

128

INVESTIGATION OF INHIBITOR TREATMENT OF GALVANIZED STEEL

A THESIS

Presented to
the Faculty of the Graduate Division

by
Guillermo Alfredo Aguayo

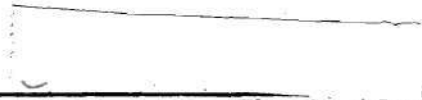
In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemical Engineering

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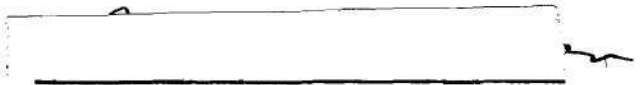
INVESTIGATION OF INHIBITOR TREATMENT
OF GALVANIZED STEEL

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SUMMARY

The purpose of this investigation was to present a measure of the relative effectiveness of several inhibitor treatments for galvanized steel. This was done by immersing galvanized steel specimens in different inhibiting solutions and testing the specimens, at frequent intervals, to determine their degree of corrosion after exposure to atmospheric conditions.

A reflection indicator system was constructed which allowed the specimens to be analyzed, in order to determine their degree of corrosion by means of their ability to reflect light (the more light reflected, the less corrosion and vice-versa). The reflection indicator system consisted of a box to which a light bulb and an exposure meter were attached. The specimens were placed on the cover of the box; light was then allowed to shine on them. This light reflected into the exposure meter, which, by indicating the intensity of the reflected light, measured the degree of corrosion of the specimens.

The specimens were marked for identification purposes, pickled (that is, immersed in an inhibited 10% H_2SO_4 solution) and galvanized by dipping in a molten zinc bath through a $Zn(H_3N)_2Cl_2$ flux. The specimens were cooled in a water bath and finally were dipped in their respective inhibiting solutions. They were allowed to dry in air and readings were taken to measure their reflectiveness. Then they were placed on a stand for exposure to atmospheric conditions.

Three series of runs were performed during the course of this investigation. Each run consisted of different inhibiting solutions containing

mixtures, in different concentrations, of CrO_3 and H_3PO_4 , CrO_3 and NaF , or of solutions containing CrO_3 alone. Several solutions were subjected to various temperature treatments to study the influence of temperature variations on the inhibiting properties of the solutions. In each run several plates or specimens were left untreated for comparison purposes.

The results were evaluated by comparing the average decrease in light reflectiveness occurring for specimens treated with the various inhibiting solutions and subjected to atmospheric conditions for the same period of time.

The results of this investigation agreed well with theoretical observations, that is, higher concentrations of CrO_3 provided better corrosion protection than lower concentrations. These results also agreed with work involving the use of CrO_3 and NaF mixtures.

The experimental data and calculated results are presented in Tables 1 through 14 and in Figures 2 through 15. From these results different inhibiting solutions can be evaluated over the same time interval, thus presenting a correlation of the different solutions and an evaluation of their effectiveness.

The results obtained from the three runs performed proved to be consistent throughout the experiment. These results led to the following conclusions:

1. Solutions containing mixtures of CrO_3 and NaF provided the specimens with the best corrosion protection.
2. Solutions containing CrO_3 alone provided better protection than those solutions containing mixtures of CrO_3 and H_3PO_4 .
3. The higher the concentration of CrO_3 in a solution the

better the corrosion protection it provided the specimens.

4. Solutions that were maintained at their boiling point provided much better corrosion protection than the solutions that were kept at room temperature.

5. The temperature of the specimens before dipping had no influence in the improvement of corrosion protection.

6. Specimens that were not treated with any inhibiting solution deteriorated at a rate much faster than those treated with inhibiting solutions.

7. Chromic acid concentrations of less than 10 gms./lt. did not provide the surface of the specimens with an orange color, whereas concentrations of 10, 15, and 20 gms./lt. did.

It is recommended that more experimental work should be done with respect to determining the influence that the dipping time of the specimens has on providing the specimens with a better corrosion protection.

CHAPTER I

INTRODUCTION

The preservation of the superficial characteristics of brilliance and corrosion resistance of galvanized steel has always been a problem for both producers and users.

White rust is a zinc corrosion product which is harmful to the galvanized surface in several ways. Depreciation of the product and reduced electrochemical protection of the steel base result. The formation of white rust is damaging because it extracts zinc from the coating and converts it into basic carbonates of zinc of variable composition, thus shortening the life of the ferro-zinc couple (3). This formation is brought about by complex chemical reactions and electrochemical phenomena with the presence of oxygen and atmospheric humidity, and by various aggressive ions.

The factor mostly responsible for the corrosion of the galvanized coat is the differential oxygenation, that is, the formation of local couples of oxygen concentration. This phenomenon is known as "oxygen concentration cell" and, since is well known in electrochemistry its details are omitted (4). The purpose of the galvanized coat is to make the steel cathodic to the zinc (since zinc is less noble than steel it will corrode first in case of a discontinuity in the galvanized coat). The effort of galvanized steel producers to eliminate or retard this damaging phenomenon is therefore understandable.

Chemical surface treatments of various kinds play an important role in the metal finishing industry. Surfaces can be protected in aqueous conditions by the addition of inhibitors. An inhibitor may be defined as "a chemical substance or mixture, which, when added to an environment, usually in small concentrations, effectively decreases corrosion" (5).

The development of protective finishes for galvanized steel has been carried out and encouraged mainly by the steel producers themselves. A great number of treatments of various types have been devised over the past thirty years. An increasingly prominent group of these are the protective chromate conversion treatments (6), (7), (8) and phosphate coatings (9), applied to steel or galvanized steel. Wetting agents help to bring an inhibited solution to metal surfaces that are covered with rust or scale, since they materially help in the diffusion of the inhibited solution to the metal through rust and porous scale (10).

It is the purpose of this investigation to present a measure of the relative effectiveness of several inhibitor treatments for galvanized steel. The problem was raised in view of the many difficulties encountered by many producers and users of galvanized steel connected with the formation of white rust. It is obvious that the amount of research done in order to provide galvanized steel with a suitable inhibitor is enormous. Different treatments were found in the literature search, (11), (12), (13), (14), (15), (16) but only those which used chromic acid were considered.

Nature of Chromatic Coatings.--(1) The theory of passivity and inhibition deals with the formation of a resistant film on the anodic or cathodic

areas of a metal specimen. The chromates act mainly as anodic inhibitors.

All chromate conversion treatments use chromic acid or one of its soluble salts, which contain chromium in the hexavalent state. Other chemical can be added to activate the reaction between the chromium salts and the metals. These are known as activators. If the clean metal surface is immersed in such a solution, a thin film or conversion coating is produced; this has the desirable characteristic of retarding corrosion of the metal surface. The term "conversion coating" refers to the fact that surface metal is converted into a non-metallic form in the film producing reaction.

Relatively little is known about the composition and structure of chromate films. A few generalizations can be made, however. It is fairly well established that most films are gel-like rather than crystalline. Films are soft and absorptive while freshly formed and still wet. On drying they set or harden, and become rather non-wettable and impervious to aqueous solutions. The hardening process continues at a slow rate for some time after drying. Colored films owe their color to the presence of hexavalent chromium compounds within the film structure. Corrosion resistance of a chromated depends in part on the corrosion resistance of the metal itself. Most chromate solutions operate at, or nearly at, room temperature. Temperature control is not critical. Corrosion of the galvanized surface is effectively retarded by chromates.

In addition to affording corrosion protection, chromates treatments in many cases enhance the appearance of the metal surface by providing metallic bright or attractively colored finishes. Chromates also make excellent bases for paint and other organic finishes which do not

adhere to untreated metals.

Most chromate treatments in use at present, except those used for magnesium, are of the propriety type. Users are supplied with powdered compounds or liquid concentrates, from which working solutions are made up and operated according to manufacturer's recommendations. A variety of formulations, tailored to meet specific requirements, are available.

Phosphate Coatings.--(9) Phosphate coatings are used to convert the surface of the metal to a less active compound of the metal, such as the phosphate. If properly done this results in better adhesion of an organic coating, such as paint, and reduces the spread of corrosion from pinholes in the organic coating. As in other coatings of this nature, however, phosphate coatings are not sufficiently resistant to be used alone under exposed conditions, but form a strongly adherent base for organic protective coatings.

CHAPTER II

DESCRIPTION OF APPARATUS

The apparatus involved in the determination of the degree of corrosion of the galvanized steel specimens consisted of three components: a stand or wooden frame where the specimens were placed so they would be directly exposed to the existing atmosphere conditions, a reflection indicator system where the specimens were placed and examined to determine their degree of corrosion, and a wooden rack which transported the specimens from the stand to the site where the reflection indicator system was situated and vice-versa.

The Stand or Wooden Frame.--The purpose of the stand was to support the specimens so that they would be exposed to existing atmospheric conditions. The stand consisted of a frame formed by boards 2" by 4", it had a length of six feet and an inclination of fifty-five degrees from the horizontal so that the sun's rays would impinge perpendicularly on the specimens at this latitude. The frame had seven boards positioned horizontally and parallel to each other. The specimens were fastened to the boards by means of plastic clothespins, which proved to be very helpful in facilitating the removal and placing of the specimens on the boards. The capacity of the frame was one hundred specimens.

It is to be noted that the specimens were held by the clothespins from the bottom so as to avoid extraneous materials from falling on the specimens.

The Reflection Indicator System.---The purpose of the reflection indicator system was to determine the degree of corrosion of the specimens by measuring the reflectivity of each specimen as a function of time. This was done by allowing light to strike the specimens and measuring the intensity of the light reflected off the specimens at various time intervals by means of a light exposure meter. A diagram of the system is shown in Figure 1.

The reflection indicator system consisted of wooden box, a 100-watt electric light bulb, a General Electric exposure meter (type DW-48), which could record a maximum light intensity of 70 foot-candles, a mirror, and a powerstat for adjustment of the light intensity.

The wooden box was a trapezoidal shaped box which measured fifteen and a half inches long, seven and a half inches high, seven and a half inches at its narrow end, and twelve and a half inches at its wide end. A panel which formed a forty-five degree angle with the bottom of the box was inserted, and the exposure meter was attached to this panel by means of a brass strip. This strip had a hole cut out so the sensitive light-cell of the exposure meter could be fitted into it. A hole with the same dimensions as that on the brass strip was cut out on the panel so as to permit the exposure meter to collect the light reflected from the specimen being tested.

The electric light bulb was placed at the narrow end of the box and against its back wall.

On the cover of the box a hole was cut out just above the light meter so that each specimen could be positioned over the hole to cover it, thus exposing a portion of its surface to the light emitted by the bulb.

Due to the forty-five degree inclination of the panel with the exposure meter placed perpendicularly to the panel, the light reflected from the specimen on the lid above the meter impinged perpendicularly on the exposure meter.

Standardization of the Reflection Indicator System.---The reflection indicator system was adjusted or standardized so that the exposure meter would indicate its maximum reading when the brightest possible plate was placed in the specimen position. Such a plate was a freshly galvanized plate which was not dipped in an inhibiting solution.

Obviously this freshly galvanized plate could not be used over and over again as a permanent standard or reference point, because the formation of zinc corrosion products on it would impair its brightness, i.e., its reflectivity would decrease; therefore a permanent reflector was chosen. This permanent reflector was selected to give the same maximum reading as the freshly galvanized plate with the same amount of light. For this purpose a mirror was selected. The resulting deflection registered by the exposure meter for the light from the mirror was greater than the maximum reading on its scale. It was found, therefore, necessary to cover a portion of the surface of the mirror with a black tape to reduce the intensity registered until the exposure meter would indicate only its maximum reading when the mirror was placed on the box. When this adjustment had been completed the mirror could be used as a non-tarnishing standard equivalent to a newly galvanized plate.

A powerstat was connected in series with the electric bulb, in order to supply the bulb with a constant controlled voltage; as a result the intensity of the light emitted by the bulb was kept constant at all times.

The exposure meter was standardized throughout the recording of reflectivity readings by placing the mirror on the box and adjusting the powerstat so that the light reflected off the mirror would indicate a maximum reading of 70 foot-candles on the exposure meter.

The Wooden Rack.--The purpose of the wooden rack was to transport the specimens from the stand to the site where the reflection indicator system was located and back.

