

ADSORPTION ISOTHERM STUDIES
OF UNSUPPORTED ORGANIC FILMS

by

LAWRENCE EDWIN HOLBOKE

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APPROVED:

Redacted for Privacy

Associate Professor of Chemistry

In Charge of Major

Redacted for Privacy

Chairman of Department of Chemistry

Redacted for Privacy

Chairman of School Graduate Committee

Redacted for Privacy

Dean of Graduate School

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ADSORPTION ISOTHERM STUDIES OF UNSUPPORTED ORGANIC FILMS

INTRODUCTION

History of Protective Films

Paint is perhaps one of the most ancient contrivances of man (2, p. 350-356). There exists today, in Western Europe, paintings executed by our primitive ancestors some 50,000 years ago. Although these prehistoric paints are extremely crude, they are obviously durable. In the period between 8000 B.C. and 1000 B.C., the Egyptian civilization became highly adept in the art of preparing and applying coatings for decorative and protective purposes, as the remaining artifacts of their culture so adequately evidence.

Although the advanced art of the Egyptians passed with time, and the world drifted into the shadow of the dark ages, the need for protection of surfaces against the elements continues. Around 500 A.D. to 1500 A.D. we find many recipes, most of them deep secrets, for the manufacture of rust preventing compounds to be used on the steel armor of the day.

In the Far East, lacquers and varnishes of high quality were being developed independently. Many articles with a "Japan" finish are in an excellent state

of preservation today, after several hundred years. These oriental lacquers used pigments similar to those common in Western practice, and a binder obtained from Rhus Vernicifera, a varnish tree.

The nineteenth century brought the first hint of the technological race now in progress; the quality, quantity, and variety of paint products increased enormously compared to that of prior times. There was, however, very little science in the manufacture of paint, and almost without exception, only naturally occurring oils, pigments, and resins were used.

Synthetic materials made their appearance at approximately the beginning of the present century. Large quantities of nitrocellulose were left unused at the end of the First World War, and in a short time methods were found to convert it to useful lacquers. At about the same time, tung oil began to be imported. Tung oil can be used with lower grade resins in order to produce a lower cost varnish with good quality. Soon a low cost synthetic resin, abietic triglyceride, which heretofore had been unuseable was prepared and sold as a varnish component in large quantities. The Second World War cut short the importation of tung oil and in order to keep up production of vital paints, ways of improving the characteristics of the domestic drying oils were

necessary. Fortunately, they were found.

Corrosion

Paint has always been used to protect iron and steel from attack by water and air, with varying degrees of success. Some coatings applied to ferrous metals will fail within days or even hours under severe conditions. There are also on record cases of paint providing adequate protection of steel structures for forty to fifty years.

As the technology of paint advanced, so did the art of food preservation. From the first real "tin" can, evolved the modern low cost steel container which is produced, distributed, and used profusely.

One of the greatest problems of the canning industry is that of preventing corrosion and the corresponding adulteration and spoilage of preserved food. In order to achieve this, coatings are applied to the inside of the can which, it is hoped, stop or greatly reduce the rate of corrosion. At first metallic coatings were used, and to some extent they are still used, but the greater part of the cans used today are protected by a very thin layer of a non-pigmented synthetic resin varnish. There are many types of resins used for this purpose, and each type has merits, but no coating is completely effective.

THE PROBLEM AND METHOD OF ATTACK

Filiform Corrosion

As stated previously, steel, even when protected by a paint film, is still subject to rusting. In the particular case of a steel can with a thin varnish film and high concentrations of water vapor, a very common type of failure is known as filiform corrosion. As the name suggests, a filament of rust is formed which eventually will destroy the useful surface of the steel. This type of corrosion was named by C. F. Sharman (4, p. 621-622)(5, p. 1126-1127) and has been described by Van Loo et al. (7, p. 277-283).

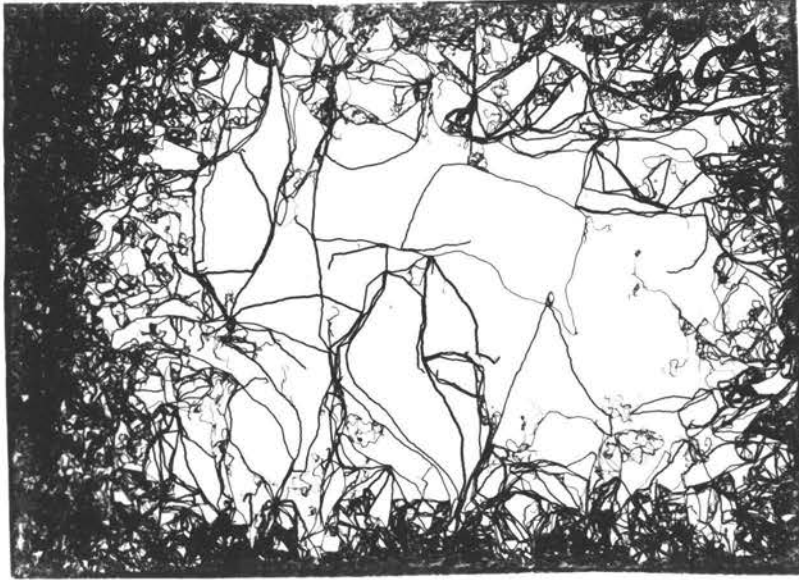
In filiform corrosion a defect in the protective film appears to start the process. Soon a small "head" appears which moves underneath the film leaving a raised thread of hydrated ferric oxide behind. The head is the main subject of interest since in it take place the reactions which start the process and which keep it in action. The head is green in appearance, the front semicircular and the rear V shaped. In the progress of this action one filament never crosses another, but is deflected away from the dry rust deposit.

This type of corrosion takes place when the relative humidity is above 65%, and under films which are

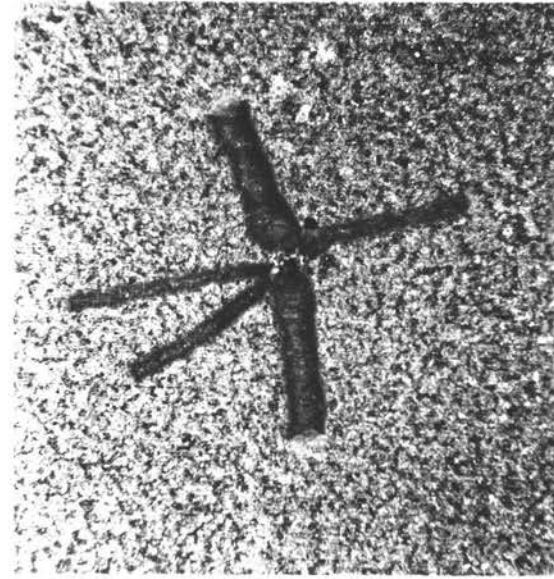
permeable to gases. It is independent of light, grain structure of the underlying metal, and biological activity. Filament growth is faster under thicker films and with wider filaments at high humidities. Figure 1A and 1B display typical examples of filiform corrosion.

