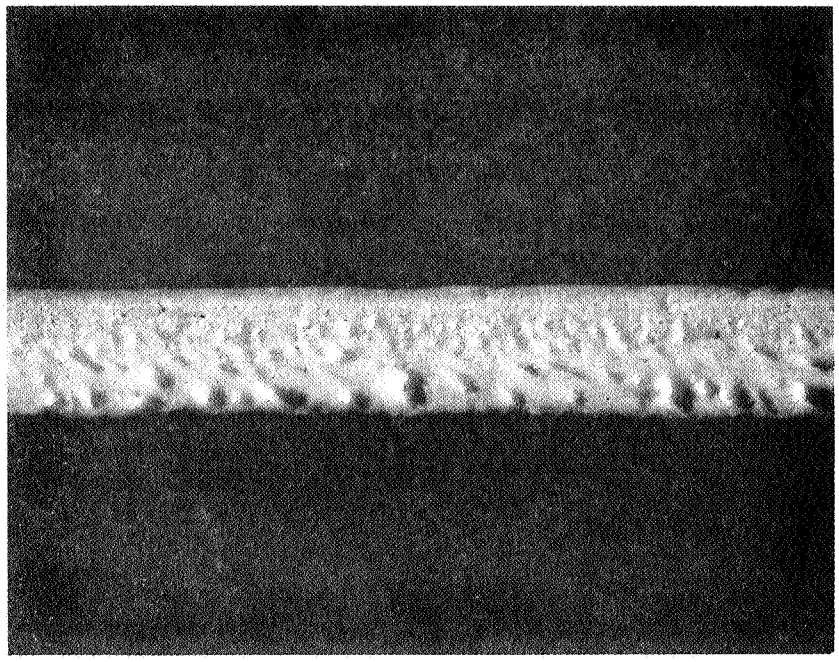
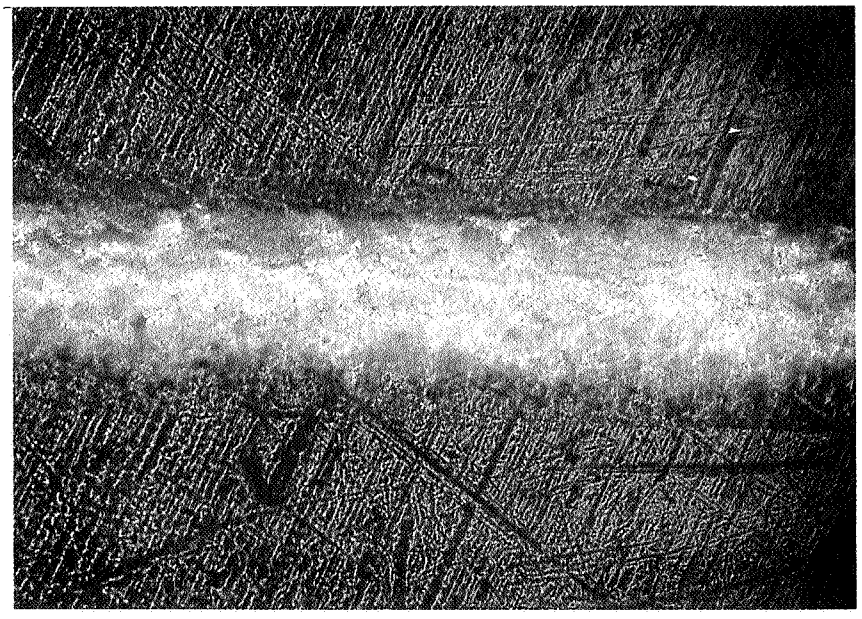