CHAPTER III

EXPERIMENTAL PROCEDURE

In preparation for a data run, specimens four inches long, two and a half inches wide, and 1/8 inches thick were cut out of plain carbon steel plates. The plates were then marked for identification purposes and taken to the pickling and galvanizing facilities of the Atlantic Steel Company, where they were immersed in an inhibited 10% H₂SO₄ solution for about twenty minutes to get rid of the scales on the surface, and then they were galvanized by being immersed in a molten zinc bath through a Zn(H₃N)₂Cl₂ flux.

Extreme care was taken in skimming the surface of the molten zinc before pulling the specimen from the galvanizing bath; too rapid pulling would cause a rough galvanized surface on the specimen and a decrease in brightness, i.e., a dull surface.

The specimens were cooled by dipping in a water bath at room temperature and finally they were dipped in their respective inhibiting solutions for approximately ten seconds. They were allowed to dry in air and then readings were taken to measure their reflectiveness. They were immediately placed on the stand for exposure to atmospheric conditions. The specimens were tested at frequent intervals which can be seen from Figures 2 through 15 for their reflectiveness by means of the reflection indicator system and their registered deflections were recorded.

Three series of runs were performed in the course of this investigation:

The First Run.--Twelve solutions were made up containing mixtures of CrO_3 and H_3PO_4 in different proportions. Seven solutions contained mixtures of CrO_3 and H_3PO_4 , and five contained different concentrations of CrO_3 alone. Three plates were used per solution and five were kept untreated as control specimens. The plates were placed on the stand, care being taken that the side of the plate that was used in taking the reflectiveness reading was exposed facing the sun and the rain.

The Second Run.--This run consisted of nineteen solutions. Six solutions contained different concentrations of chromic acid alone; seven solutions contained different mixtures of chromic acid and phosphoric acid; and two solutions contained different concentrations of chromic acid and sodium fluoride. Another solution was divided in two parts, one part was heated to its boiling point and three hot and three cold plates were dipped in it; the other part was kept at room temperature and three hot plates were dipped in it. By hot plate it is meant a plate that was not immersed in water after being galvanized. Finally three plates were immersed for five minutes in a solution to study the influence of dipping time in the effectiveness of the inhibiting solution. In this run three plates were kept untreated.

The Third Run.--The third run consisted of eight test studies utilizing four different solutions. Two solutions contained chromic acid in different concentrations and two solutions contained mixtures of chromic acid and sodium fluoride. These four solutions were used once at room temperature and a second time at their boiling point thus making a total of

eight test series. As usual three plates were kept untreated.

The results of the runs are detailed in Chapter V. The experimental data and calculated results are presented in Tables I through 14 and Figures 2 through 15. A list of the different solutions used is presented in Table 1 in the Appendix.

CHAPTER IV

EVALUATION OF RESULTS

The calculations or evaluations involved in the determination of the degree of effectiveness of the different inhibiting solutions used are very simple.

Since the steel specimens were galvanized manually, it was virtually impossible to obtain the same quality or type of galvanized surface on every specimen; therefore the quality and characteristics of the galvanized surface varied with every specimen. These differences in the galvanized surfaces caused different amounts of light to be reflected off each specimen; therefore, the only way in which the effectiveness of the different inhibiting solutions could be related was by comparing the average decrease in light reflectiveness caused by different inhibiting solutions over the same length of time.

The average relative humidity and precipitation per week were recorded so as to aid in the evaluation of the results.

Reflectiveness readings of the specimens were taken at frequent intervals. Since several plates were used per solution, the average reflectiveness readings of the plates was used in computing the average decrease in light reflectiveness.

The light reflectiveness readings, which were taken immediately after the plates were galvanized, immersed in the inhibiting solution, and allowed to dry, were used to calculate the average decrease in light

reflectiveness, together with the readings taken at the end of the desired time interval.

The experimental data and calculated results are presented in Tables 1 through 14 and in Figures 2 through 15. From these tables and figures different inhibiting solutions can be evaluated over the same time interval, thus presenting a correlation of the different solutions used and an evaluation of their effectiveness.

A correlation and discussion of the results obtained is presented in the chapter entitled "Discussion of Results." The conclusions formulated are listed in Chapter VI.

CHAPTER V

DISCUSSION OF RESULTS

The data obtained from the work described in Chapter IV are outlined in a series of Tables and Figures in the Appendix. These are grouped so as to exhibit the change in reflectivity of a specimen with time of exposure to atmospheric conditions and to delineate the protection provided to the specimens by varying the concentration of the chemical constituents of the inhibiting solutions, namely, that of CrO_3 , H_3PO_4 and NaF .

Figures 6 to 15 exhibit changes of reflectivity of specimens with time of exposure. Various plots are also made for specimens treated with solutions of various compositions. Figures 2 to 5 exhibit data derived from the preceding Figures and Tables 9 to 13 which show principally the variation of reflectance with composition of the solution.

The remaining Figures exhibit data obtained for other peripheral findings related primarily to the effects on corrosion of the use of hot and cold solutions.

The results obtained from this investigation proved to be consistent throughout the three runs performed. From the results obtained from runs 1 and 2 it was evident that the addition of phosphoric acid to solutions containing chromic acid did not improve the corrosion resistance properties of the specimens. For fixed concentrations of phosphoric acid, corrosion protection increased as the concentration of chromic acid in the solution

increased. On the other hand, for fixed concentrations of chromic acid, an increase in the concentration of phosphoric acid did not increase consistently the corrosion protection of the specimens.

For solutions containing chromic acid alone, the results from runs 1 and 2 proved without the shadow of any doubt that an increase in the concentration of chromic acid provided the specimens with an increase in corrosion protection.

The initial light reflectivity readings showed that the solutions containing phosphoric acid had on the average higher initial values, but they deteriorated at a faster rate.

After one week of exposure to atmospheric conditions, it was observed that the specimens that were dipped in solutions 10-A₁, 11-A₁, and 12-A₁, i.e., the solutions that had the highest chromic acid concentration, exhibited an increase in reflectiveness readings, this situation was observed only in the results obtained from run 1, it did not occur in run 2. The reason for this behavior was that a portion of the film deposited on the surface of the specimens was washed away by rainfall, rendering the surface of the specimen brighter. The portion that was washed away was an excess of chromate deposit due to the heavy concentration of chromic acid in the respective solutions. It should be noted that the specimens that were immersed in these solutions were tinted with an orange color due to the high concentration chromic acid present in the solutions. This color film tends to fade out as the exposure time to atmospheric conditions increased. The reason why this same situation did not occur with solutions 10-A₂, 11-A₂, and 12-A₂, of run 2 is because a heavier rainfall occurred during the week right after the

specimens from this run were placed on exposure, as a result, a greater amount of the protective film was washed away and the surface corroded at a rate slighter faster than that of the specimens in run 1, treated with solutions having the same concentration.

In view of the results obtained from run 1 it was concluded that solution 9-A₁ gave the best results for this run. This particular solution (5 gms/1 t. of CrO₃) presented the best combination of corrosion and brightness of all the solutions used in run 1. This solution was used in preparing the additional solutions that constituted the part of run 2 devoted to various temperature conditions.

The solutions used in run 2 confirmed the results of run 1 that an increase in the concentration of chromic acid resulted in an increase in corrosion protection for the specimens. However, the principal results determined from run 2 were that the addition of sodium fluoride to a solution containing CrO₃, in a ratio of 0.27 grams of sodium fluoride per gram of chromic acid, improved the corrosion resistance of the specimens considerably and kept their surface brighter and for a longer period of time. The results obtained from the solutions containing mixtures of sodium fluoride and chromic acid were reproduced closely in run 3, that is, the results obtained from run 3 confirmed the conclusions regarding the effectiveness of the solutions containing mixtures of chromic acid and sodium fluoride.

The results obtained from the experiments designed to study the effect of temperature variations of the solutions or plates on corrosion protection of the specimens showed that by bringing the inhibiting solution to its boiling point a better corrosion protection is obtained than that

when the solutions were not heated, and that the temperature of the specimen up to 460° C had no influence in providing better corrosion protection.

The specimens that were treated with solution 1-C₂, that is, the solution that presented a high concentration of chromic acid, 15 gms./l t., and which was heated to its boiling point, were heavily tinted by the chromic acid. This same situation occurred for specimens that were dipped in solution 1-B₂ (20 gms./ l t. of CrO₃), although this solution was not heated.

Solutions 2-C₃ and 3-C₃, which had mixtures of chromic acid and sodium fluoride and were heated to their boiling points, presented a better corrosion protection than solutions 2-B₃ and 3-B₃ which had the same concentrations, but were not heated. However, treatment with the latter solutions yielded a higher degree of brightness to the specimens.

Run 3 confirmed the results obtained in run 2, that hot solutions provided a better corrosion protection than cold solutions, and that solutions containing mixtures of CrO₃ and NaF provided much better corrosion protection than that provided by solutions containing CrO₃ alone. In addition, these solutions yielded specimens with a brighter surface.

The combined results from the three runs showed that solution 2-B₃ provided the specimens with the best combination of corrosion protection and surface brightness. Detailed conclusions regarding the results are given in Chapter VI.

The results of this investigation agreed well with the theory (1) that higher concentrations of chromic acid provide better corrosion protection than lower concentrations, and with previous experimental work involving the use of CrO₃ and NaF mixtures (2).

The specimens that were not provided with any inhibitor treatment deteriorated at a rate notably faster than the rate exhibited by other specimens.

The errors occurring in the course of this investigation were fairly minor. One type of error was committed in reading the scale of the exposure meter. The estimated error in reading a value off the exposure meter was plus or minus one foot-candle.

Another source of errors was the contamination of the surface of the specimens with extraneous materials other than the corrosion products, but this source of errors was reduced satisfactorily by checking the results by a series of similar tests. This was done as explained previously by checking the results obtained from run 1, by run 2; and checking the results obtained from run 2 by run 3.

Since previous (17) observations of metals in the atmosphere indicate that the rate varies with seasonal changes in natural atmospheric conditions, the length of time the specimens remain wet, the intermittent removal of water-soluble salts by heavy rainfall, etc., the average relative humidity and the precipitation per week were recorded to aid the reader in interpreting the results.

In order to reduce errors introduced from defective specimens, several plates were used per inhibiting solution. An average of all the readings of the different plates was taken in calculating the results. It was found necessary to reject the readings obtained from specimens on solutions 5-A₁, 11-A₁, 5-A₂, due to their faulty surface condition, i.e., the plates were rough and warped. Observations were made in these special cases in order to explain the nature of the defective plate. These observations are found in Tables 6 and 7.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The conclusions resulting from this investigation may be summarized as follows:

1. The most effective treatment found was solution 2-B₃ which contained a concentration of 5 gms./1 t. of CrO₃ and 1.35 gms./1 t. of NaF. This solution provided the specimens with the brightest surface and excellent corrosion protection which maintained their surface bright for the longest period of time.

2. Solutions containing mixtures of NaF and CrO₃ in a ratio of 0.27 gms of NaF per gm. of CrO₃ provided the best corrosion protection. Solutions containing CrO₃ alone provided better corrosion protection than those containing mixtures of CrO₃ and H₃PO₄. Solutions containing mixtures of CrO₃ and H₃PO₄ provided the specimens with higher initial light reflectivity readings, but the readings decreased faster.

3. The higher the concentration of CrO₃ in an inhibiting solution, the better the corrosion protection it provided the specimens.

4. Solutions that were maintained at their boiling point provided much better corrosion protection than the solutions that were kept at room temperature.

5. The temperature of the specimens before dipping had no influence in the improvement of corrosion protection.

6. Specimens that were not treated with any inhibiting solution deteriorated at a rate notably faster than those treated with inhibiting

solutions.

Even though it was found that a dipping time of five minutes improved the corrosion protection of the specimens, more experimental work should be tried on this subject. However, it is thought that a dipping time of more than five or ten minutes will not improve appreciably the corrosion protection of galvanized surfaces.

The recommendation is made that in the light of the results achieved by the addition of NaF to CrO_3 , more experimental work should be tried on this subject. The influence of different concentrations should be examined more exhaustively, as well as the protection afforded by NaF alone.