A Mechanism

A mechanism for filiform corrosion has been advanced by W. H. Slabaugh and Morris Grotheer (6, p. 1014-1016). According to this theory, water vapor from the atmosphere above the film permeates the film by osmotic action carrying soluble ions present in the film with it as it does so. These ions, now in water solution, are deposited on the iron surface, probably with a certain amount of atmospheric oxygen. A partial oxidation of the iron takes place causing a very concentrated FeII solution with dark green color to be formed. The pressure due to osmosis now becomes quite high, since the vapor pressure of the solution is lowered greatly because of its concentration. The pressure is great enough to break the film to metal bond in the weakest spot around the initial head. The subsequent lifting of the film in the direction of the weakest bond causes the movement which is observed. After the solution diffuses to the under surface of the film, atmospheric oxygen completes the oxidation and ferric oxide is formed which immediately

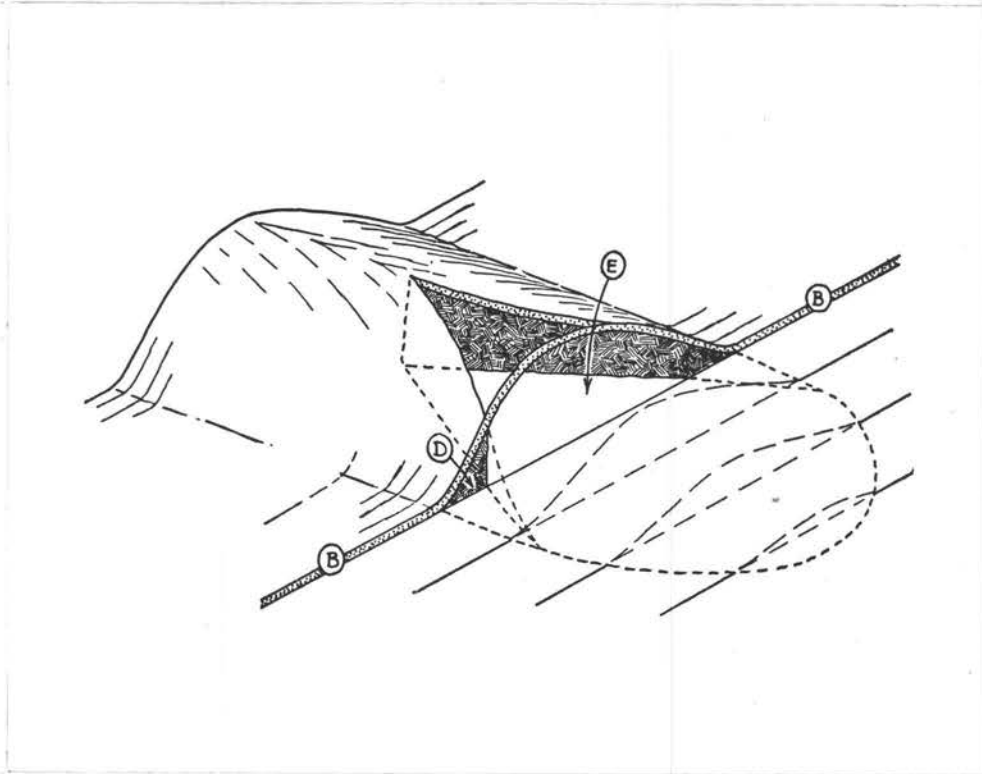


**COATED STEEL PLATE SHOWING
APPEARANCE OF FILAMENTS (1 X)**



**PHOTOMICROGRAPH OF SEVERAL
FILAMENTS, SHOWING ORIGIN AT
COATING DEFECT (20 X)**

FIGURE 1A



SKETCH OF A FILAMENT (100 X)
B. CROSS SECTION OF HEAD
D. FERRIC OXIDE DEPOSIT
E. HEAD, CONTAINING Fe^{II} SOLUTION

FIGURE 1B

coordinates the necessary water from the solution to become the familiar rust filament.

The Role of the Film

In view of the proposed mechanism, it would seem that the characteristics of the film used to protect steel which corrodes holds the key to the problem. Since water vapor and other gases must pass through it, a study of the permeability should be useful in determining ways of stopping filiform. Another characteristic of the film which should be of great interest is the apparent presence of soluble ions. Undoubtedly, a great deal could be learned by a detailed examination of the solution present in the corrosion head. The substances found there would most certainly give clues as to their origin and manner of formation.

Perhaps the most fruitful approach is a study of the way in which water vapor is transmitted through the film. Since large pressures are apparently present in the head, the nature of the film as a semipermeable membrane exercises the controlling influence on the process.

By obtaining adsorption isotherms one might expect to obtain highly relevant information about the surface of the film, the pores which it obviously contains, and something of the way in which soluble materials are

removed from it.

The Attack

It was decided that the best way to approach the problem was from three standpoints:

- A. In order to obtain adsorption isotherms of several types of films, an apparatus is needed in which to place the films, remove the air, and admit a gas. After the films are established in a vacuum and their temperature regulated and accurately measured, a means is necessary to continuously weigh the samples as the adsorbate gas is admitted. This is a standard gravimetric adsorption apparatus, except that since the films are known to exhibit quite small adsorptive properties, it must be capable of detecting very small weight changes without at the same time decreasing the precision. As an adsorbate gas water vapor is no doubt the best choice since it can be used at ordinary temperatures and since the corrosion process is so obviously characterized by the film's physical and perhaps chemical reaction to water vapor. The first approach, then, is to construct a highly sensitive water vapor adsorption apparatus and to use it in the accumulation of adsorption data.
- B. A correlation between the adsorption characteristics of the film used to coat steel cans and the corrosion properties of the coated steel is necessary in order to

evaluate the experimental results. Therefore, there is a need for information about the manner in which the coated steel fails under a variety of conditions. This information may be gained by placing samples of film coated steel in three humidity chambers, noting the filiforms which result and by some method of comparison, obtaining the relative rates of corrosion. It is perhaps impractical to study the effect of temperature on this process since the chambers must be so large and so long a time is involved. By placing a thin layer of various substances on the surface of the film coated steel, one might obtain interesting changes in the process. Washing the coated plates in an attempt to remove soluble compounds before the humidity test might also prove to be a useful test.

C. The time relationships which exist between placement of the test panel in a high humidity atmosphere, the first failure of the film, and development of a corrosion filament are the object of the third direction of attack. The best way of recording these things is by means of motion pictures. In order to speed up the action, relatively long intervals between pictures are needed. Slight magnification is also necessary to make the subject easily visible. This technique may also bring to light new aspects of the process which would otherwise be unnoticed because of their slowness.

EXPERIMENTAL METHOD AND APPARATUS

Adsorption Apparatus and Use

Figure 2 and 3 illustrate the apparatus used to obtain the adsorption data. It is a standard gravimetric type. The sample of film (a) hangs suspended freely on a thin glass rod (b) with a hook on both ends. Three small clips cut from a discarded spring fasten the bundle of film to the rod. The hook prevents it from slipping off the end. The other end of the rod is hooked through a loop at the end of the spring (c). The spring is composed of 300 to 400 turns of copper beryllium wire 0.010 inch thick and wound on a one-half inch form. In order to make a useful spring, heat treatment was necessary. The treatment used consisted of four parts:

1. Wind the wire on a form which conducts heat rapidly, such as an iron rod or, better, a copper tube.
2. Quickly heat to $760 - 780^{\circ}$ C., and remove after two or three minutes if an iron rod form is used or about forty-five seconds if a copper tube is used.
3. Immediately quench in cold water.
4. Reheat to 316° C. for three hours and cool.

The spring thus formed has a sensitivity of about one mg./mm. at 30° C. and a maximum load of 200 - 300 mg.

if the rate of drift is to be kept small. The drift rate after aging was found to be 0.1 - 0.2 mm. per day with maximum load.

The upper end of the spring is fastened to another glass hook sealed into the closed end of a ground glass joint section (d). This section fits into a long glass tube (e) which extends down to enclose the stretched spring and ends in a ball joint (f). The function of the upper joint is to permit removal and insertion of the spring from the top where it is most convenient, rotation of the entire suspension, and adjustment of spring length. Inserting a link between the hook and the spring end, thus making the spring longer, or hooking the spring further down, making it shorter, is accomplished here. At the ball joint is attached a short length of tubing with another closed end. This encloses the sample.