Fig. 29—Schematic sketch of continuous coating machine



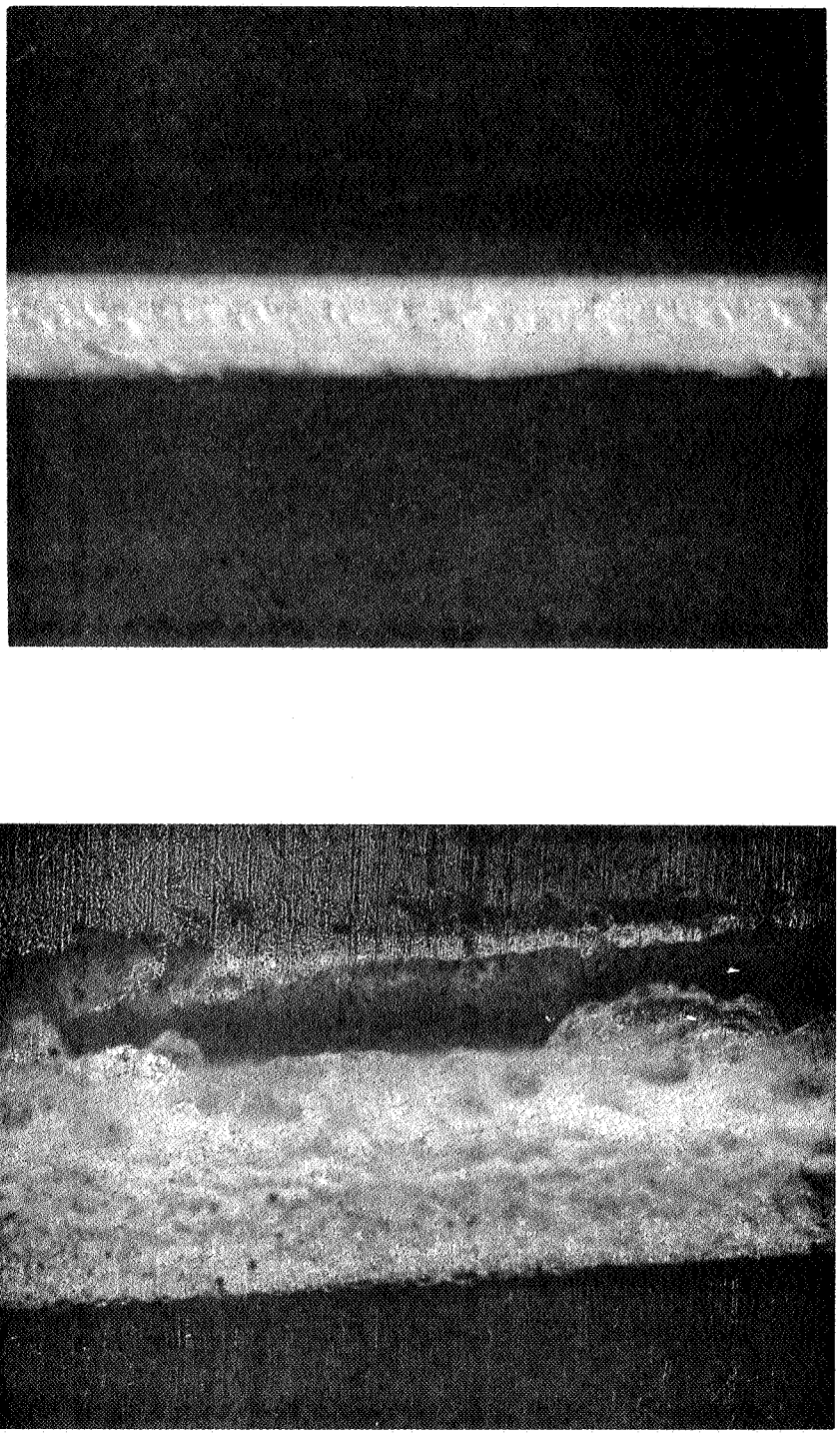
100X Unmounted Edge - Razor Cut



200X Mounted in Paraffin - Microtome Cut

Sample: 5 g $Zr(OH)_4$/15 g Polysulfone/100 ml DMAC, Water Cast No. 87-11-29-3

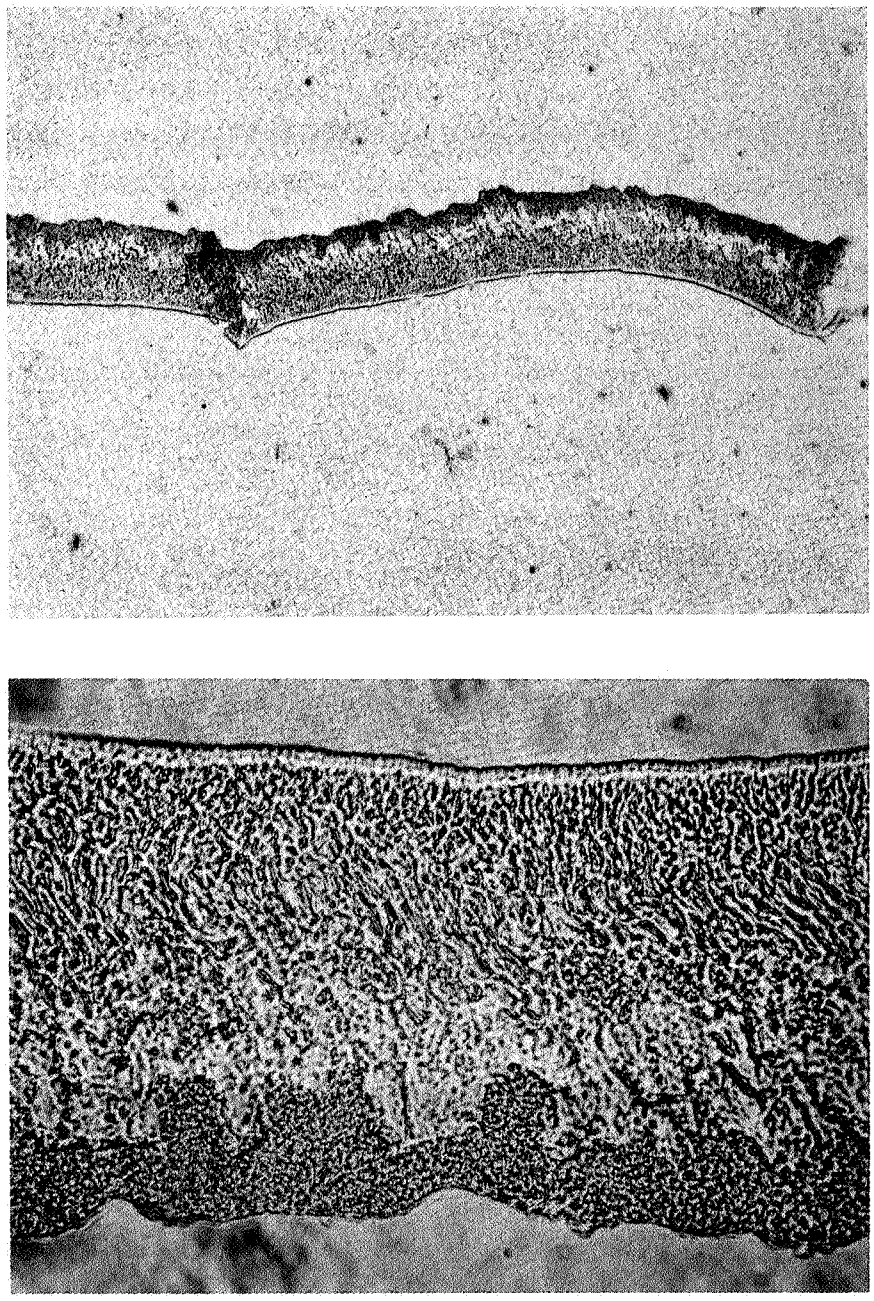
Figure 30



200X Mounted in Paraffin - Microtome Cut