APPENDIX

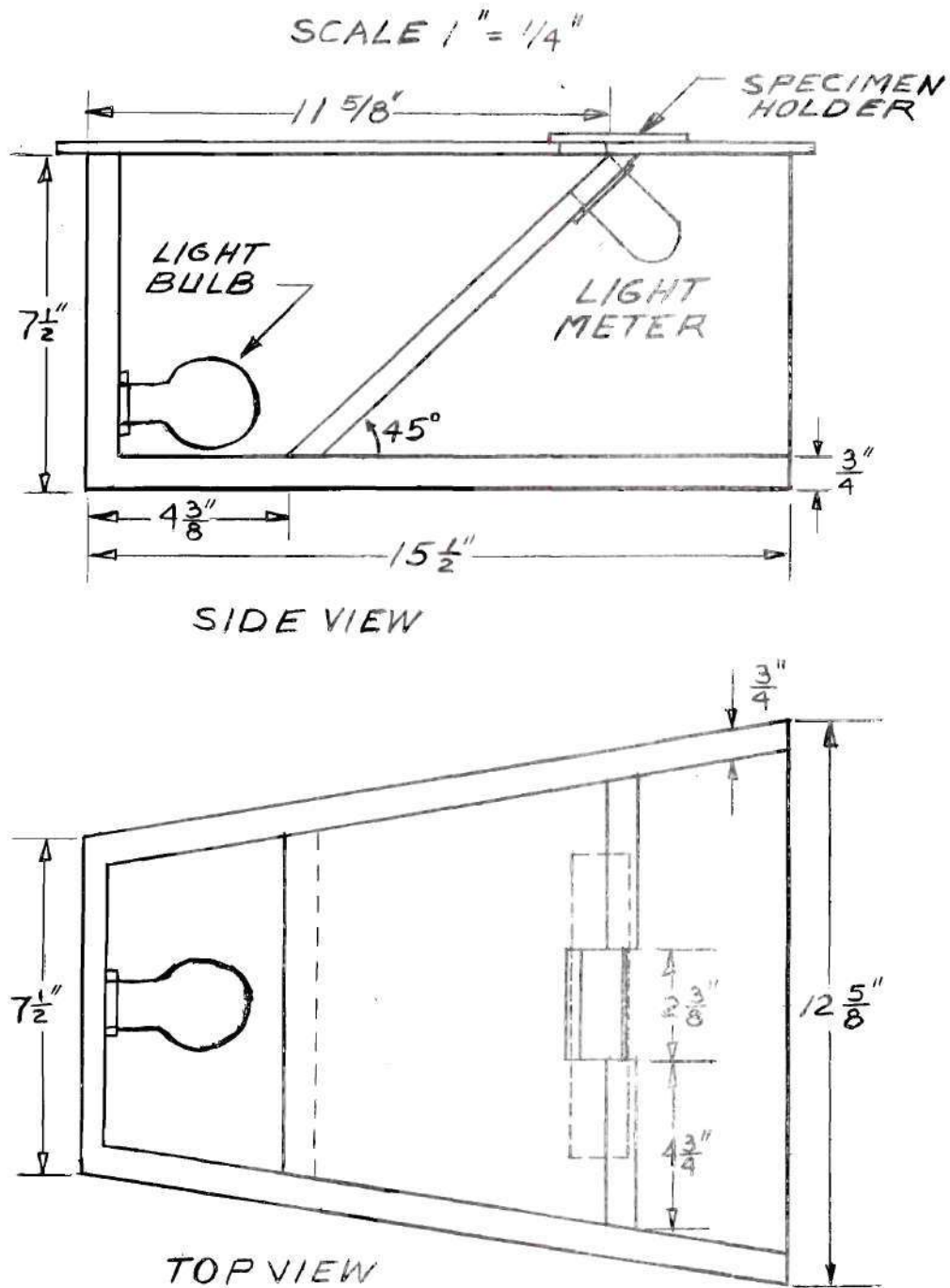


Figure 1. Diagram of Reflection Indicator System

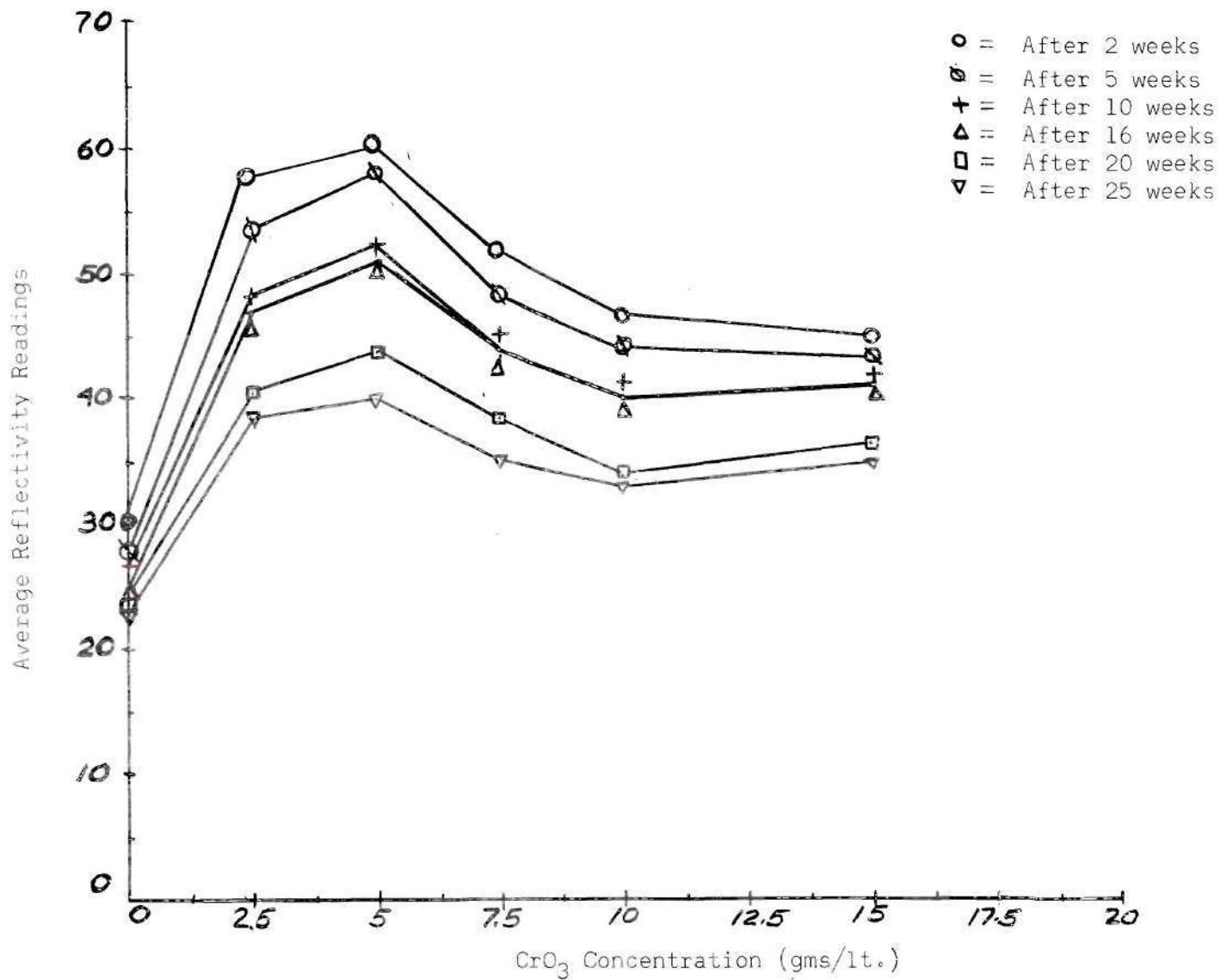


Figure 2. Average Reflectivity Readings Versus CrO₃ Concentration Data - Run No. 1

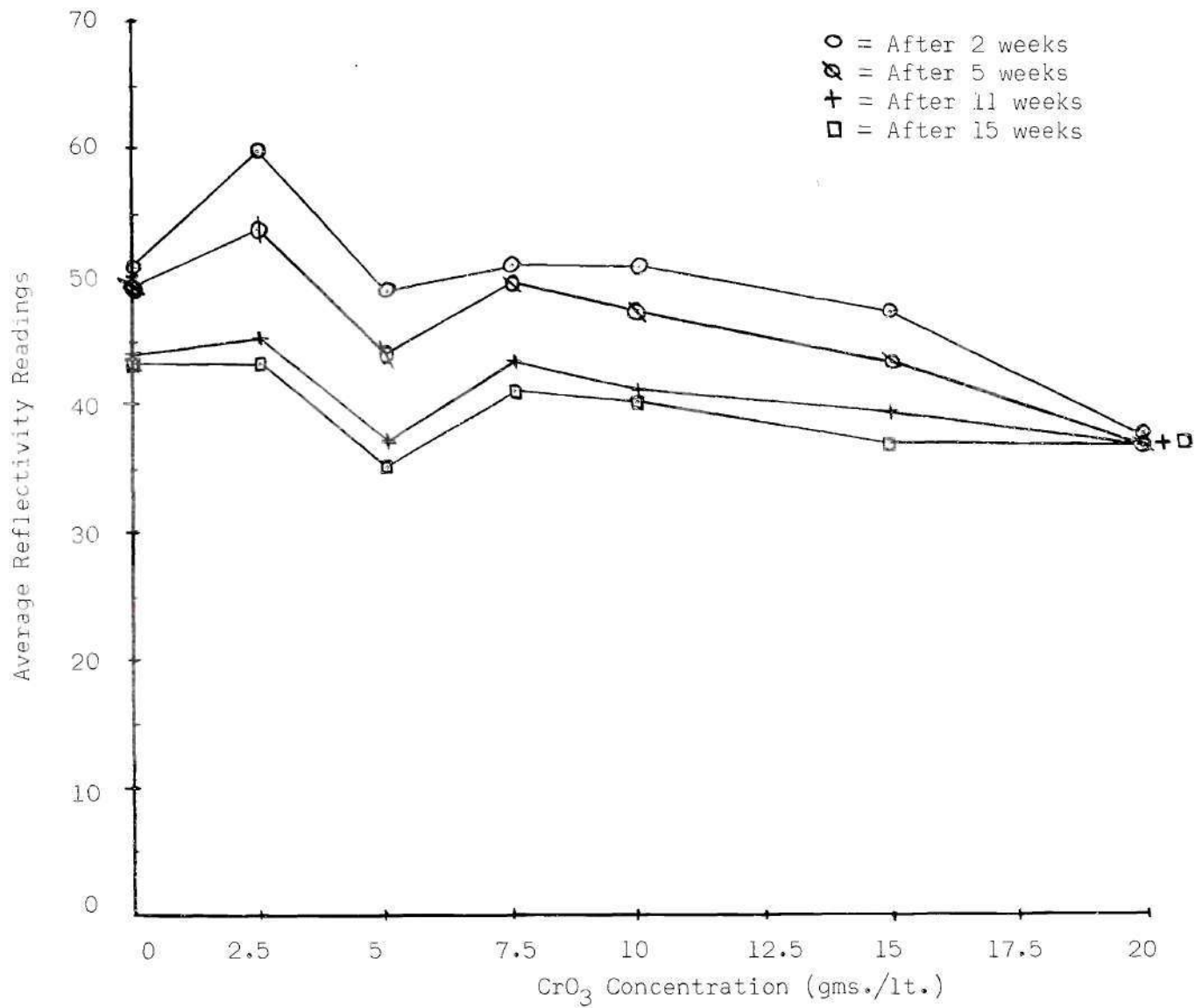


Figure 3. Average Reflectivity Readings Versus CrO₃ Concentration Data - Run No. 2