Nine such columns are used, four on each side house the eight springs with their attached sample, and the central one contains a thermometer, in order to measure the temperature of the air bath. All nine columns pass through a wooden box, lined with aluminum foil and faced with glass. Each column is connected through a separate stopcock to the vacuum system. The stopcocks permit localization of small leaks. It was

necessary to lap the ball joints with silicon carbide compound to prevent fine leaks from developing.

Copper-beryllium springs are quite sensitive to temperature changes. To keep the temperature constant, a blower (g) circulated air over a cooling coil (h), a lamp bulb (i), and through the enclosure. The lamp is controlled through an electronic relay (j) by a bi-metallic thermo-regulator (k) mounted at the center of the bath.

Considerable difficulty was experienced in maintaining a temperature which was adequately constant. The thermo-regulator and thermometer respond so slowly to air temperature changes, that many adjustments were required in order to reproduce the 30° C. chosen. A certain amount of drift in the thermoregulator was noted this required periodic adjustment even after the correct temperature was initially reached. The temperature as noted on the thermometer in the center tube did not vary more than 0.1 - 0.2 degree with close attention, which caused a spring movement of about 0.1 mm.

The lower tube sections, containing the film samples, are immersed in a water bath (e) which is maintained at the proper temperature by an arrangement similar to that used for the air bath. This temperature was very constant and did not vary more than 0.1 degree, barring

equipment failure. A pump (n) circulates water from the reservoir (m) to the far end of the bath, whereupon it flows over the sample tubes, through a siphon, and back to the reservoir. Large tubes are used to insure rapid circulation, and as a result no detectable temperature difference existed in the system.

The means of measuring spring extension is shown in Figure 3. The thin glass rod between the end of the spring and the sample holds a short rod segment which is slightly larger in diameter. Clear cement holds the segment in place. Behind the column is mounted a light source which consists of a six volt automobile lamp (o) and a condensing lens of the type used in eight millimeter motion picture projectors (p) supported in an aluminum frame. In front of the tube is a telephoto lens of six inch focal length. The condensing lens focuses the lamp filament image on the rear element of the telephoto lens, and after proper adjustment, an image of the two rods is projected on a chart (q) fastened to the wall of the laboratory. In this way a magnification of approximately thirteen times is achieved. The inset of Figure 3 shows the appearance of the projected image. A circular field is produced and when the weight of the sample changes, the image of the rod moves thirteen times as far as the rod itself. The segment cemented to the

support rod is cut so that its image is slightly shorter than the diameter of the field, thus when the top of the rod image disappears, the bottom comes into view and the working range is nearly doubled. The chart is covered with a rough surfaced clear plastic sheet so that pencil markings may be easily erased when a run is finished. Each column is so equipped and current for the lamps is distributed by a solenoid actuated rotary switch. A push button above the chart controls the solenoid and switches current from one lamp to the next, from the first through the eighth and then repeats. Readings of all eight columns can be made within one minute.

In order to find the adsorption curves of one to eight samples, the films are first weighed on an analytical balance to the nearest milligram, placed in the columns, temperatures regulated, spring length adjusted, and the chart positions marked. Then pumping is started. A two stage mechanical pump was sufficient to reach a pressure of one to ten microns.

After a time when all adsorbed material is thought to be removed, the chart is again marked. By using previously obtained calibrations, the true dry weight of the sample is calculated. There is an error in weight by this method since when the air is removed so is its buoyancy on the suspended objects. The error was calculated to be about 2 milligrams, which was found to be

insignificant. Changing the temperature of the water bath had no effect on the chart readings.

Now the run is started. The tube (r) containing previously degassed water is opened, and closed when approximately the desired pressure is noted on the oil manometer. This reading is 15.5 times larger than the mercury manometer reading and so is much more accurate at low pressures. It was found that a gas of some sort diffused very slowly out of the oil and caused a small error in the pressure reading, of two to four mm. of oil in 48 hours. This also was neglected as insignificant. After sufficient time for equilibrium, the chart is marked, the manometer read and recorded, and more vapor admitted. The chart readings are converted into weight changes by use of the spring calibrations. Continuation of this process results in a complete isotherm.

Preparation of Films

The films were supplied as varnish coatings on CMQ steel plate selected for uniformity of surface and composition. Table I gives the identification and approximate weight of the coatings.