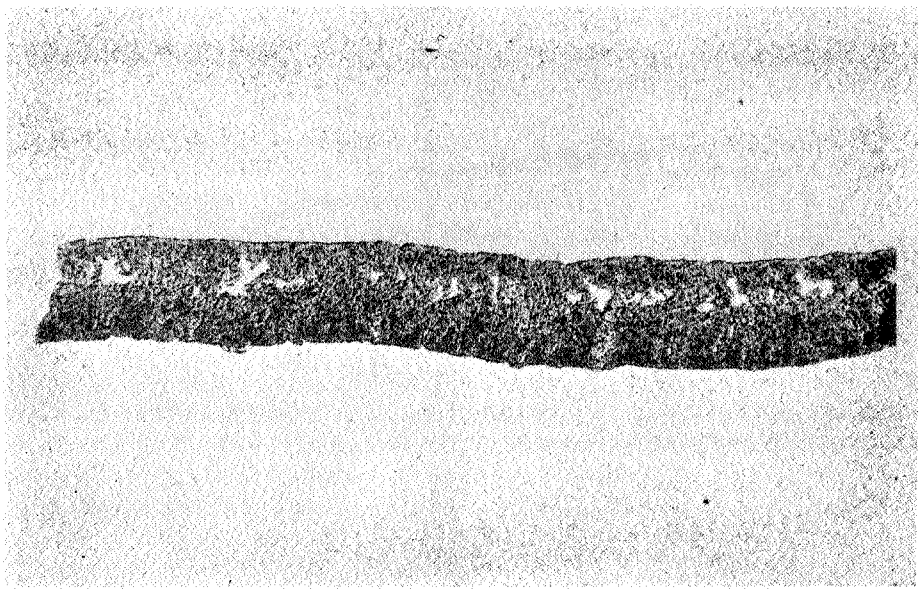
Sample: Unfilled, 15 g Polysulfone/100 ml DMAC, Water Cast No. 83-11-17-2

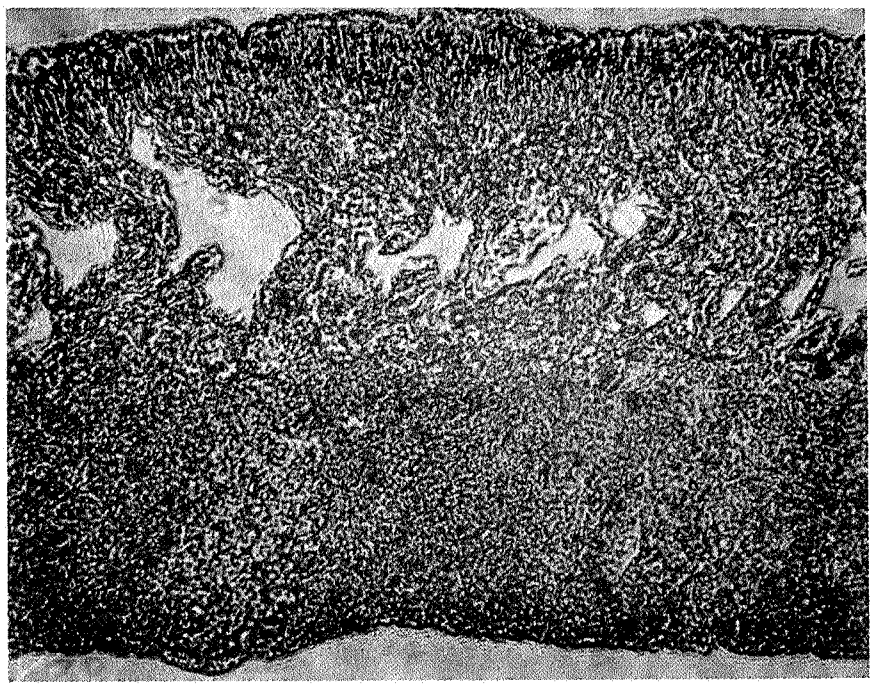
Figure 31



Microtome Cut 7μ thick
Sample: Unfilled, 15 g Polysulfone/100 ml DMAC, Water Cast
No. 83-11-17-2

Figure 32





Microtome Cut 7μ thick
Sample: Filled, 5 g $Zr(OH)_4$/15 g Polysulfone/100 ml DMAC
Water Cast No. 87-11-29-3