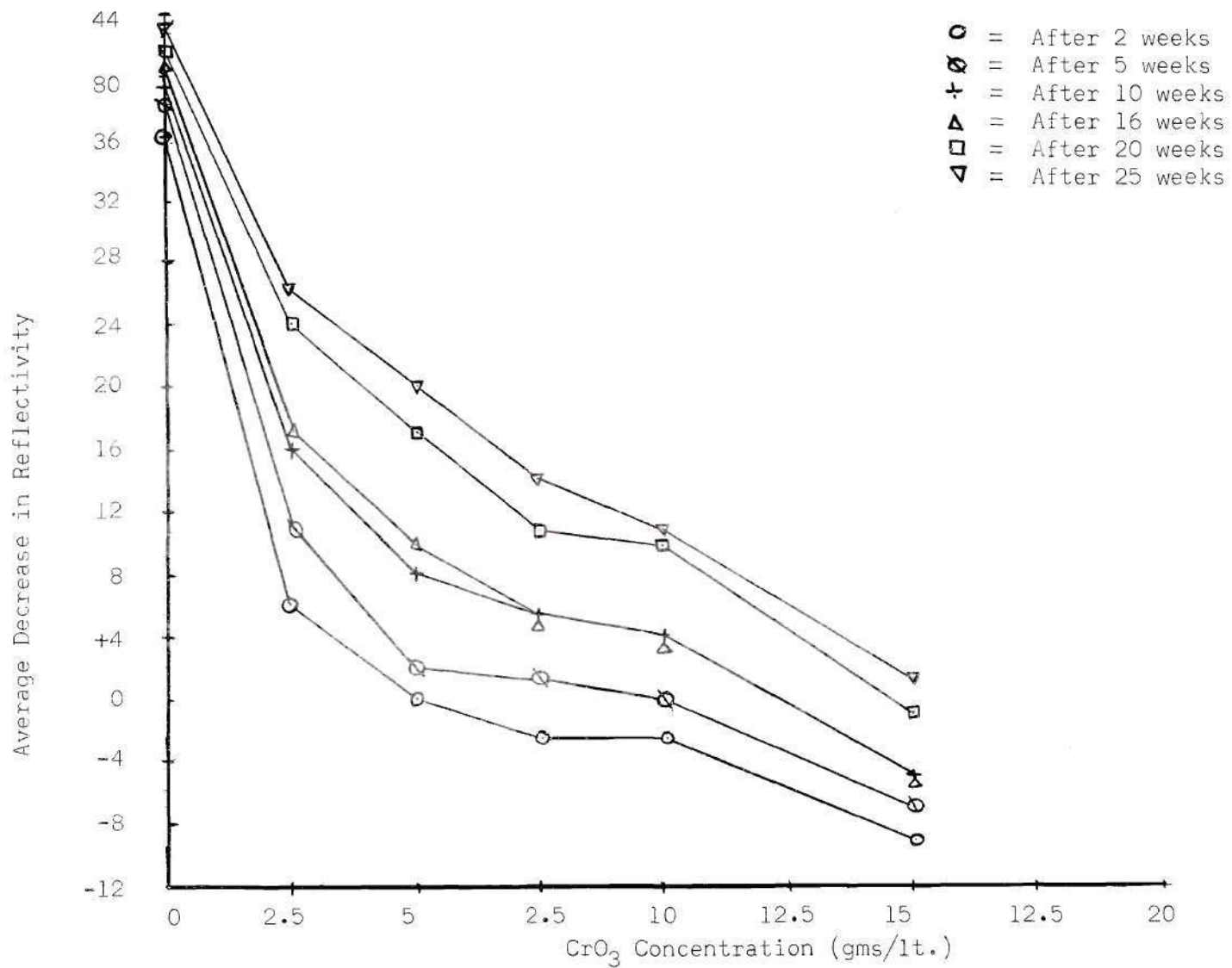


Figure 4. Average Decrease in Reflectivity versus CrO₃ Concentration Data - Run No. 1

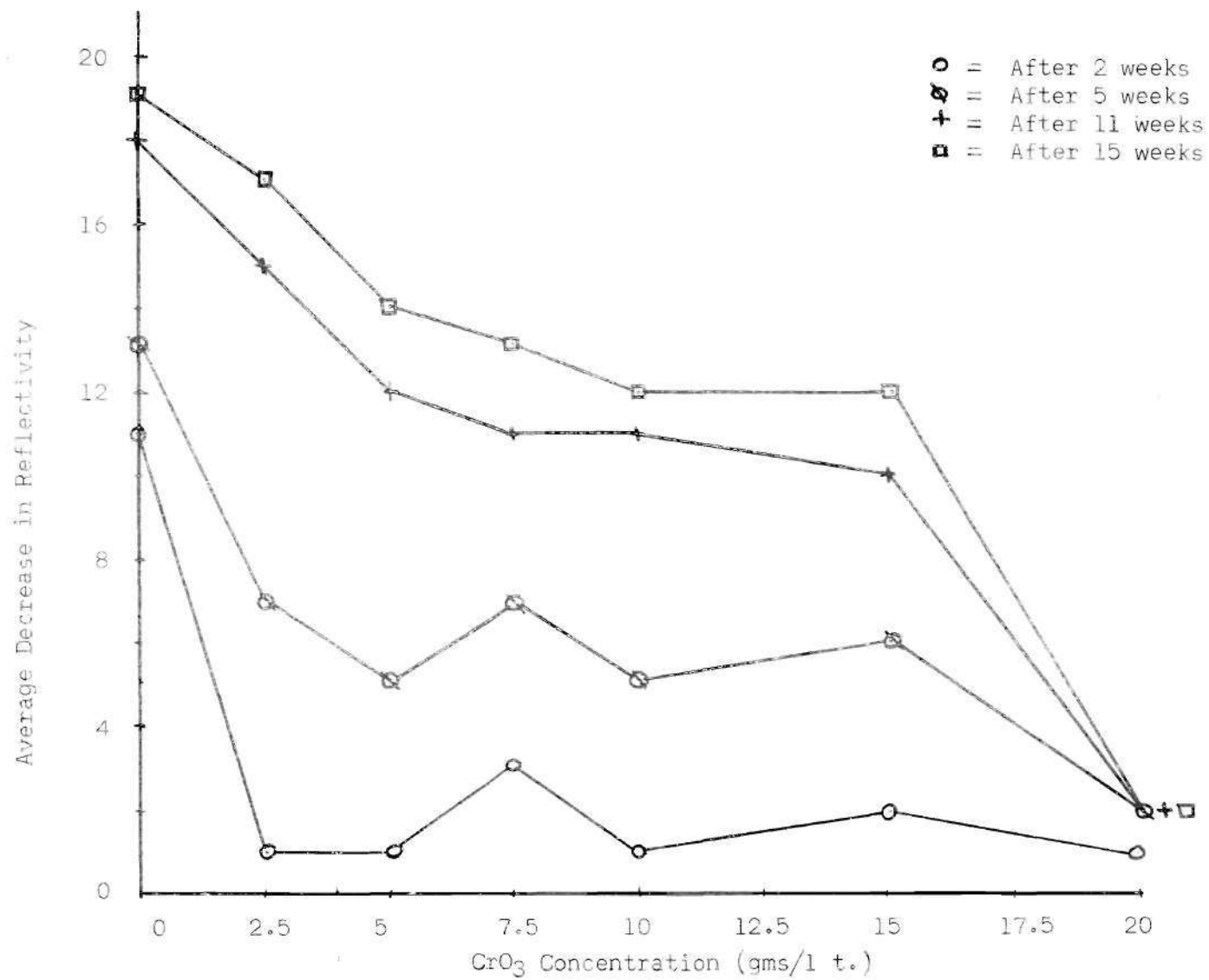


Figure 5. Average Decrease in Reflectivity Versus CrO₃ Concentration
Data-Run No. 2

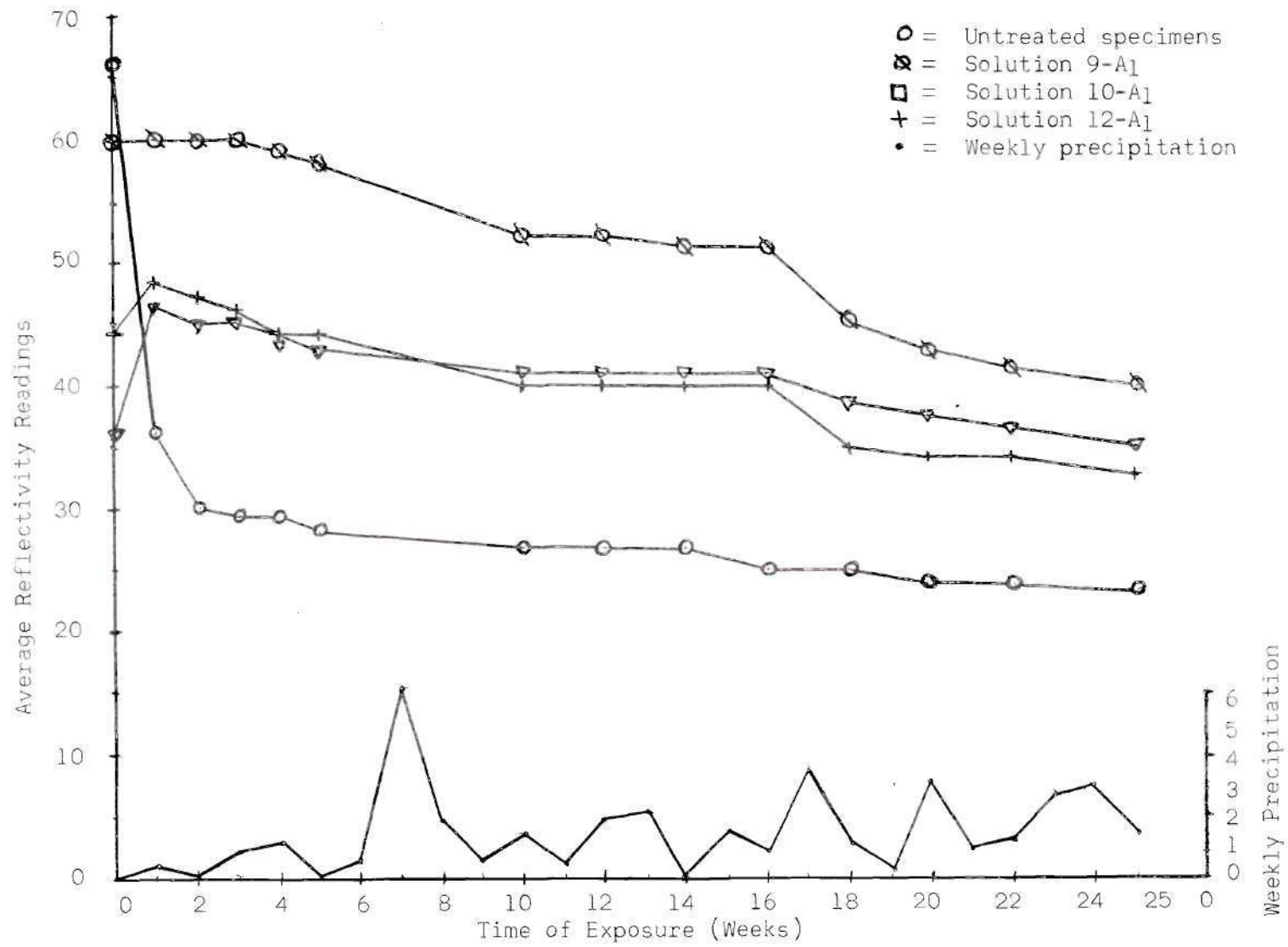


Figure 6. Average Reflectivity Readings Versus Time of Exposure For Solution Containing only CrO₃. Data-Run No. 1