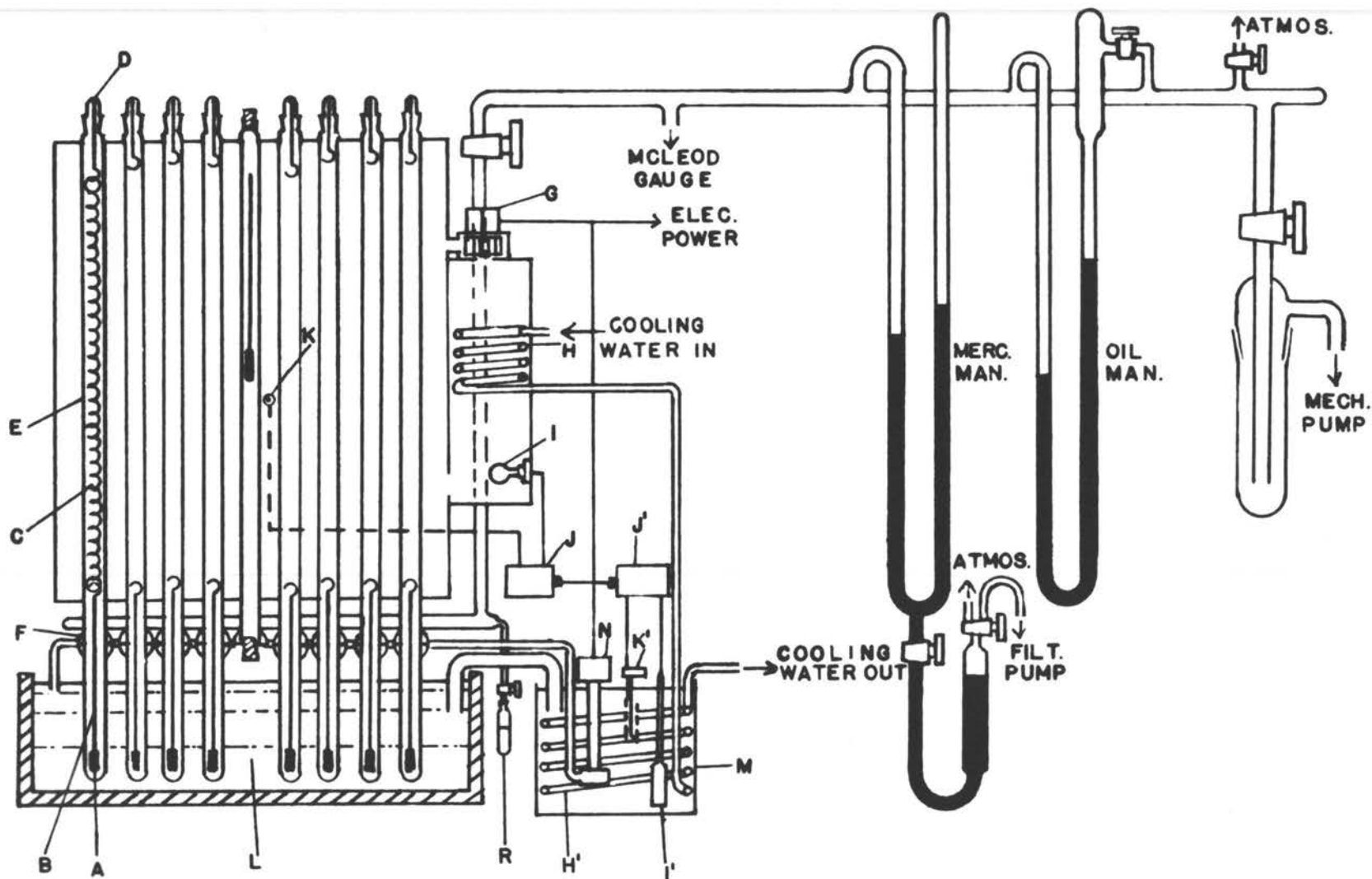


FIGURE 2 ADSORPTION APPARATUS

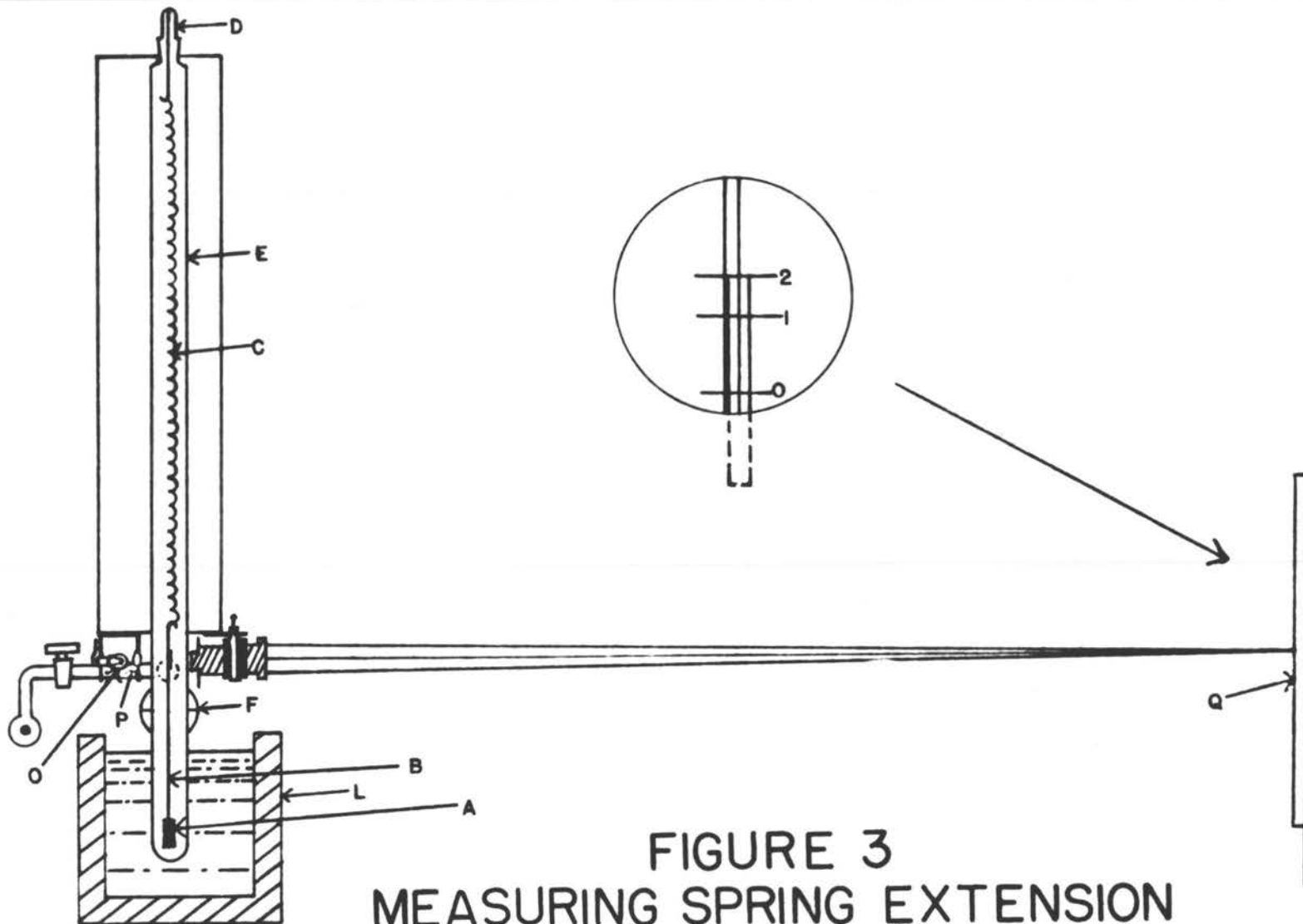


FIGURE 3
MEASURING SPRING EXTENSION

Table I

DESIGNATION OF POLYMER FILMS

Film Number	Type	Weight mg./4 in. ²
I	Oleoresinous F-9	22
II	Phenolic P-2	17
III	Vinyl X-21 Heavy	26
IV	Vinyl X-21 Light	13
V	Alkyd 10-E-55016	22
VI	Epoxy E-5	17
VII	Hydrocarbon DX-15	18
VIII	Hydrocarbon DX-15B	20

An electrolysis method was used to remove the coatings. Plates three by four inches were first placed in a steam bath for one to three hours, depending on the type of coating, then electrolyzed in a 1% sodium carbonate solution using a potential of six volts. A platinum foil was the positive electrode, and the steel panel the negative electrode. Electrolysis continued until hydrogen formed on the steel surface completely loosened the film. There is probably a change in the character of the films due to this treatment, but it is an efficient method that is generally accepted. An attempt was made to apply varnish to plates with a layer

of a mercury-tin amalgam on the surface, but it was not successful.

The greatest difficulty was experienced in trying to keep the films made in this way in one piece. After removal from the electrolysis bath, the plates were immersed in distilled water and the films slipped off. After washing, the films were dried on a frame of glass rod, either at room temperature or in an oven at 80° C. or less. Upon drying, the film almost invariably stuck to the frame, and it was necessary to cut around the edges to remove it. Several of the films are very fragile and brittle when dry. Film II gave the greatest difficulty in this connection. With sufficient time and patience, however, approximately 250 mg. of each type was obtained in large enough pieces to permit suspension from a spring without the use of a bucket.

Corrosion Tests

Three humidity chambers were used to find the relative corrosion rates of the various coated panels at 70, 80, and 90 percent relative humidity. These chambers were large glass cylinders with a flat glass plate sealed to the top with grease. Saturated salt solutions kept the humidity constant; ammonium nitrate and potassium chloride for 70%, ammonium sulfate for 80% and sodium carbonate decahydrate for 90%. No attempt

was made to control the temperature of these chambers, even though a temperature change caused a humidity change, since only a comparison of corrosion rates was desired. The variation in room temperature was not great enough to cause important errors.

Three by four inch plates with the eight different types of coatings were placed in each chamber. Forty-eight additional plates were placed in the 80% chamber. Each of the eight types were treated in six ways. The treatment consisted of applying a two percent solution of:

- a. sodium chloride
- b. sodium hydroxide
- c. sulfuric acid
- d. potassium chromate
- e. thiocurea

The sixth treatment was a 14 day immersion in running water (w). Only half of the plate was treated, the other half being left as a comparison. The solutions also contained two percent detergent which was necessary to wet the film with a break free layer of solution.

Exposure of all the plates was started at the same time, and they were periodically examined. After a reasonable amount of corrosion had occurred, a plate was removed and placed in a dry box to stop the action. All

plates still in the chambers after nine months were also removed. The time of exposure, the treatment, and the humidity were marked on each plate.