Figure 33

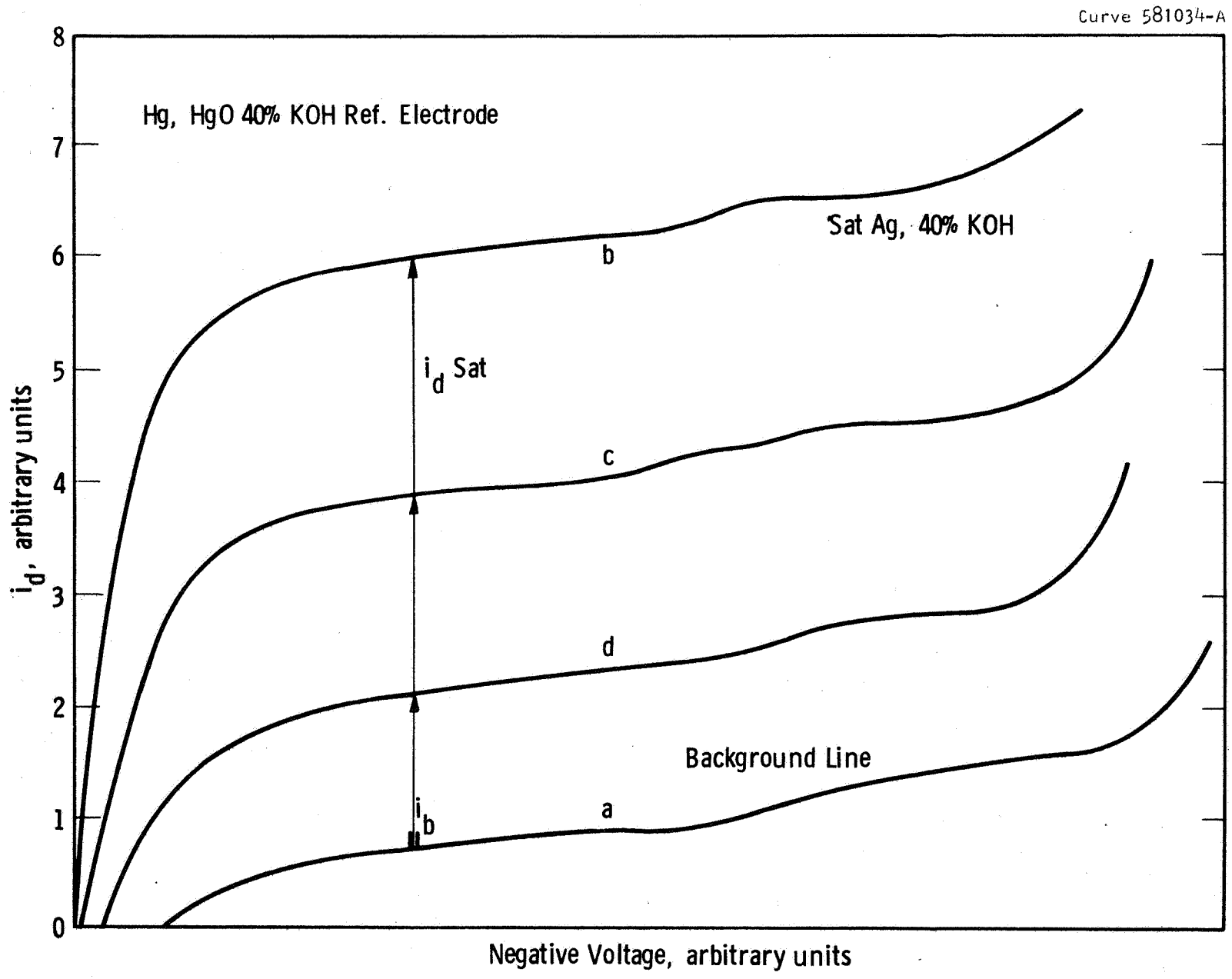


Fig. 34—Polarograms of different silver concentrations

Curve 581033-A

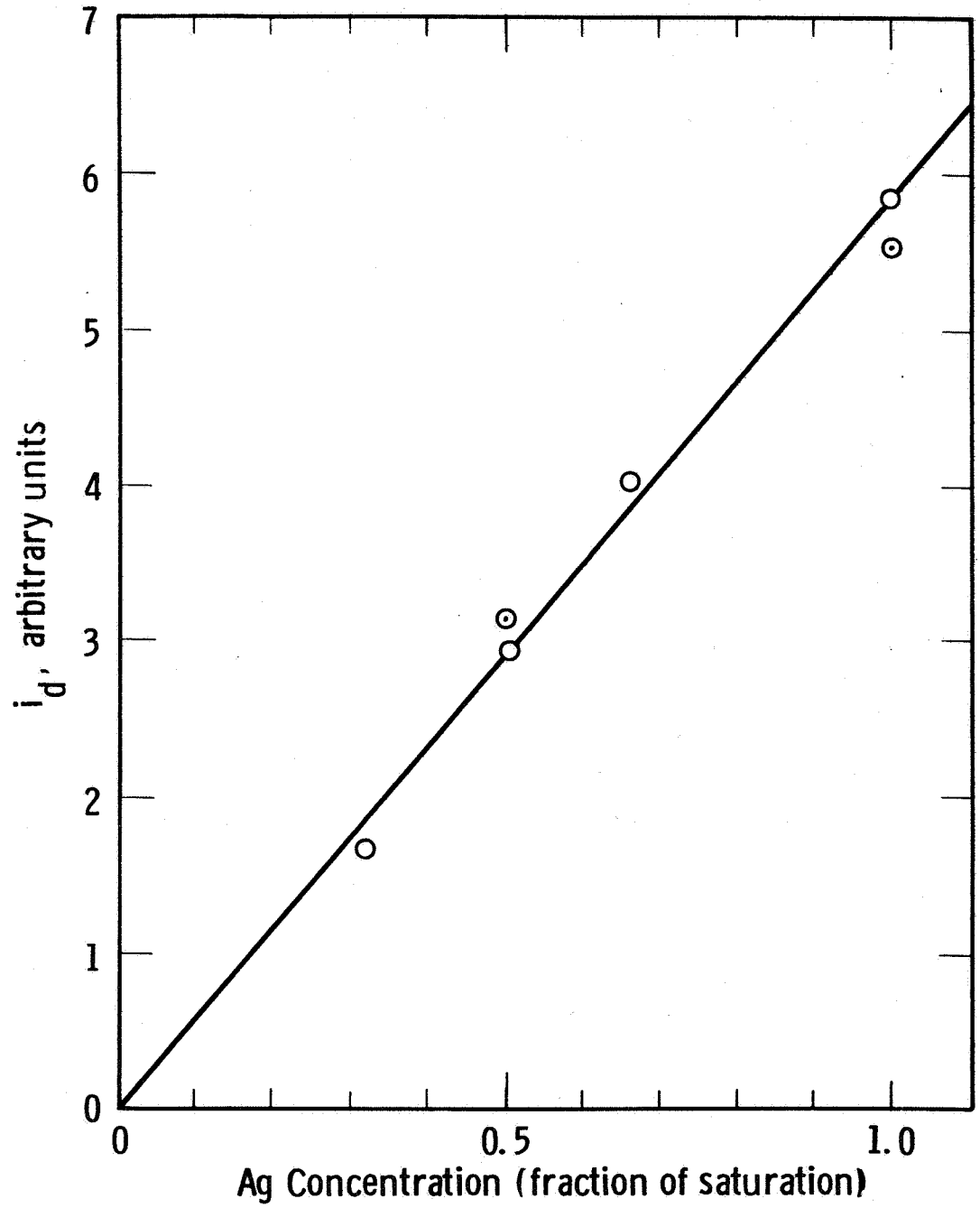