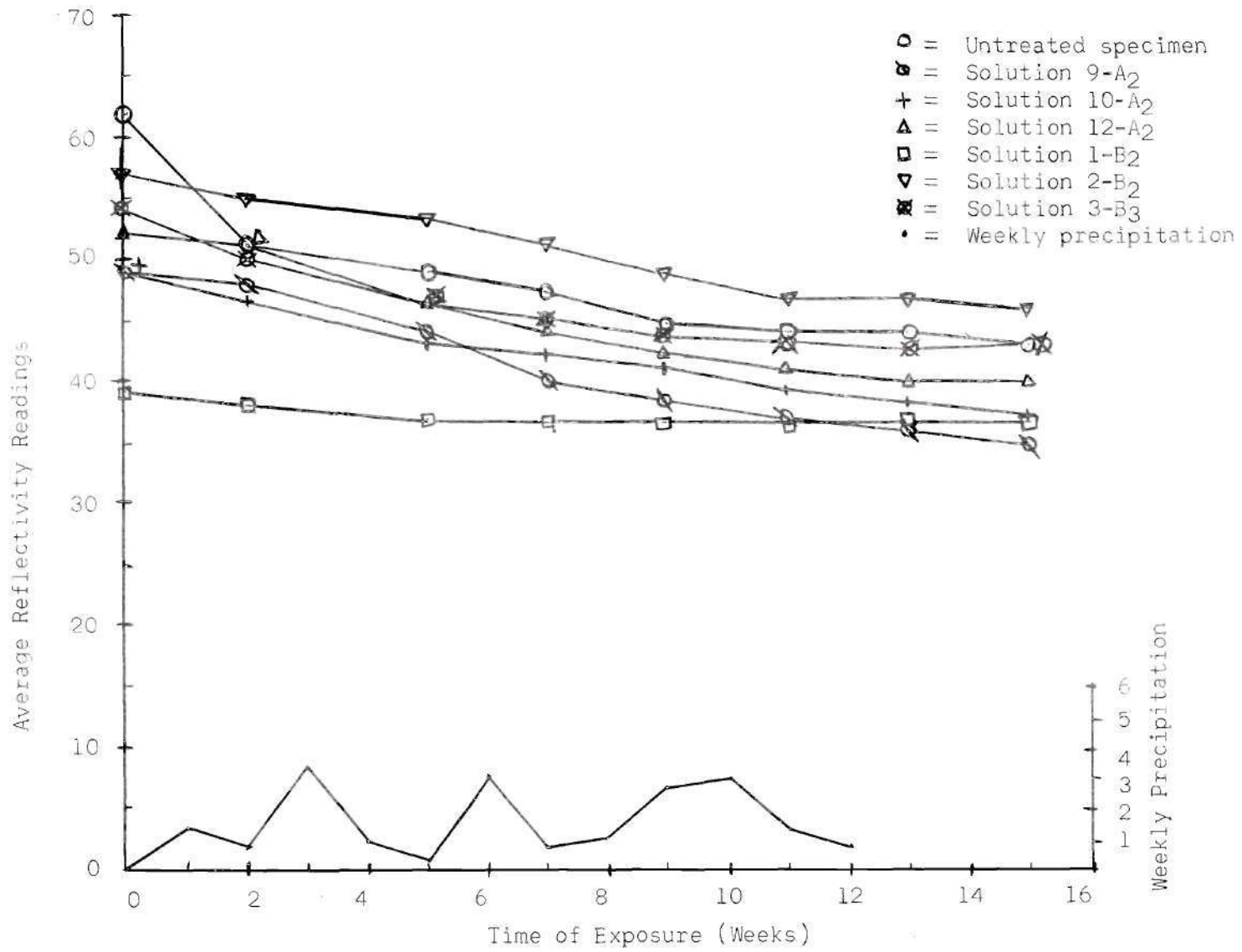


Figure 7. Average Reflectivity Readings Versus Time of Exposure. Data-Run No. 2

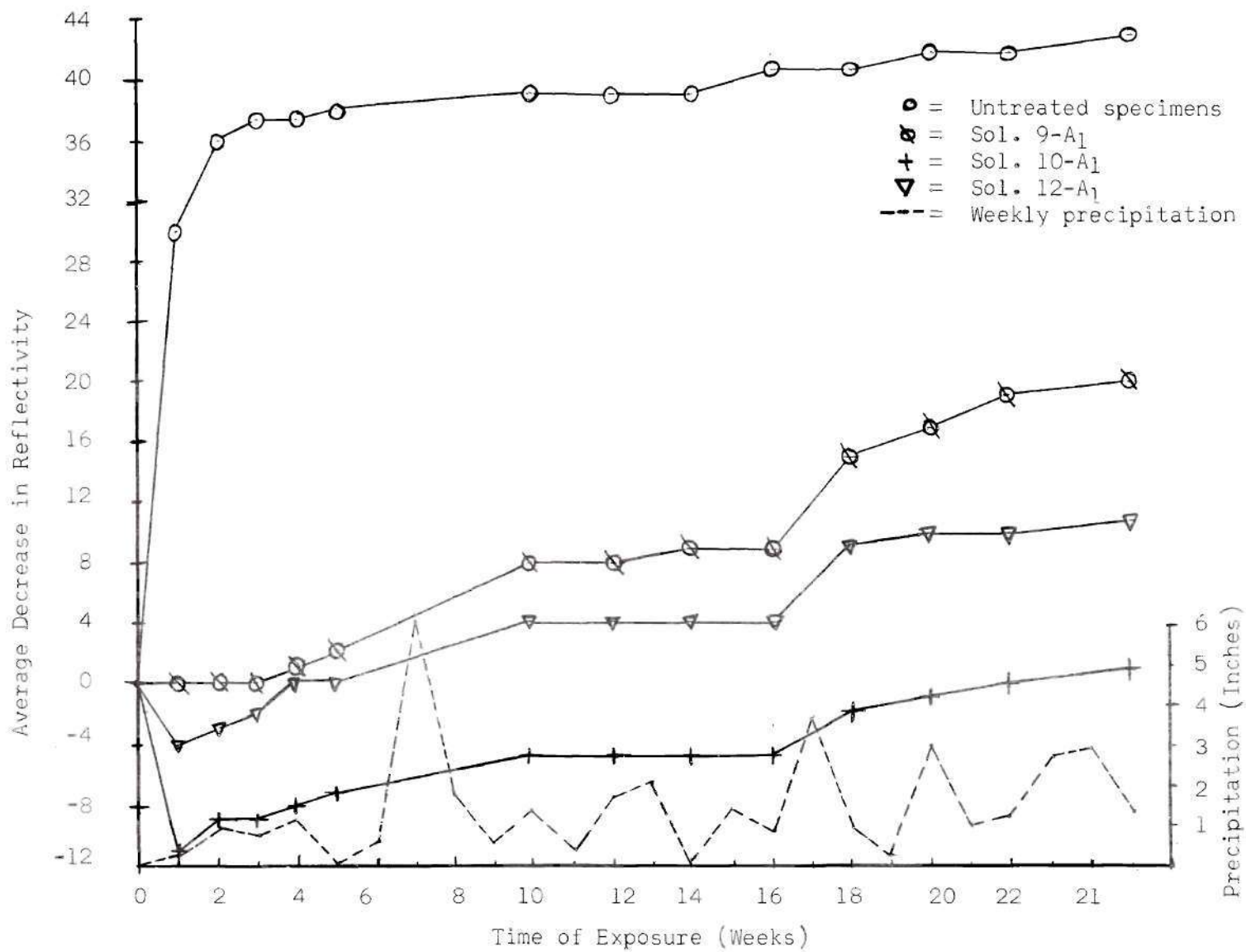


Figure 8. Average Decrease in Reflectivity Versus Time of Exposure for Solution Containing Only CrO_3 . Data=Run No. 1

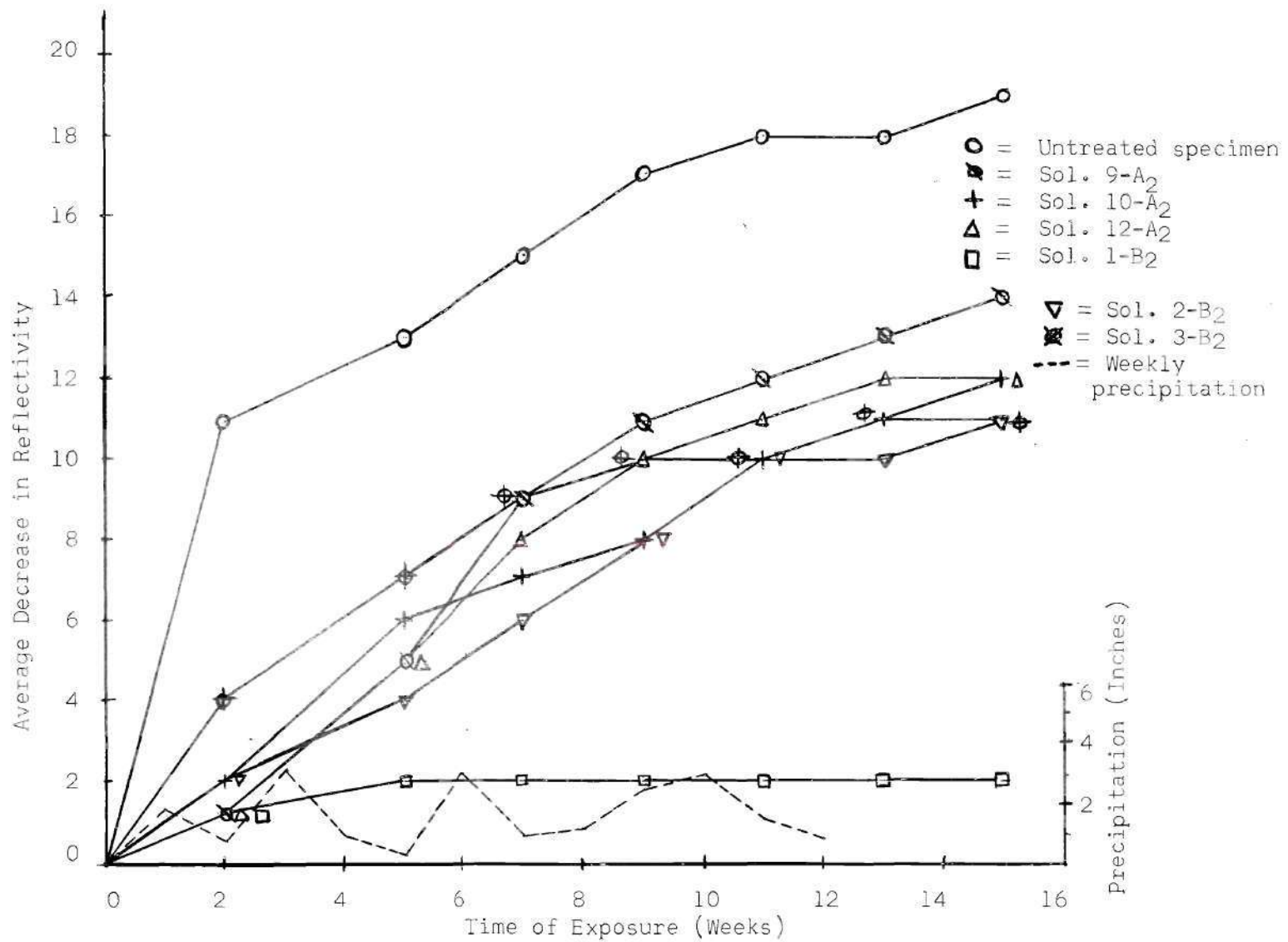


Figure 9. Average Decrease in Reflectivity Versus Time of Exposure. Data-Run No. 2

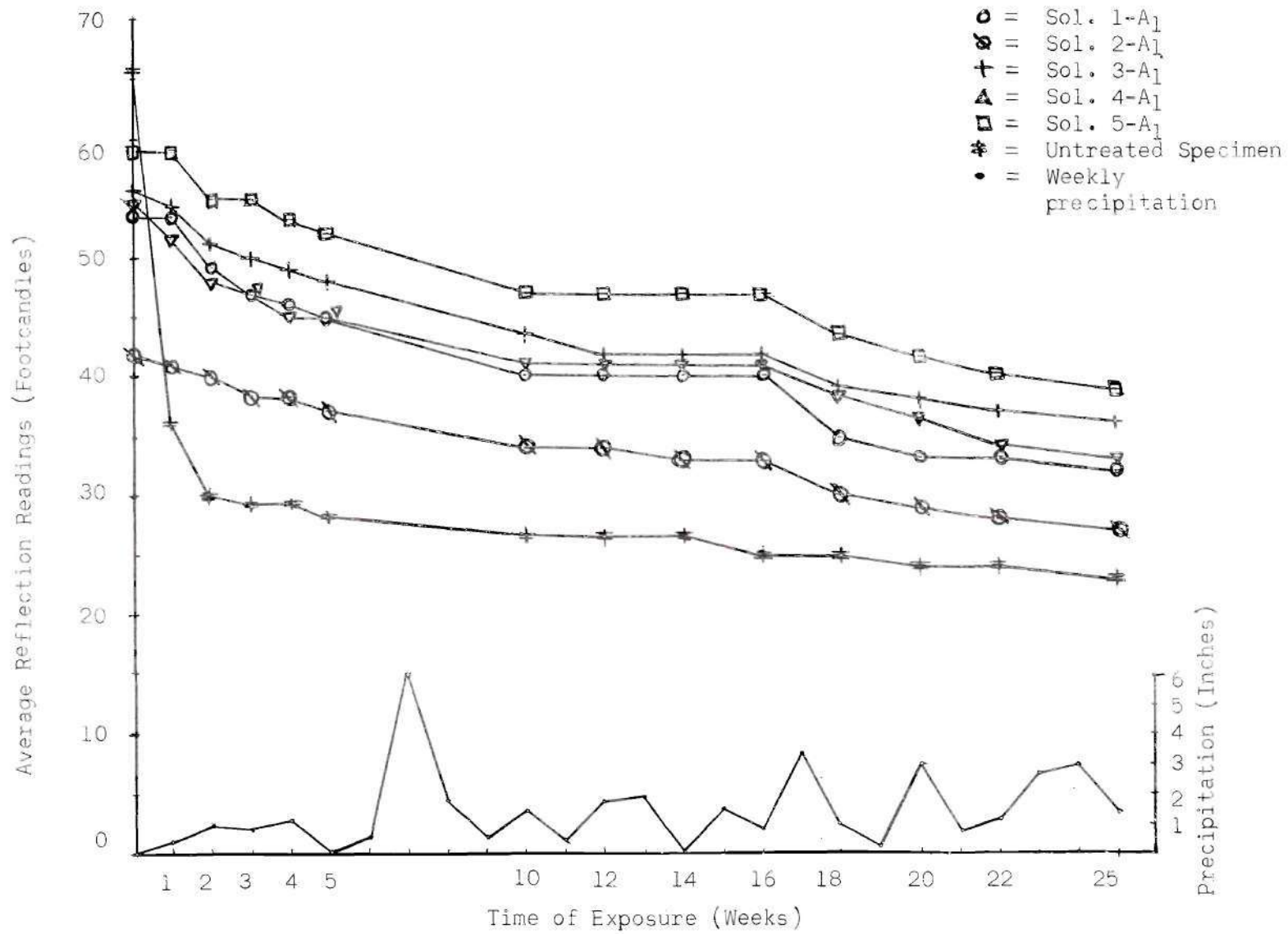


Figure 10. Average Reflectivity Readings Versus Time of Exposure for Solutions Containing CrO_3 and H_3PO_4 Mixture. Data-Run No. 1