Photography

The most convenient corrosion system to follow photographically was a vinyl film with sodium chloride coating at 90 percent relative humidity. Filiforms grow rapidly and are about one millimeter wide. They are very characteristic of this type of corrosion.

A sixteen millimeter motion picture camera with "through the lens" focusing was used. A solenoid operated cable release actuated the single frame release on the camera. Light was provided by a ring of ten six volt flashlight lamps. Current for the lamps originated in three two volt lead-acid cells connected in series and was controlled by a relay. The wet cells were kept continually charged by a trickle charger supplying 0.25 ampere. The lamps consumed 0.5 ampere each for a total of five amperes. The filament temperature was measured with a pyrometer and found to be around 3500°, so that color film balanced for a 3400° source was used without compensation.

The solenoid and relay were connected to a timing unit consisting of a recycling timer and two thermostatic delay relays. In operation, the lamps are turned on,

followed in three seconds by operation of the solenoid, which causes the camera to photograph one frame. After two seconds more, the solenoid is released and in another three seconds the lamps are extinguished. The complete cycle is repeated at intervals depending on the gear combination used in the recycling timer. A fifteen minute interval was found to be satisfactory for an apparent rate of growth suitable for detailed examination.

Two methods for obtaining magnification were used. The first utilized extension of the standard lens so that image distance was smaller than object distance. This was unsuccessful because the lens did not have sufficient resolution and flatness of field in that arrangement.

The second method used a three inch telephoto lens on the camera with the standard one inch lens fastened to the front so that the light passed through the one inch lens in a reverse fashion. The two lens arrangement resulted in much better pictures.

THE DATA

Adsorption

Several adsorption runs were made. The curves obtained showing the least divergence of points are reproduced in Figure 4. Along the abscissa is plotted the pressure of water vapor in millimeters of mercury. Along the ordinate is weight change of the sample in milligrams per gram of film. The temperature of the samples was held at 27° C. The adsorption and desorption curves were made in approximately 14 steps, each with a 60 minute interval between to allow equilibrium to take place. A period of 12 hours elapsed between the end of the adsorption curve and the start of desorption during which time the pressure decreased spontaneously and the weight increased.

The two vinyl films, III and IV, showed such very little adsorptive properties that no meaningful data could be obtained. Indeed, the buoyancy effect of the water vapor proved to be greater than their weight change at lower pressures, and the increased adsorption at higher pressures near the top of the curve still did not provide measurements greater than the errors of the system. The buoyancy effect on the other samples was relatively very small and was neglected.

It is observed that neither end of the curves meet in most cases. Even extended pumping periods did not cause the springs to return to their original positions. This behavior was not due to spring drift since the original drift figure, 0.1 mm/day, grew smaller as time passed and at the time of the run was practically immeasurable over periods of a week or two. Also, the wide variance of nonreturn characteristics is a negative indication of drift, since all springs had nearly equal drift rates.

Curves were also obtained at 17° and 37° C. using the same techniques as at 27°. Three of these are displayed in Figure 5. The axes are the same here except for an expanded ordinate scale in order to better show the 37° plots. The other samples' behavior bears a similar relation to the 27° data as the three shown do. The average slope increases as temperature decreases, as does the shift in endpoints. The shape does not change appreciably with temperature. The 27° curves were omitted for clearness sake. They lie approximately midway between the 17° and 37° lines.

While the apparatus was still being adjusted and improved, partial isotherms were obtained over a long period of time using films I, II, and VII. These had varying intervals between readings but usually were