Fig. 35—Relation between i_d and silver concentration

Curve 581035-A

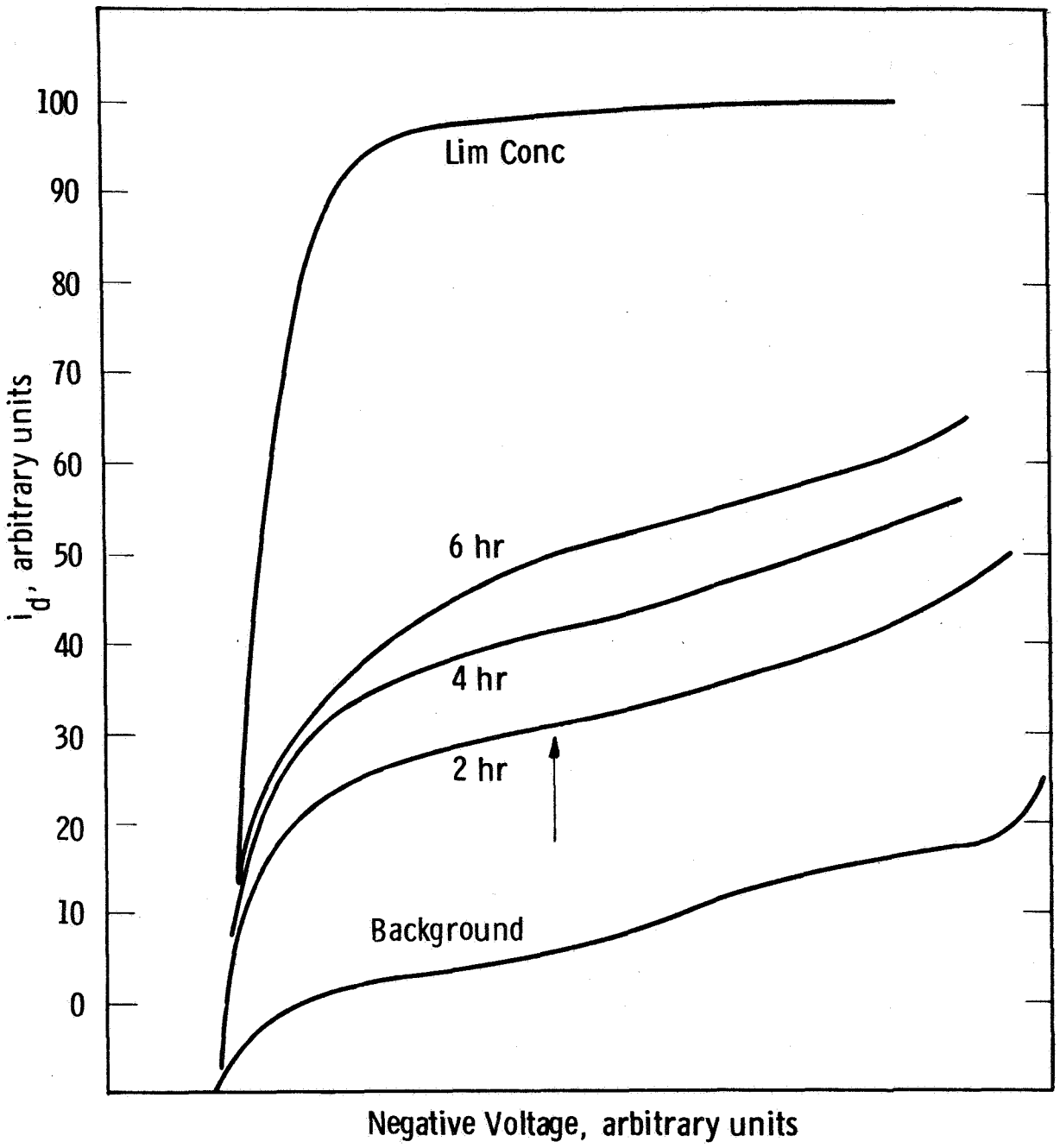


Fig. 36—Polarograms of Ag in 40% KOH