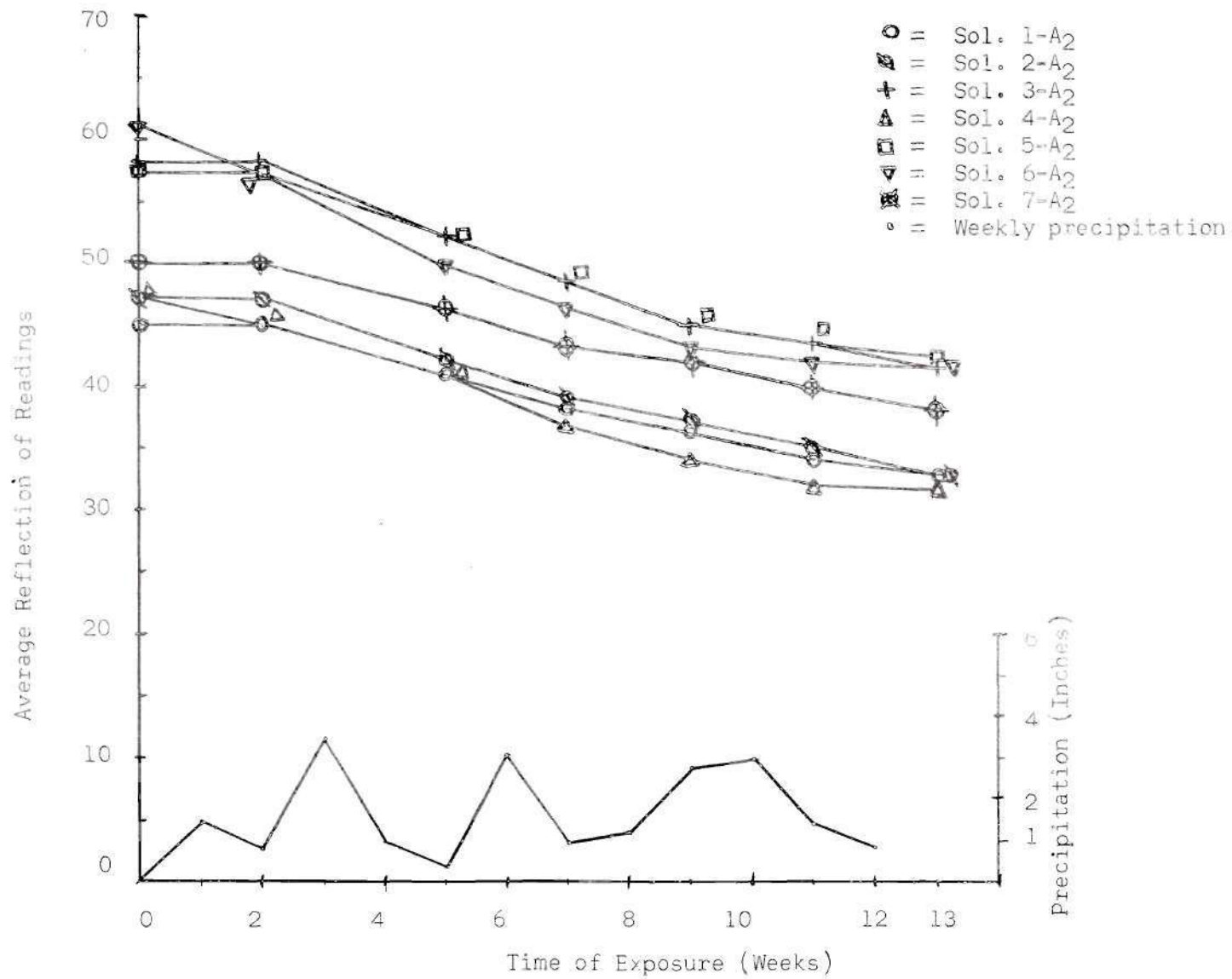


Figure 11. Average Reflectivity Readings Versus Time of Exposure for Solution Containing CrO_3 and H_3PO_4 Mixture. Data-Run No. 2

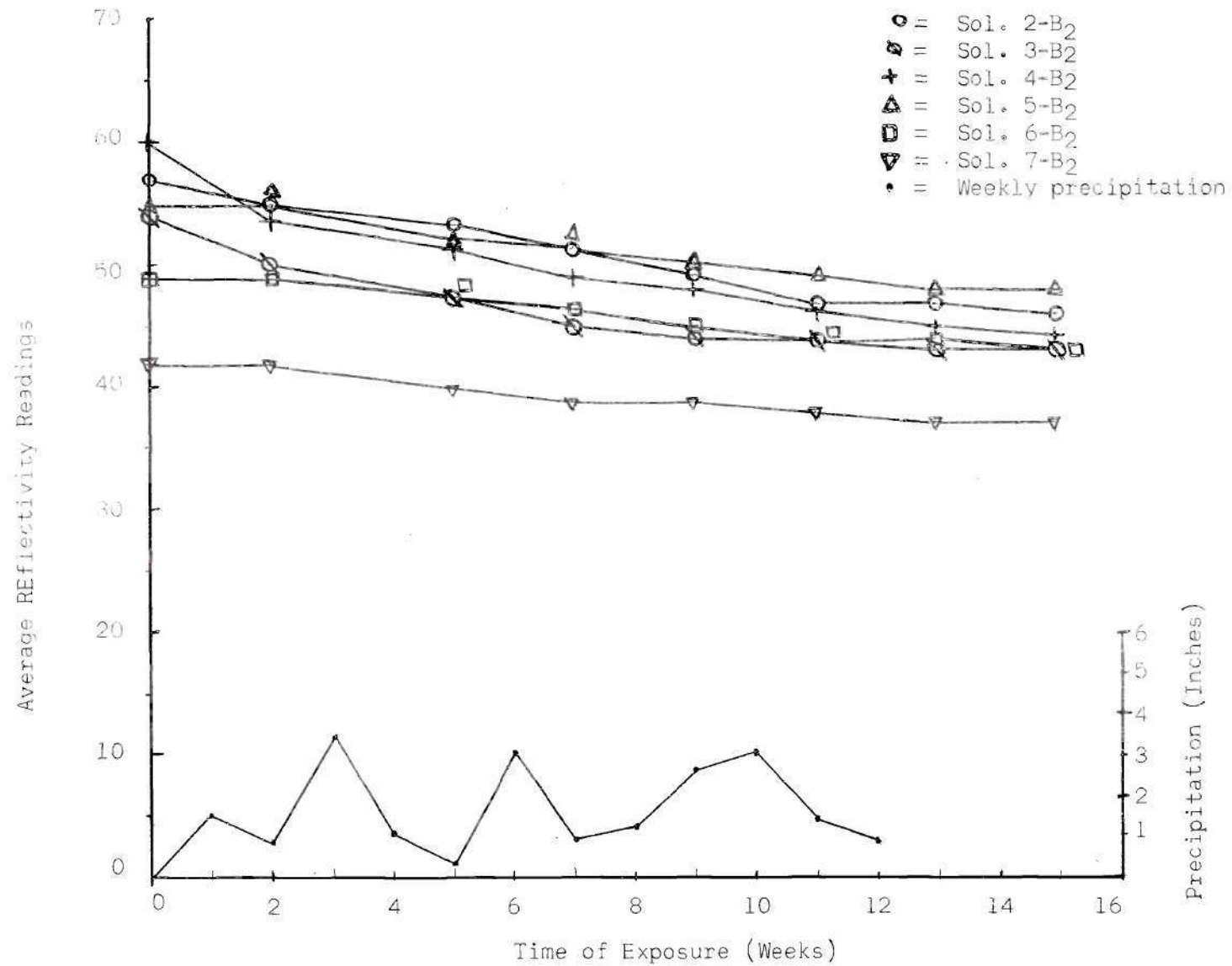


Figure 12. Average Reflectivity Readings Versus Time of Exposure for Solution 2-B₂ through 7-B₂. Data-Run No. 2

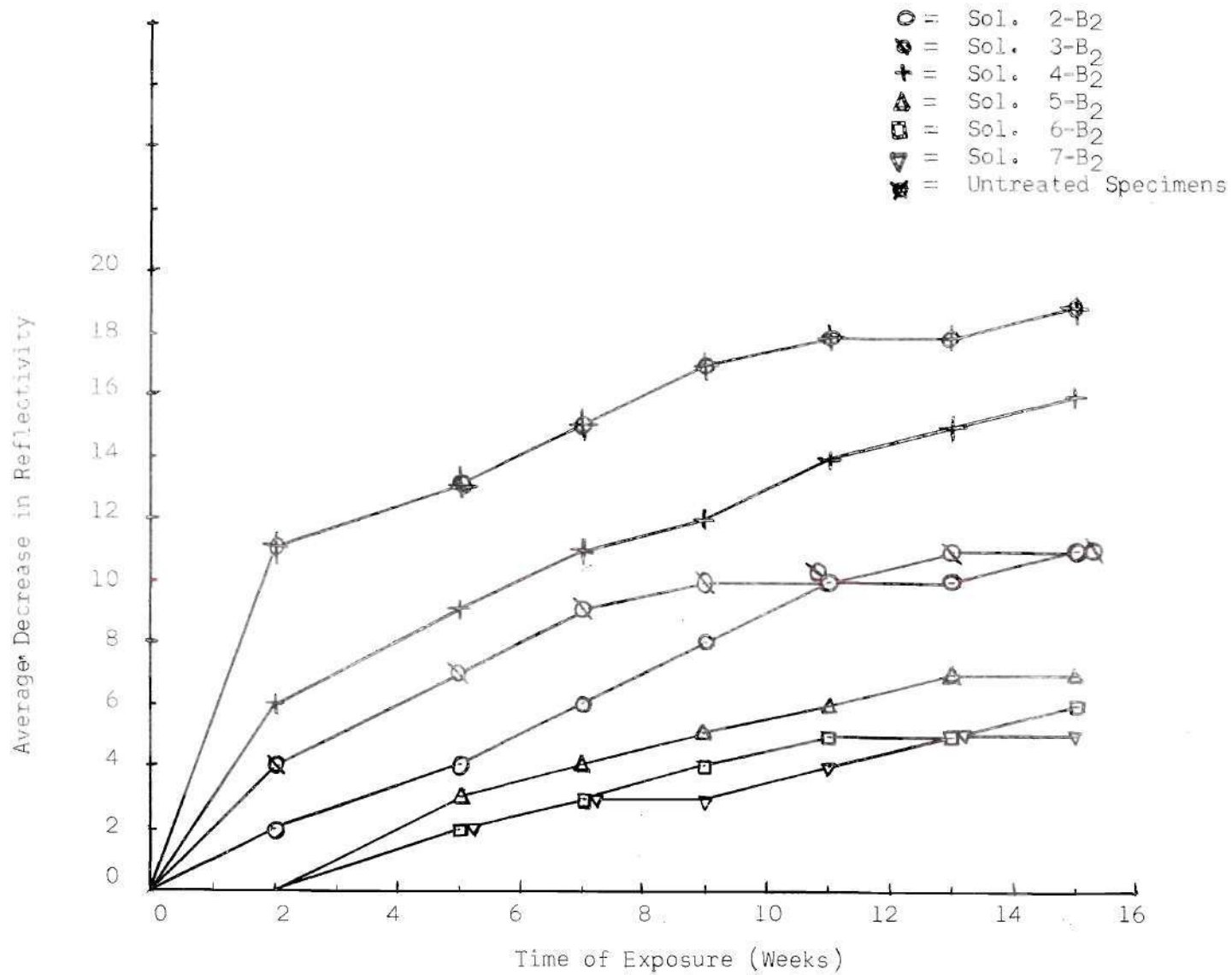


Figure 13. Average Decrease in Reflectivity Versus Time of Exposure for Solution 2-B₂ through 7-B₂. Data-Run No. 2