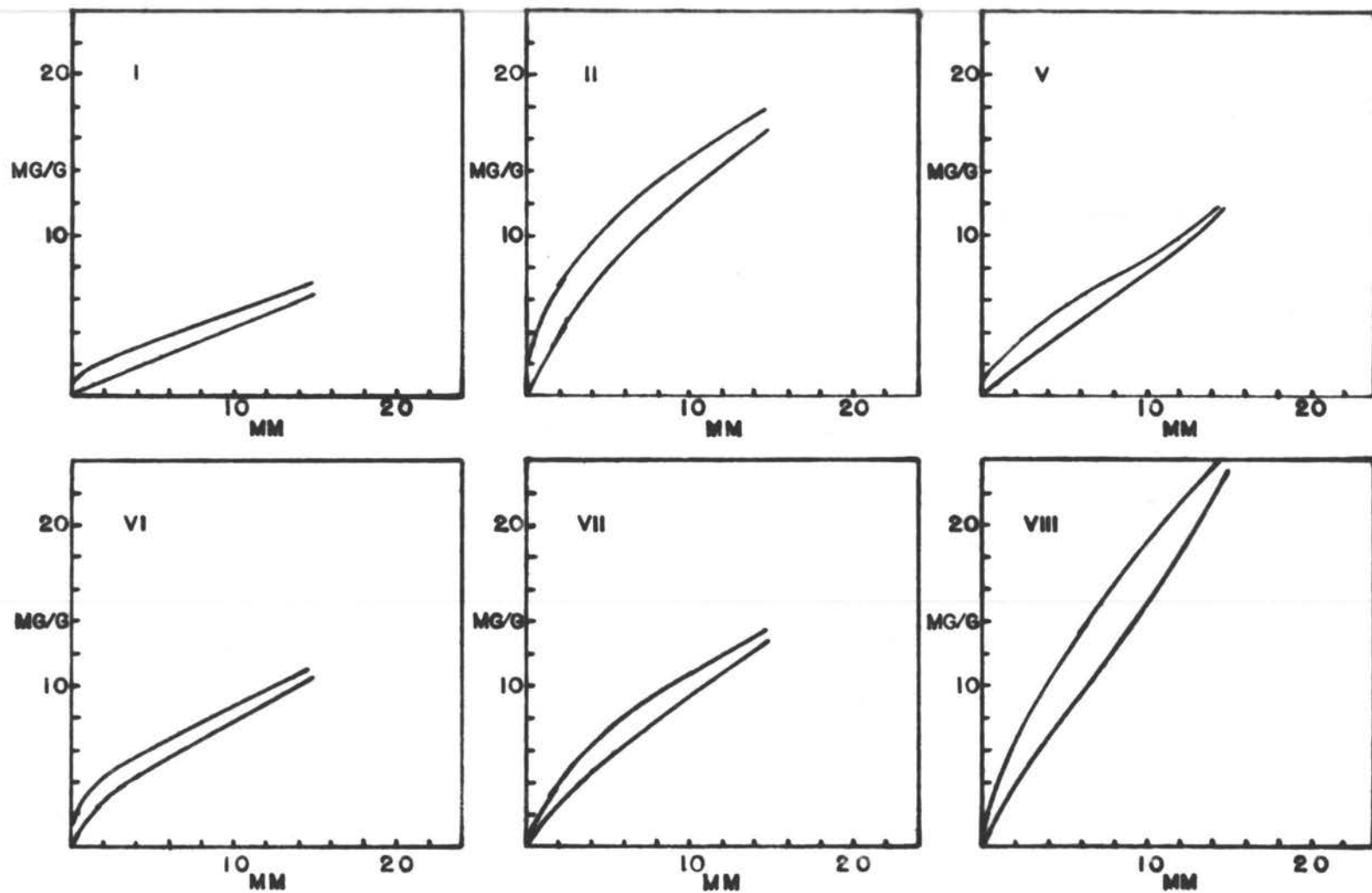


FIGURE 4

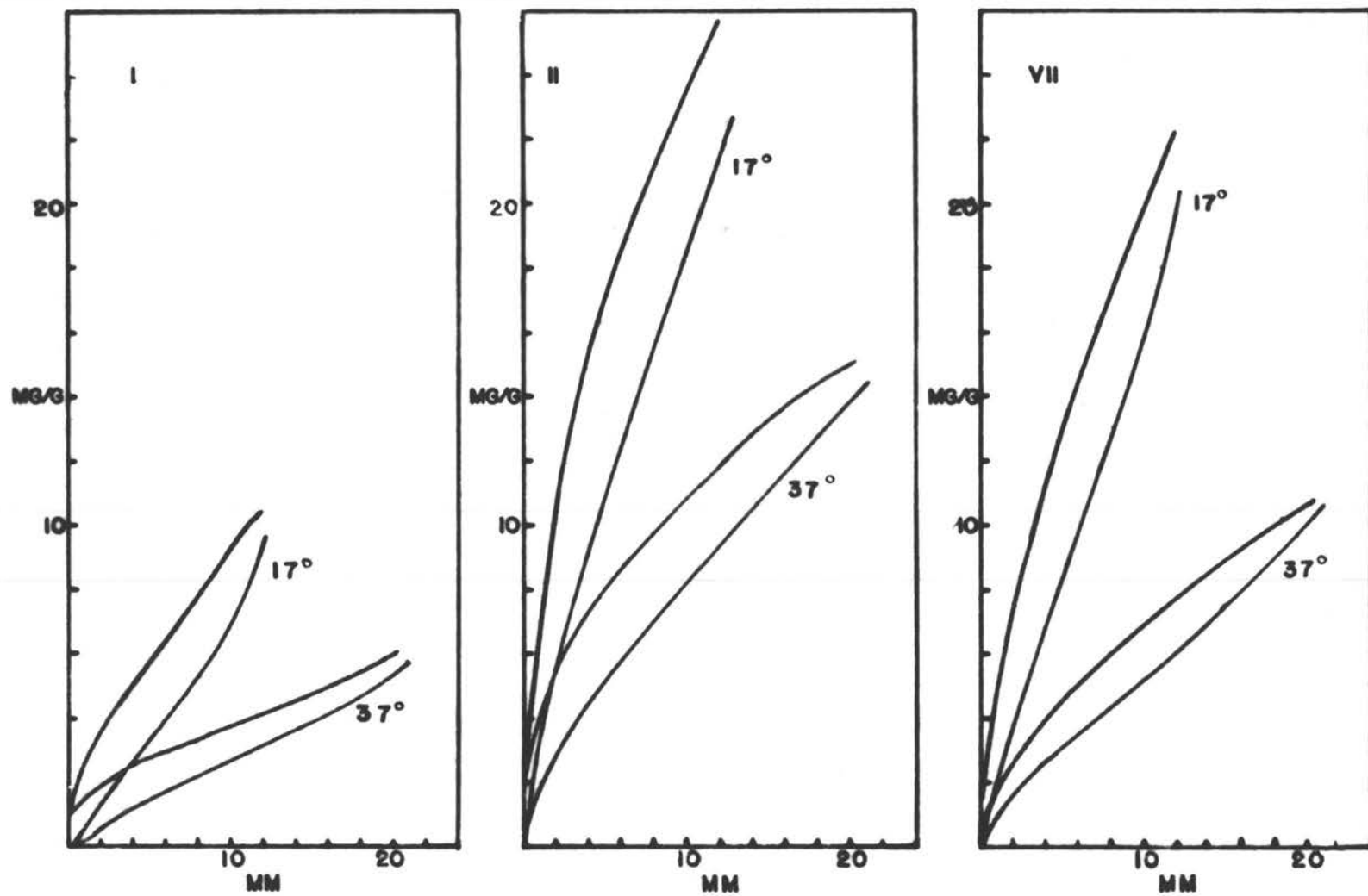


FIGURE 5

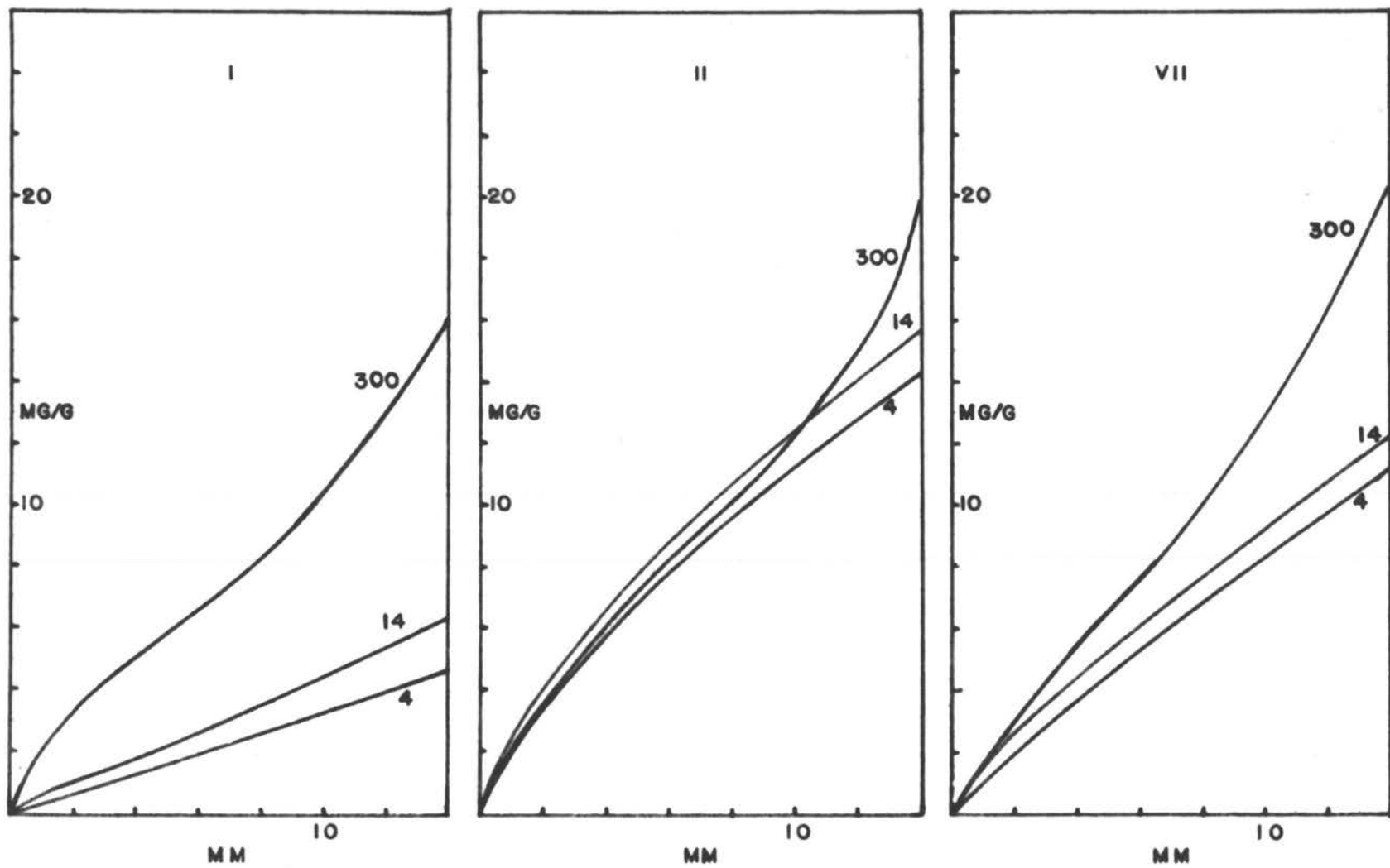


FIGURE 6

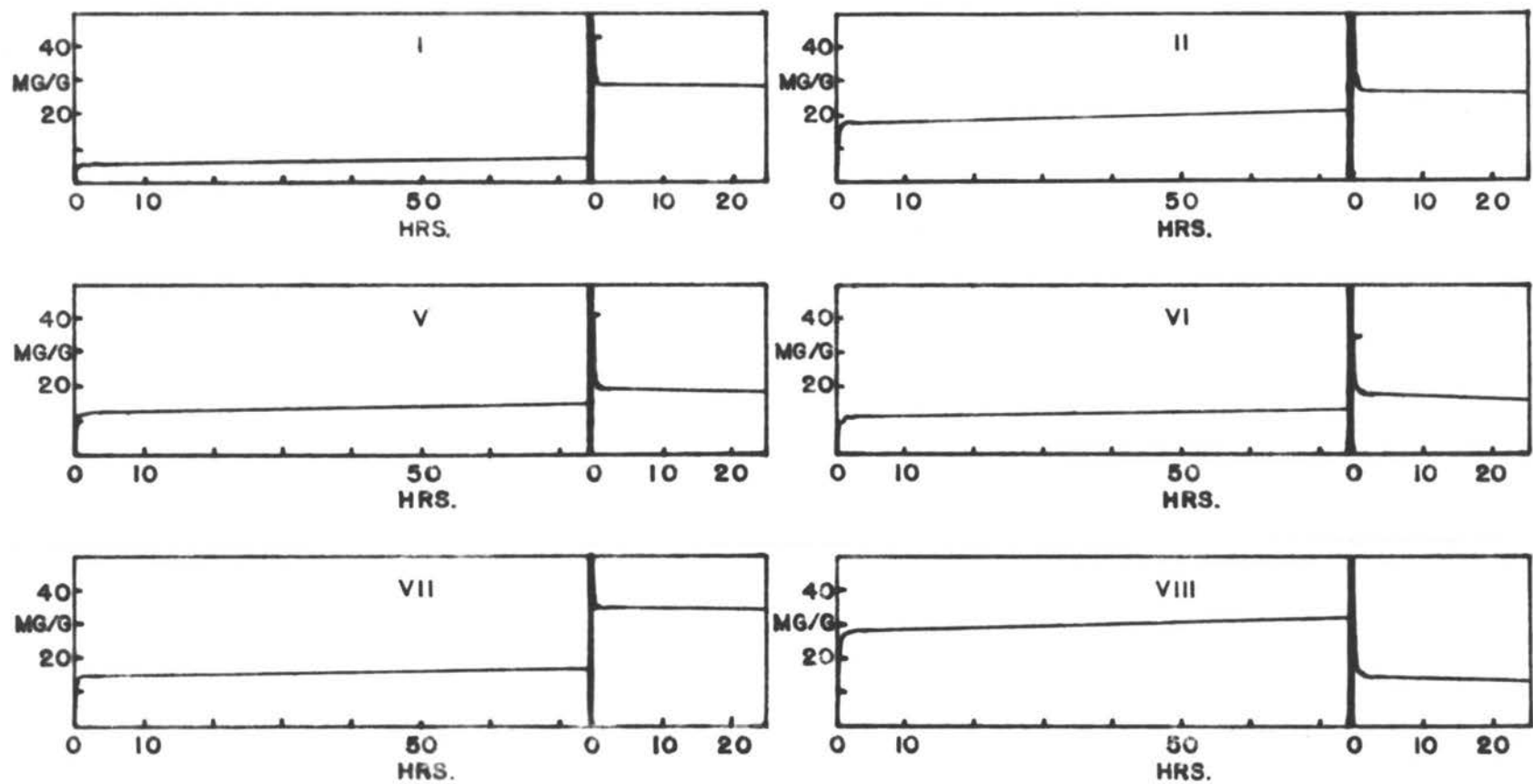


FIGURE 7

several hours. They reached only to 14 mm. of pressure because of leaks developing in the system.

The points gathered then were rather widely scattered and therefore were not seriously considered since it was thought that when apparatus improvements were completed, this scattering would cease.

Later, when improvements were finished, isotherms on all films were done at three different temperatures using a 30 minute equilibrium period. This was considered quite sufficient since diffusion of water vapor through the films has been shown to take place very rapidly (3)

In spite of the high diffusion rate, the films still appeared to gain weight upon standing for periods longer than 30 minutes. In order to find a satisfactory interval, a rather rough experiment was carried out to determine the relation between adsorption to equilibrium conditions and the time involved. The experiment seemed to show that 60 minutes would be a better interval. Accordingly, complete adsorption-desorption isotherms were run at three temperatures using a 60 minute interval. These are the subject of Figures 4 and 5. Prior to this time, desorption isotherms were not attempted.

The endpoint shift and apparent hysteresis still pointed to a lack of equilibrium.

Then the early long-time curves were recalled. It was thought that a comparison of these, the 30 minute and the 60 minute plots, would give an indication of the time required for true equilibrium. Figure 6 compares these isotherms. The time required to reach 14 mm. pressure is marked near the corresponding curve. Obviously, equilibrium is not reached in any reasonable length of time, at least in the case of I and VII. Drift cannot account for the divergence for it is not rapid enough; also the lack of divergence in II negates that possibility.

It seemed as though a very slow reaction was taking place between the film and water vapor. A kinetic study of the films appeared to be the next reasonable step. A plot of sample weight as a function of time is shown in Figure 7. At time 0 at the far left of the plots a pressure of 9.6 mm of vapor was admitted at 17° C. and more for the first few hours to keep the pressure constant. All the films immediately adsorbed a certain amount, but then a slow continuous increase began which was considerably greater than the spring drift rate. At 74 hours, the solid line indicates a raise of temperature to 27° C., pressure to 21mm, and a lapse of ten days. Film number II, VII, and VIII gained such a large amount that they were no longer measureable. The weight of the