Increase in i_d with diffusion time

Curve 581039-A

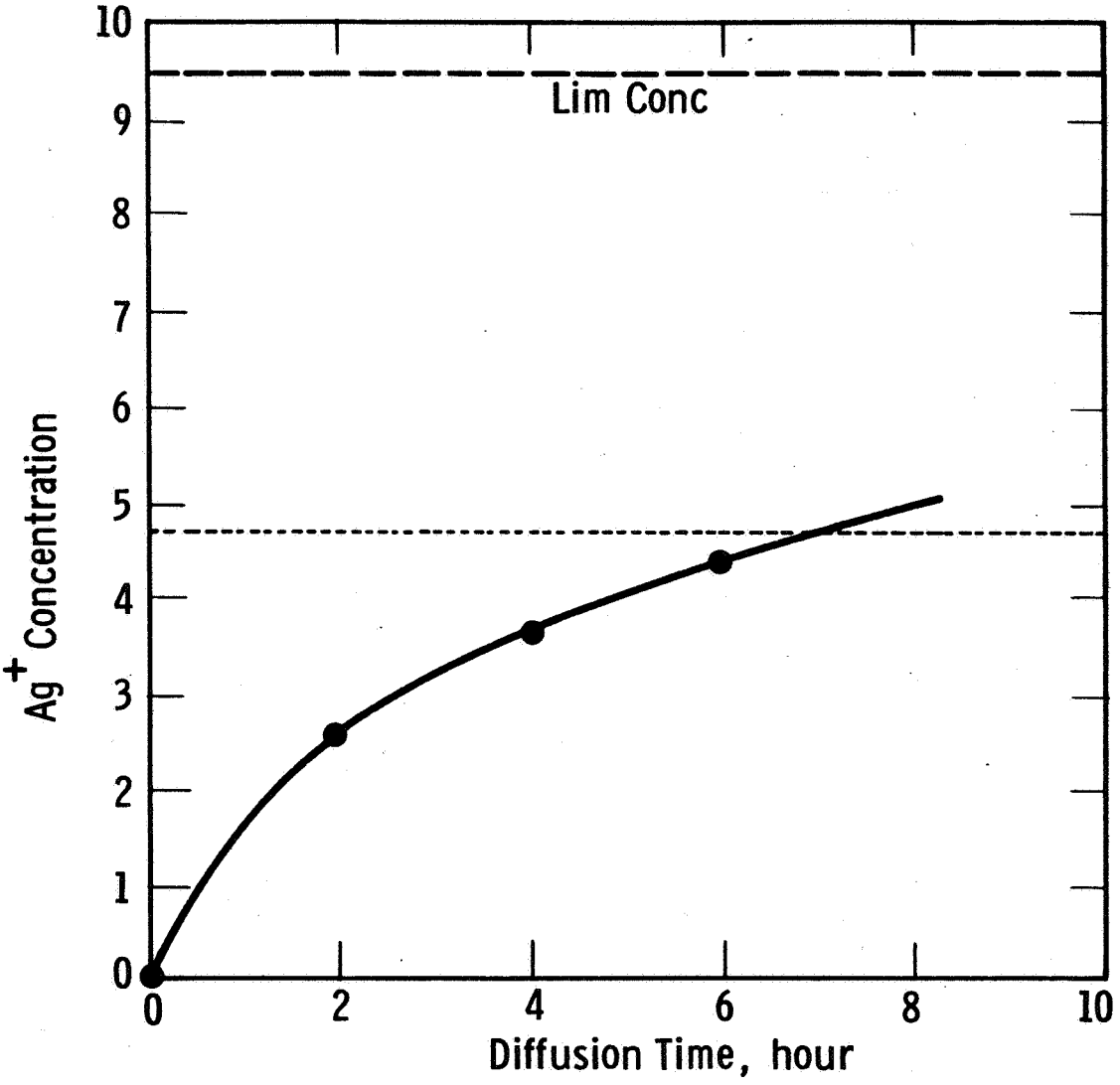
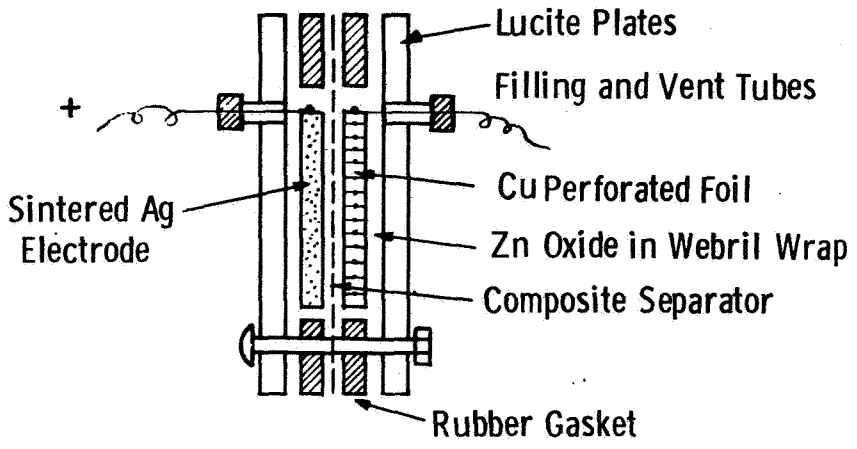