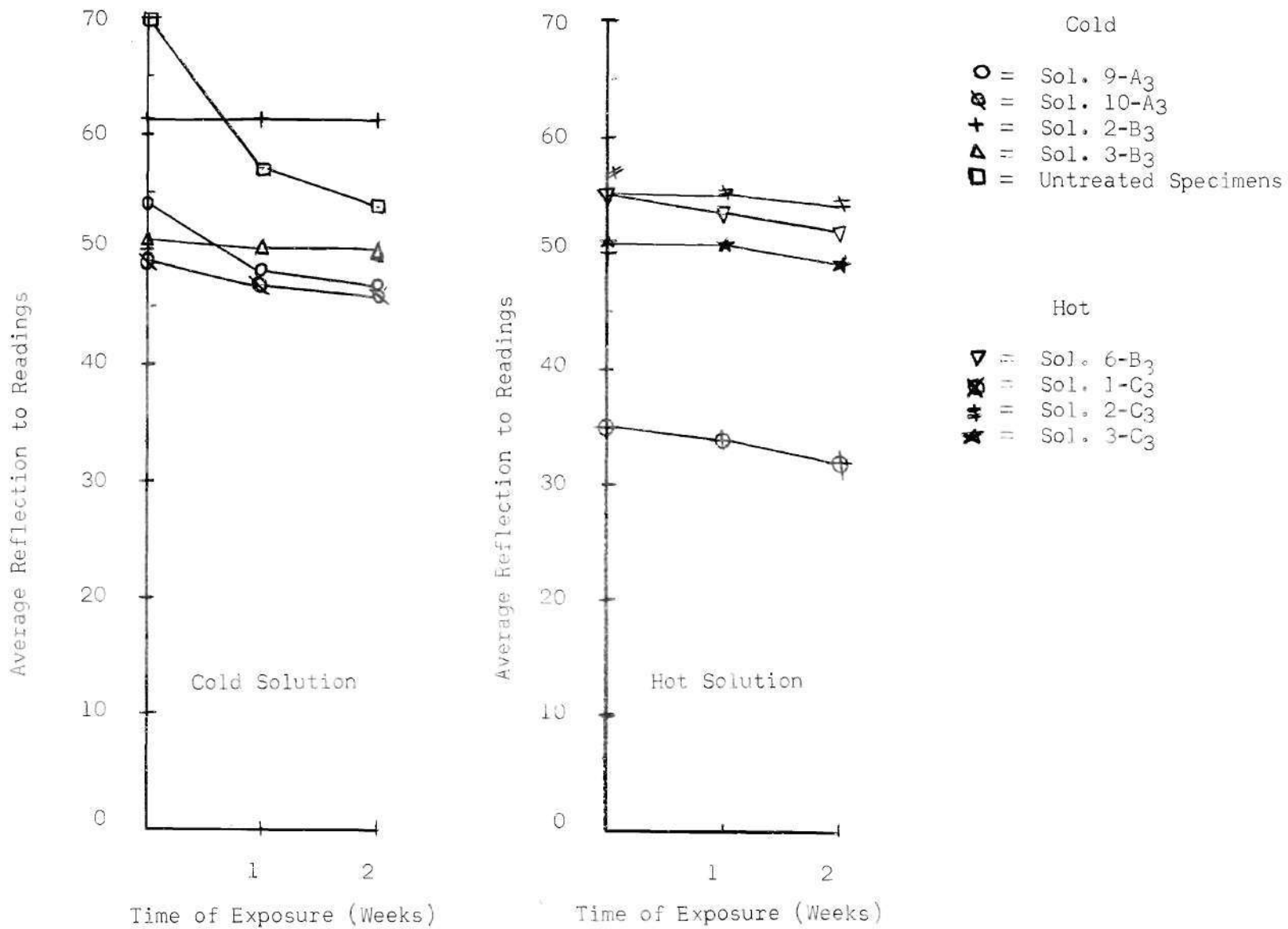


Figure 14. Average Reflectivity Readings Versus Time of Exposure for Hot and Cold Solutions. Data-Run No. 3

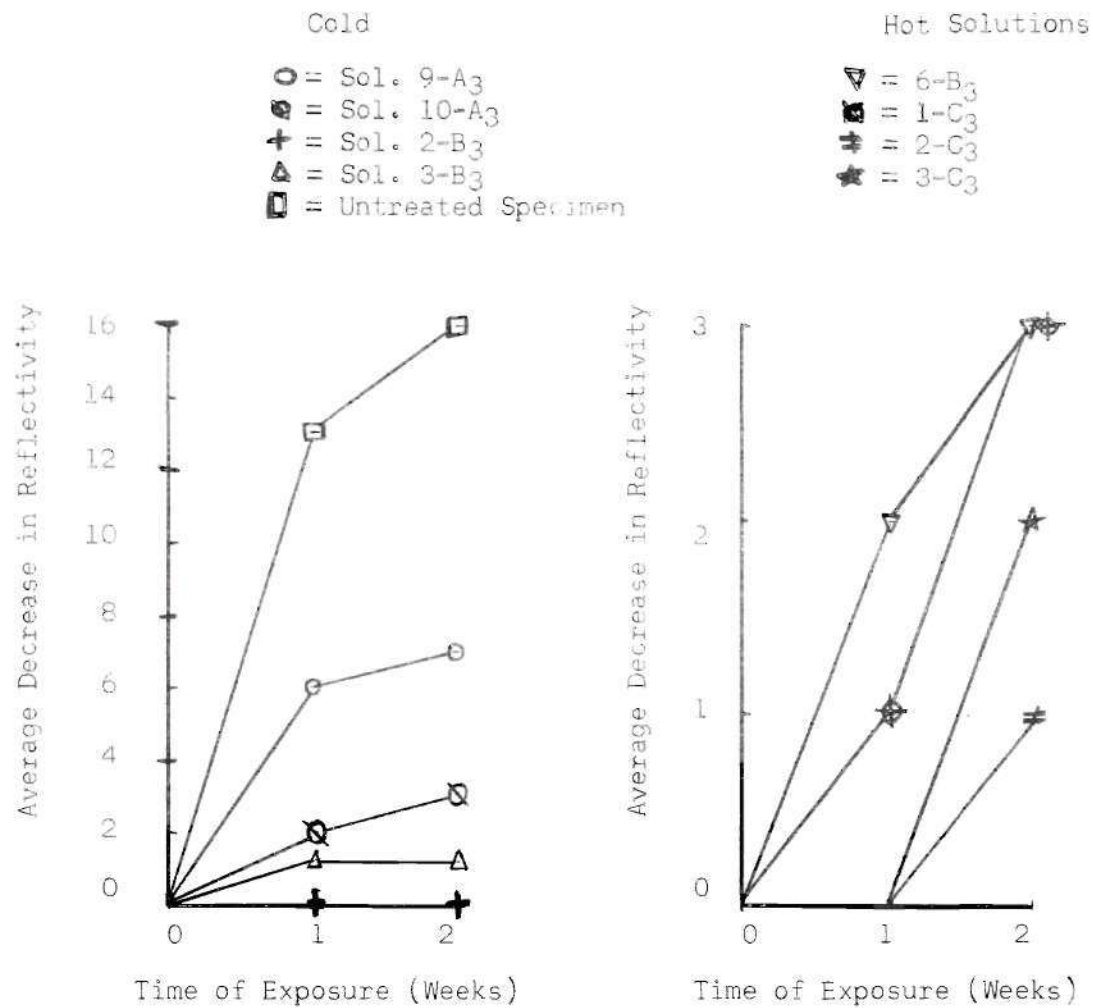


Figure 15. Average Decrease in Reflectivity Versus Time of Exposure for Hot and Cold Solutions. Data-Run No. 3

Table 1. Composition of Solutions Used for Test No. 1
(Concentrations in Grams per Liter)

Solution No.	CrO ₃	H ₃ PO ₄
1-A ₁	7.5	2.0
2-A ₁	7.5	5.0
3-A ₁	2.5	5.0
4-A ₁	2.5	10.0
5-A ₁	7.5	10.0
6-A ₁	2.5	15.0
7-A ₁	7.5	15.0
8-A ₁	2.5	-
9-A ₁	5.0	-
10-A ₁	15.0	-
11-A ₁	7.5	-
12-A ₁	10.0	-

Table 2. Compositions of Solutions Used for Test No. 2
(Concentrations in Grams per Liter)

Solution No.	CrO ₃	H ₃ PO ₄	NaF	Treatment
1-A ₂	7.5	2.0	-	
2-A ₂	7.5	5.0	-	
3-A ₂	2.5	5.0	-	
4-A ₂	2.5	10.0	-	
5-A ₂	7.5	10.0	-	
6-A ₂	2.5	15.0	-	
7-A ₂	7.5	15.0	-	
8-A ₂	2.5	-	-	
9-A ₂	5.0	-	-	
10-A ₂	15.0	-	-	
11-A ₂	7.5	-	-	
12-A ₂	10.0	-	-	
1-B ₂	20.0	-	-	
2-B ₂	5.0	-	1.35	
3-B ₂	15.0	-	4.05	
4-B ₂	5.0	-	-	Hot plate - Cold sol.
5-B ₂	5.0	-	-	Hot plate - Hot sol.
6-B ₂	5.0	-	-	Cold plate - Hot sol.
7-B ₂	5.0	-	-	Cold plate - Cold sol. (5 min. dip)

Table 3. Composition of Solutions Used for Test No. 3
(Concentration in Grams per Liter)

Solution No.	CrO ₃	NaF	Treatment
9-A ₃	5.0	-	
10-A ₃	15.0	-	
2-B ₃	5.0	1.35	
3-B ₃	15.0	4.05	
6-B ₃	5.0	-	Cold plate-Hot sol.
1-C ₃	15.0	-	Cold plate-Hot sol.
2-C ₃	5.0	1.35	Cold plate-Hot sol.
3-C ₃	15.0	4.05	Cold plate-Hot sol.