others is shown by a small horizontal line.

After the ten day period, the vapor was removed and the amount of desorption shown occurred with an inverted form of the adsorption curve. The wide variance of nonreturn again points away from spring drift as an explanation.

All the evidence so far pointed toward a very slow, possibly irreversible, hydrolysis reaction. In order to prove this assumption the film samples were removed and reweighed, it being obvious that they must be considerably heavier than when first installed in the columns.

Every sample was found to have exactly the same weight as recorded earlier. This was indeed surprising. The only possible explanations for the apparent weight gain were a large adsorption of water vapor either by the spring or by the glass suspension rod. The fact that the phenomenon was slow tended to discount the possibility of pure physical adsorption, since this is nearly always quite rapid on simple surfaces. The most reasonable choice appeared to be either a reaction at the spring surface or slow physical adsorption on a modified complex spring surface caused by the rigors of heat treatment. The very small amount of glass present made it seem extremely unlikely that it could be responsible.

In the small amount of time available, an experiment

was conducted to determine the effect of high humidity on the springs. All eight springs were loaded with glass weights of approximately the same weight as the samples the springs previously supported. Four of the columns were evacuated and the other four were filled with water vapor to reach about 90 percent relative humidity. The positions of the springs were marked at the outset and every 24 hours thereafter. At this writing, two springs have been exposed 72 hours, two 48 hours, and four for 24 hours.

All the springs experienced a small initial drift which disappeared after an hour or two. The dry springs did not go beyond this point. The springs exposed to water vapor in all cases continued to lengthen with the passage of time. However, the greatest change appeared to occur during the first 24 hours.