Fig. 37—Relation between silver concentration i_d and diffusion time in hour

Curve 581049-A



Cell Construction

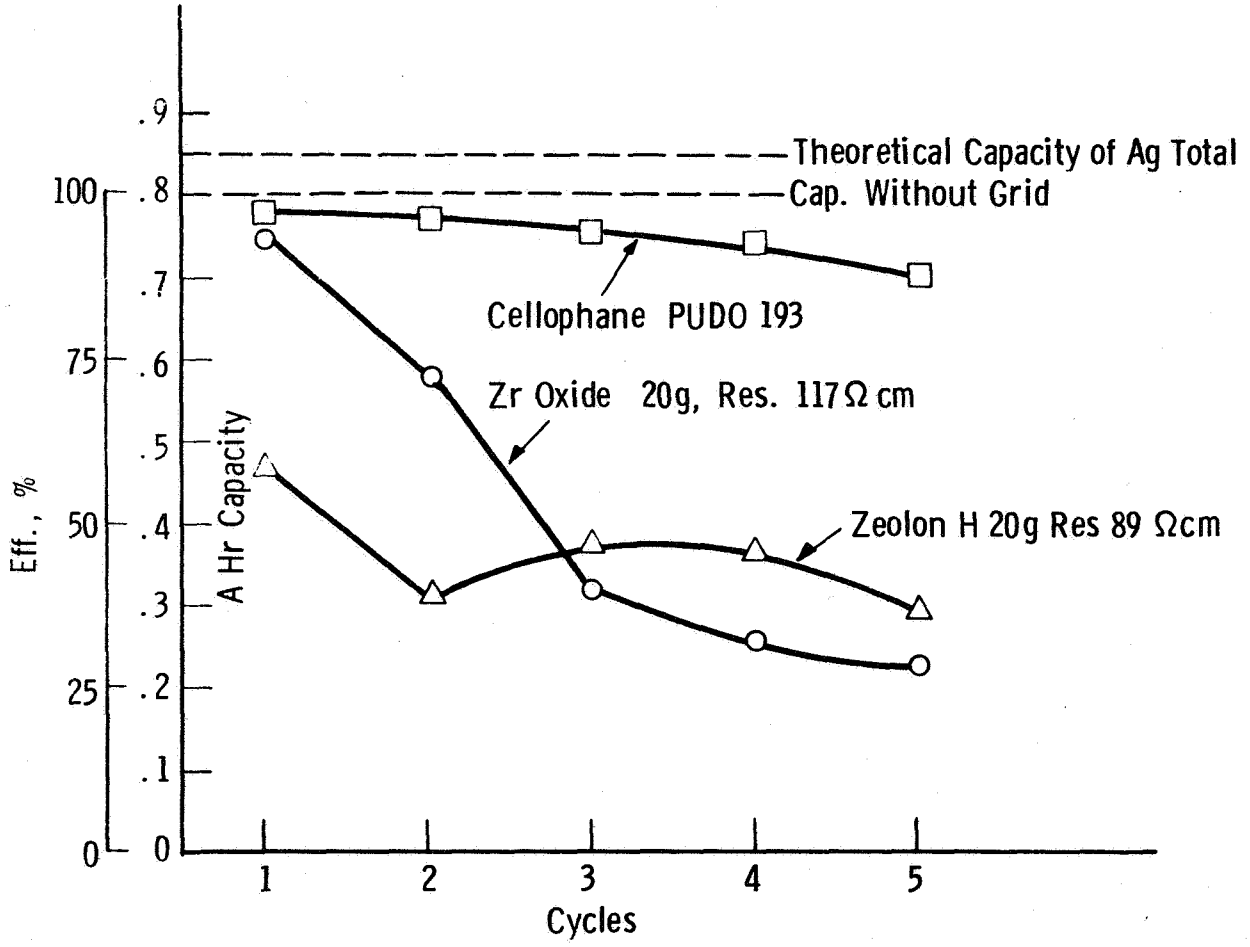


Fig. 38—Performance of a simple Ag-Zn cell with composite separator

Curve 581041-A