Table 4. Atmospheric Conditions for Test No. 1

Time of Exposure Weeks	Average Precipitation Inches	Average Relative Humidity %
1	0.33	54
2	0.09	72
3	0.81	52
4	1.16	84
5	0.00	65
6	0.54	64
7	6.19	78
8	1.72	90
9	0.48	65
10	1.31	62
11	0.39	70
12	1.73	60
13	1.82	75
14	0.00	86
15	1.42	65
16	0.77	63
17	3.41	70
18	0.98	81
19	0.22	72
20	3.00	82
21	0.81	55
22	1.07	48
23	2.62	79
24	2.95	62
25	1.37	73
26	0.75	52

Table 5. Atmospheric Conditions for Test No. 2

Time of Exposure Weeks	Average Precipitation Inches	Average Relative Humidity %
1	1.42	65
2	0.77	63
3	3.41	70
4	0.98	81
5	0.22	72
6	3.00	82
7	0.81	55
8	1.07	48
9	2.62	79
10	2.95	62
11	1.37	63
12	0.75	52

Table 6. Light Reflectivity Readings for Run No. 1

Solution	Initial Readings	Weeks of Exposure												
		1	2	3	4	5	10	12	14	16	18	20	22	25
1-A ₁	60	60	55	53	52	51	44	44	44	44	39	37	36	35
	49	49	45	44	42	41	37	37	37	37	32	31	31	30
	51	51	46	45	45	44	40	40	39	39	33	32	32	31
2-A ₁	40	39	37	35	34	34	31	31	31	31	27	26	26	25
	43	42	40	39	39	37	34	34	34	34	31	30	29	28
	44	43	42	41	40	39	36	36	35	35	31	30	30	28
3-A ₁	53	52	50	47	46	46	41	41	41	41	39	39	38	36
	54	52	48	47	46	45	40	40	39	39	36	35	35	34
	62	58	56	55	54	52	48	47	46	45	41	40	39	38
4-A ₁	55	53	48	46	44	44	40	40	39	39	36	34	32	31
	57	55	51	51	48	48	44	44	44	44	42	40	38	36
	51	49	46	44	43	43	39	39	39	39	36	34	32	31
5-A ₁	55	55	50	50	49	48	43	43	43	43	41	39	38	36
	30*	30	30	30	30	30	30	30	30	30	28	28	28	27
	63	62	60	59	56	56	50	50	50	50	45	43	42	41
6-A ₁	45	44	43	41	41	41	38	38	38	38	33	31	30	29
	57	55	55	54	51	51	47	47	46	46	41	38	38	37
	53	52	50	46	45	45	42	42	42	42	37	35	35	34
7-A ₁	50	50	49	46	46	46	43	43	42	42	38	37	37	36
	56	56	55	53	51	51	46	46	46	46	43	41	41	41
	51	50	48	46	45	45	41	41	41	41	38	36	35	35
8-A ₁	68	65	61	59	58	56	51	50	49	49	44	41	39	39
	63	61	58	56	54	53	49	49	48	48	43	40	39	39
	60	58	54	51	50	49	45	45	44	44	40	38	37	36
9-A ₁	59	59	59	59	58	56	51	51	50	50	45	43	41	40
	61	61	60	59	59	58	52	52	51	51	45	43	41	40
	60	60	61	61	59	59	52	52	51	51	45	43	41	41
10-A ₁	35	46	46	46	45	45	42	42	42	42	39	38	37	36
	34	45	43	42	41	41	39	39	39	39	35	35	34	33
	40	49	46	46	45	44	42	42	42	42	39	38	37	36
11-A ₁	47	50	49	46	46	46	43	43	42	42	38	37	36	35
	25*	31	30	30	29	29	29	29	29	29	27	27	26	26
	50	55	54	51	49	49	45	45	45	45	41	39	37	36
12-A ₁	45	51	49	48	46	46	41	41	41	41	36	35	35	34
	45	48	46	45	43	43	40	40	39	39	35	34	34	33
	41	46	45	44	42	42	39	39	39	39	34	33	33	32
Untreated	68	30	26	26	26	26	26	26	26	26	25	25	25	24
	70	41	35	35	34	33	29	29	29	29	27	26	26	25
	65	33	29	29	28	28	26	26	26	26	24	24	23	23
	66	38	29	29	28	28	26	26	26	26	24	24	23	23
	60	37	30	30	29	29	26	26	26	26	24	24	23	23

*Plate Warped

Table 7. Light Reflectivity Readings for Run No. 2

Solution No.	Initial Readings	Weeks of Exposure						
		2	5	7	9	11	13	15
1-A ₂	45	45	41	39	36	34	33	-
	41	41	37	35	33	31	31	-
	49	49	44	41	38	36	35	-
2-A ₂	45	45	41	39	38	34	33	-
	51	51	45	42	39	37	36	-
	45	45	40	37	35	33	31	-
3-A ₂	63	63	57	51	47	45	44	-
	53	53	48	45	42	40	39	-
	57	57	51	48	46	43	41	-
4-A ₂	47	45	41	37	34	33	33	-
	41	40	36	32	30	29	29	-
	53	50	45	41	37	35	35	-
5-A ₂	58	58	53	49	45	43	42	-
	55	55	50	47	44	42	41	-
	31*	31	30	30	29	28	27	-
6-A ₂	65	60	53	49	47	45	44	-
	53	49	43	41	39	37	36	-
	66	61	55	49	47	45	44	-
7-A ₂	46	46	42	39	37	36	35	-
	54	54	50	48	46	44	41	-
	50	50	45	43	42	40	38	-
8-A ₂	61	59	53	48	46	45	44	44
	61	61	55	50	48	46	44	44
	59	56	51	48	45	44	41	40
9-A ₂	49	49	45	43	41	39	38	37
	56	55	50	45	42	41	40	40
	43	41	36	33	32	31	31	31
10-A ₂	54	50	46	44	43	41	40	39
	46	44	41	40	38	36	35	34
	48	46	43	42	41	40	39	38

(Continued)

Table 7. Light Reflectivity Readings for Run No. 2 (Continued)

Solution No.	Initial Readings	Weeks of Exposure						
		2	5	7	9	11	13	15
11-A ₂	54	51	49	45	42	41	40	40
	56	52	50	45	44	43	41	41
	51	51	46	44	42	41	40	40
12-A ₂	51	51	46	44	42	41	40	40
	52	50	47	44	42	41	40	40
	-	-	-	-	-	-	-	-
1-B ₂	38	36	34	33	33	32	32	32
	39	39	39	39	39	39	39	39
	39	39	39	39	39	39	39	39
2-B ₂	53	51	49	47	45	44	44	44
	60	59	56	54	52	49	49	48
	58	55	53	51	49	47	47	46
3-B ₂	53	51	48	46	45	44	44	44
	55	51	48	47	46	45	44	44
	53	48	44	43	42	42	41	41
4-B ₂	60	56	52	51	50	49	47	46
	55	49	45	44	43	41	40	39
	64	58	55	53	51	49	47	46
5-B ₂	54	54	52	51	50	49	49	48
	59	59	56	54	52	51	50	49
	51	51	48	48	47	47	46	46
6-B ₂	48	48	46	45	45	44	44	43
	44	44	42	40	40	39	39	39
	54	54	52	52	51	50	49	48
7-B ₂	40	40	38	38	37	35	35	35
	40	40	38	38	38	38	37	36
	46	45	44	42	41	40	40	39
Untreated	60	45	42	40	38	37	37	36
	55	50	47	45	43	42	42	41
	70	59	57	56	54	53	53	53

Table 8. Light Reflectivity Readings for Run No. 3

Solution No.	Weeks of Exposure		
	Initial Readings	1	2
9-A ₃	56	51	51
	56	49	47
	50	44	43
10-A ₃	51	49	49
	47	45	45
	49	47	47
2-B ₃	64	64	63
	64	54	64
	56	56	55
3-B ₃	50	49	48
	44	44	44
	60	58	57
6-B ₃	52	52	52
	55	53	53
	56	54	41
1-C ₃	33	32	30
	38	35	33
	35	34	32
2-C ₃	51	51	50
	61	61	60
	53	53	52
3-C ₃	47	47	45
	55	55	53
	51	51	49
Untreated	70	55	50
	70	66	66
	69	50	45

Table 9. Average of Reflectivity Readings for Run No. 1

Weeks of Exposure

Solution No.	Initial	Weeks of Exposure												
	Readings	1	2	3	4	5	10	12	14	16	18	20	22	25
1-A ₁	53	53	49	47	46	45	40	40	40	40	35	33	33	32
2-A ₁	42	41	40	38	38	37	34	34	33	33	30	29	28	27
3-A ₁	56	54	51	50	39	48	43	42	42	42	39	38	37	36
4-A ₁	54	52	48	47	45	45	41	41	41	41	38	36	34	33
5-A ₁	59	59	55	55	53	52	47	47	47	47	43	41	40	39
6-A ₁	52	50	49	47	46	46	42	42	42	42	37	35	34	33
7-A ₁	52	52	51	48	47	47	43	43	43	43	40	38	38	37
8-A ₁	64	61	58	55	54	53	48	48	47	47	42	40	38	38
9-A ₁	60	60	60	60	59	58	52	52	51	51	45	43	41	40
10-A ₁	36	47	45	45	44	43	41	41	41	41	38	37	36	35
11-A ₁	49	53	52	49	48	48	44	44	44	44	40	38	37	35
12-A ₁	44	48	47	46	44	44	40	40	40	40	35	34	34	33
Untreated	66	36	30	29	29	28	27	27	27	27	25	25	24	23

Table 10. Average Readings for Run No. 2

Solution No.	Initial Readings	Weeks of Exposure						
		2	5	7	9	11	13	15
1-A ₂	45	45	41	38	36	34	33	-
2-A ₂	47	47	42	39	37	35	33	-
3-A ₂	58	58	52	48	45	43	41	-
4-A ₂	47	45	41	37	34	32	32	-
5-A ₂	57	57	52	48	45	43	42	-
6-A ₂	61	57	50	46	43	42	41	-
7-A ₂	50	50	46	43	42	40	38	-
8-A ₂	60	59	53	49	47	45	43	43
9-A ₂	49	48	44	40	38	37	36	35
10-A ₂	49	47	43	42	41	39	38	37
11-A ₂	54	51	49	46	44	43	41	41
12-A ₂	52	51	47	44	42	41	40	40
1-B ₂	39	38	37	37	37	37	37	37
2-B ₂	57	55	53	51	49	47	47	46
3-B ₂	54	50	47	45	44	44	43	43
4-B ₂	60	54	51	49	48	46	45	44
5-B ₂	55	55	52	51	50	49	48	48
6-B ₂	49	49	47	46	45	44	44	43
7-B ₂	42	42	40	39	39	38	37	37
Untreated	62	51	49	47	45	44	44	43

Table 11. Average Readings for Run No. 3

Weeks of Exposure

Solution No.	Initial Readings	1	2
9-A ₃	54	48	47
10-A ₃	49	47	46
2-A ₃	61	61	61
3-A ₃	52	50	50
6-B ₃	55	53	52
1-C ₃	35	34	32
2-C ₃	55	55	54
3-C ₃	51	51	49
Untreated	70	57	54

Table 12. Average Decrease in Reflectivity for Run No. 1

Solution No.	Weeks of Exposure												
	1	2	3	4	5	10	12	14	16	18	20	22	25
1-A ₁	0	4	6	7	8	13	13	13	13	17	20	20	21
2-A ₁	1	2	4	4	5	8	8	9	9	12	13	14	15
3-A ₁	2	5	6	7	8	13	14	14	14	17	18	19	20
4-A ₁	2	6	7	9	9	13	13	13	13	16	18	20	21
5-A ₁	0	4	4	6	7	12	12	12	12	16	18	19	20
6-A ₁	2	3	5	6	6	10	10	10	10	15	17	18	19
7-A ₁	0	1	4	5	5	9	9	9	9	12	14	14	15
8-A ₁	3	6	9	10	11	16	16	17	17	22	24	26	26
9-A ₁	0	0	0	1	2	8	8	9	9	15	17	19	20
10-A ₁	+11	-9	-9	-8	-7	-5	-5	-5	-5	-2	-1	0	1
11-A ₁	+4	-3	0	1	1	5	5	5	5	9	11	12	14
12-A ₁	+4	-3	-2	0	0	4	4	4	4	9	10	10	11
Untreated	30	36	37	37	38	39	39	39	41	41	42	42	43

Table 13. Average Decrease in Reflectivity for Run No. 2

Solution No.	Weeks of Exposure						
	2	5	7	9	11	13	15
1-A ₂	0	4	7	9	11	12	-
2-A ₂	0	5	8	10	12	14	-
3-A ₂	0	4	10	13	15	17	-
4-A ₂	2	6	10	13	13	15	-
5-A ₂	0	5	9	12	14	15	-
6-A ₂	3	11	15	18	19	20	-
7-A ₂	0	4	7	8	10	12	-
8-A ₂	1	7	11	13	15	17	17
9-A ₂	1	5	9	11	12	13	14
10-A ₂	2	6	7	8	10	11	12
11-A ₂	3	7	8	10	11	13	13
12-A ₂	1	5	8	10	11	12	12
1-B ₂	1	2	2	2	2	2	2
2-B ₂	2	4	6	8	10	10	11
3-B ₂	4	7	9	10	10	11	11
4-B ₂	6	9	11	12	14	15	16
5-B ₂	0	3	4	5	6	7	7
6-B ₂	0	2	3	4	5	5	6
7-B ₂	0	2	3	3	4	5	5
Untreated	11	13	15	17	18	18	19

Table 14. Average Decrease in Reflectivity for Run No. 3

Weeks of Exposure

Solution No.	1	2
9-A ₃	6	7
10-A ₃	2	3
2-B ₃	0	0
3-B ₃	1	1
6-B ₃	2	3
1-C ₃	1	3
2-C ₃	0	1
3-C ₃	0	2
Untreated	13	16

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