Even though the data on this phase of the problem are meager, the humidity accelerated spring drift seems to account satisfactorily for all the discrepancies noted thus far. If this position is held, then it appears that the film samples actually did come to equilibrium in 30-60 minutes and so the isotherms in Figure 4 are not so far from the true ones as originally thought. There is of course a sizeable error because of the faulty spring performance, but in the relatively short time used

to make the runs, the adsorption curves provide significant characterization with which to relate the films to each other.

Corrosion

As stated earlier, all the test panels were removed from the humidity chambers after nine months whether significant corrosion had taken place or not.

The untreated panels were remarkably resistant to corrosion. As a result, the plates exposed at 70 percent and 90 per cent and those untreated ones exposed at 80 percent relative humidity were all left in the chambers the full nine months and even then little or no filiform appeared. Exceptions were those coated with films III and IV, which failed quite rapidly. Because of this state of affairs, it was not possible to compare the rate of corrosion of the untreated panels, nor to determine the effect of humidity.

A method of grading the corrosion resistance was still needed, however, and therefore the performance of the treated panels was used. All the panels having a similar treatment were placed in a descending order of failure. This was done by first separating them into groups of equal exposure time, then visually arranging the panels within a group according to the amount of corrosion present. The grouping according to time of

exposure was given precedence over the visual comparison. This process resulted in six arrangements of the eight plates. Each plate was then given one of eight numbers according to its position in a particular arrangement. A given type of plate then had six numbers. The average of these position numbers gave a relative corrosion resistance value ranging from 1 for the best to 8 for the worst. Table II lists the values resulting from this procedure.

TABLE II

Film type	Relative corrosion resistance value
I	5.2
II	6.4
III	1.4
IV	1.6
V	4.2
VI	4.0
VII	5.2
VIII	8.0

Figure 8 is a graphical presentation of the effect of various substances on the rate of filiform formation according to the method outlined on page 20. The type of coating is listed in the first column, the treatment

in the next. The letters refer to the type of treatment as listed on page 21. A heavy horizontal line indicates the effect of the treatment on the rate of corrosion as determined by comparing the treated half with the untreated half. A heavy horizontal line extending from the center (NC) may end in GR, greatly retarded; R, retarded; A, accelerated; or GA, greatly accelerated. The short lines through the NC position indicate no change of rate. As stated before, the corrosion rate was very slow in most cases, and therefore some of the panels showed no corrosion on either half. In these cases it was not possible to determine the effect of the treatment, and the line is omitted in the graph.

Motion Pictures

Many difficulties have beset this undertaking and as yet no suitable films are ready.

FILM	TREATMENT	GR	R	NC	A	GA	37
I	A B C D E W				—		
II	A B C D E W				—		
III	A B C D E W			— — —			
IV	A B C D E W		—	— — —			
V	A B C D E W			—			
VI	A B C D E W			—			
VII	A B C D E W			—			
VIII	A B C D E W			—			

FIGURE 8

ANALYSIS

Surface Area

It was thought that perhaps the surface areas would furnish a correlation to the resistance of the films to corrosion. The adsorption data, although in error, can be used to calculate the surface area of the films. For this purpose the classical method of Brunauer, Emmet and Teller is used (1, p. 309-319). This theory has been explained in nearly every discussion of surface chemistry for the past ten years, and therefore there is no real need to repeat here.

The adsorption data obtained up to about 30 percent relative humidity is used to calculate the area, and so the instrumental difficulties discussed previously are to a large extent bypassed in the isotherms made using a 60 minute interval and shown in Figure 4. The areas calculated are tabulated in Table III.

TABLE III

<u>Film type</u>	<u>Surface area M²/g</u>
I	12.9
II	33.4
V	(26.5)
VI	18.6
VII	27.4
VIII	40.8

All the isotherms gave good B.E.T. plots from 5 to 35 percent relative humidity except film V whose points exhibited considerable scatter. This was expected from the shape of the isotherm, since an S shaped curve or at least one concave downward is necessary to give a good B.E.T. analysis. The best straight line was drawn, however, and the area calculated in order to compare with the other films. An area of 10.5 square Angstroms was assumed for the water molecule. The 17° isotherms were chosen because the adsorption takes place at low pressures and the effect of high humidity on the springs was partially avoided. It was assumed that the effect would be considerably reduced at low pressures, although no rigorous experiments have been done to prove this point.

The B.E.T. plots are not reproduced here since, to be of any value, the points must be shown in their relation to the straight line chosen and this requires a large graph which is not practical on account of the number of films studied.

Heats of Adsorption

The conventional Clausius-Clapeyron equation was used to calculate the isosteric heats of adsorption in the hope that this might shed light on the situation.

TABLE IV

Film Type	Heat of adsorption Kcal/mol
I	9.5
II	6.9
V	9.7
VI	8.8
VII	10.2
VIII	10.1

These heats, given in Table IV, were calculated using the amount adsorbed to form a monolayer as determined from the B.E.T. analysis. Data at 17° and 27° were used. The high pressures necessary to form a monolayer at 37° ruled out its use due to the greater errors which would necessarily be present. Even so, there is undoubtedly a fairly large uncertainty factor involved.

If the difficulty with the springs had not been present, no doubt the adsorption-desorption curves would be closed at the ends. Then, if the desorption and adsorption were not coincident, a calculation of pore size distribution would have been possible. The unexpected spring behavior prevented this.

CONCLUSION

Correlation

Upon comparing Tables II and III, we find a certain similarity. The vinyl films, III and IV, show the lowest corrosion resistance and they were also the poorest adsorbers hence they had the lowest surface area. At the other extreme is film VIII with the highest corrosion resistance and the highest surface area. There are many discrepancies with the other comparisons, although there appears to be a significant trend.

There are surely many ways of explaining this trend. We might say that those films having a majority of large pores which pierce the film would readily pass the water vapor necessary for the corrosion mechanism to operate, and because of their size would not adsorb nearly as much vapor as small capillaries which fill readily due to the larger surface forces present. On the other hand, a film having many fine capillaries which do not pass through, would tend to adsorb water vapor easily but not transmit as much to the steel panel underneath.

Naturally, there are many bad assumptions in this theory, and until considerably more data is obtained, speculation is useless.

The adsorption heats are seen to be reasonably

close to the heat of condensation of water. Again there are variations which cannot be attributed to any definite phenomena. The fact that the heats are small remove the possibility of chemisorption.

The rapid failure of films III and IV may be explained by a partial hydrolysis of the chloride polymer to release chloride ion. The chloride ion appears to have this effect on all the films as seen in Figure 8. This may be expected since the chloride complexes with iron readily, removes any oxidized iron formed, and thus eliminates the possibility of a passivating layer.

The effect of sulfuric acid is also consistent. This is reasonable since the attack of iron by hydrogen ion is thought to be an important step in the corrosion process.

In view of this, it would be expected that sodium hydroxide would function to some extent as an inhibitor. The fact that in most cases the corrosion rate did not increase upon application of this substance, and actually decreased in one seems to bear out, at least partially, this prediction.

Potassium chromate and thiocurea are generally accepted as corrosion inhibitors; however, their action is somewhat erratic. In this case there is apparently no consistent effect. The acceleration noted may be due

to the wetting agent present in all the treatments.

Further Studies

Obviously, an investigation of the behavior of copper beryllium springs is necessary if these are to be used with any degree of accuracy. Probably much better results can be obtained with quartz springs.

The most doubtful procedure in the experiment is the method of removing the film from the steel panels because there is no way of determining what changes occur during the process. Some method should be found to produce the films without a support, thus eliminating the electrolysis step.

The corrosion experiment might be redesigned to give comparable failure in a reasonable time. This might be done by addition of a small amount of a volatile nonselective corrosion accelerating agent to the humidity chambers.

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