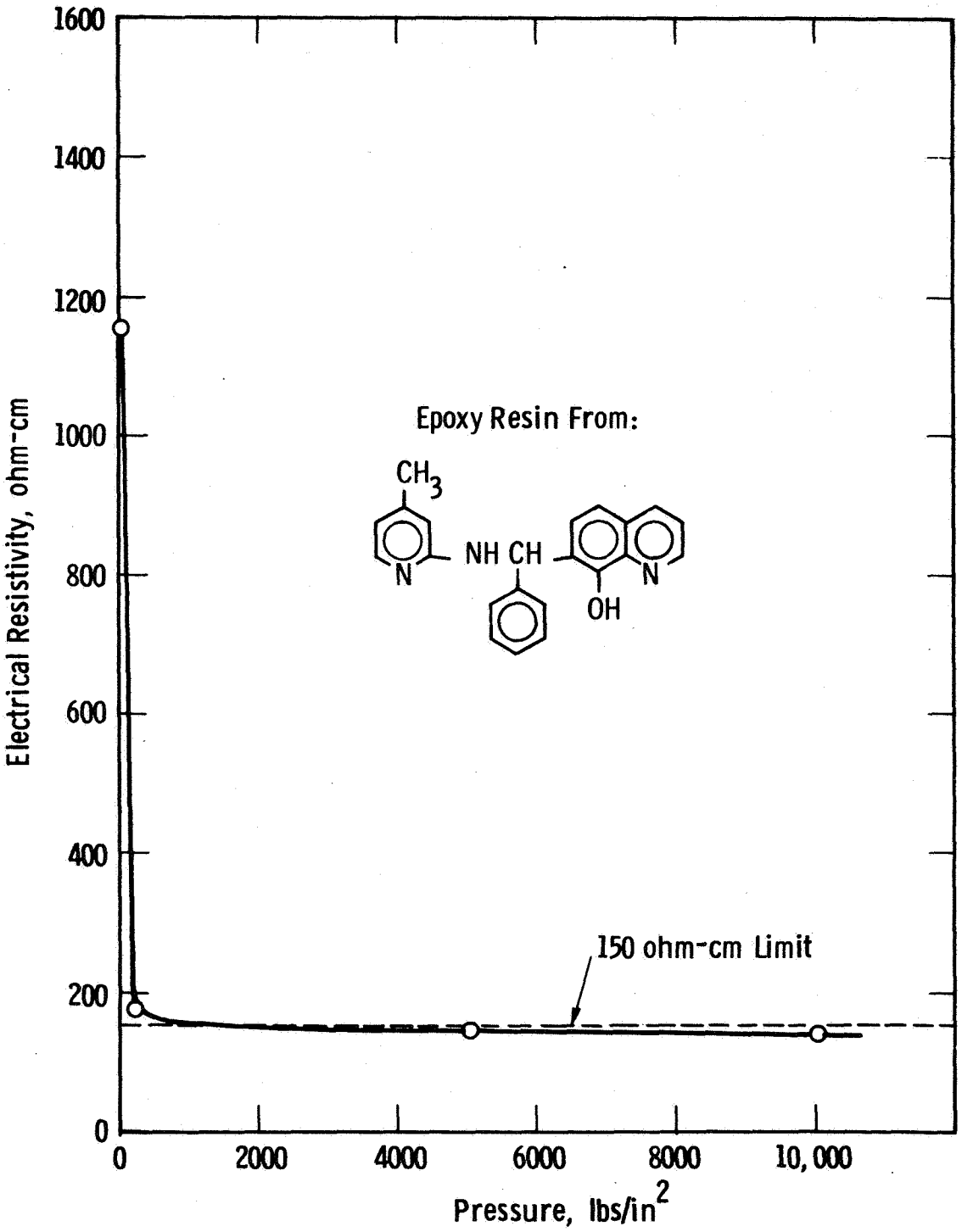


Fig. 39—Electrical resistivity as a function of applied pressure to film

Curve 581040-A

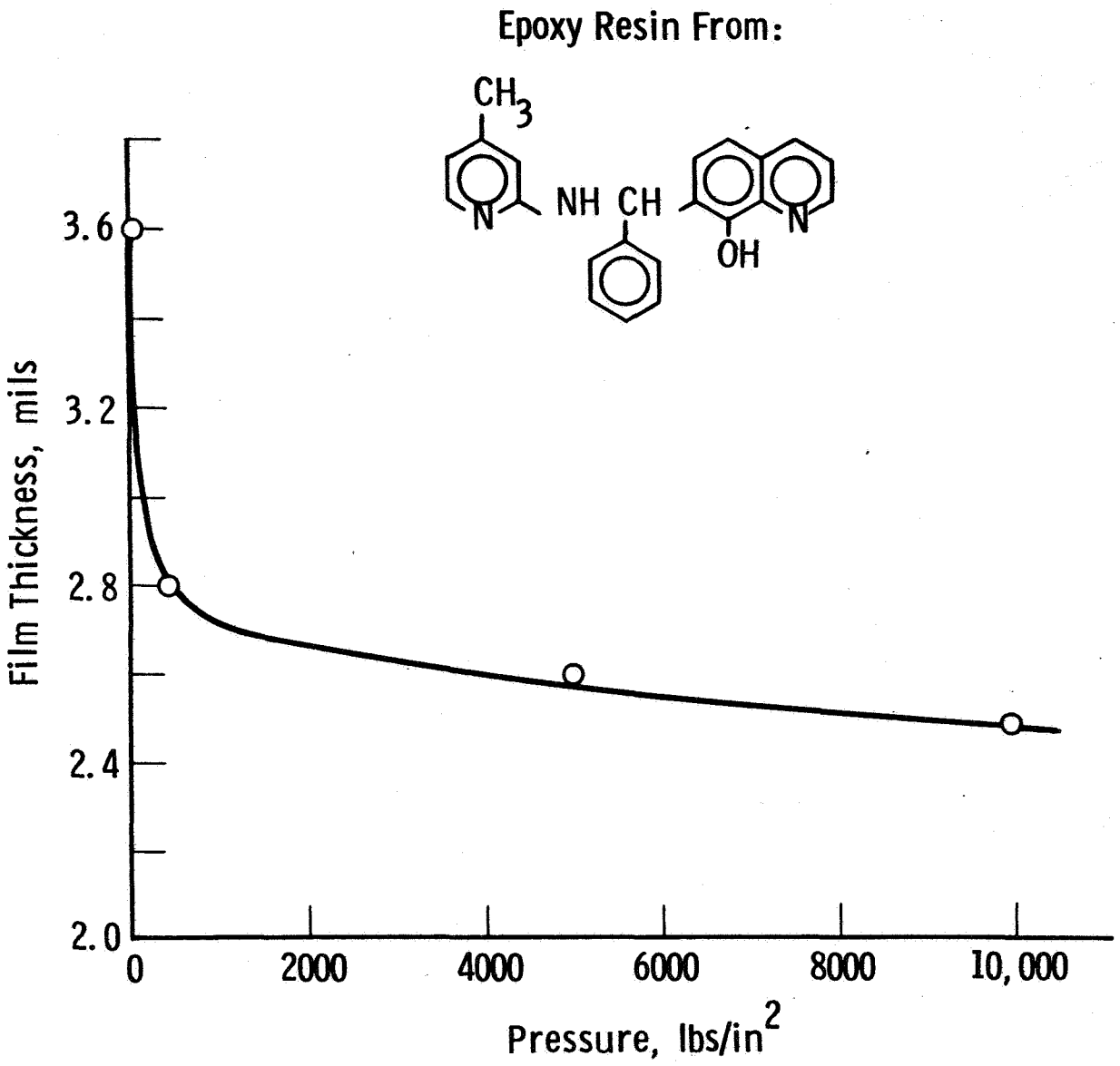


Fig. 40—Film thickness as a function of applied pressure