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MEASUREMENTS OF THE EFFECTS OF MOISTURE IN NUCLEAR TRACK EMULSION

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April 6, 1953

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ABSTRACT

In order to answer a number of specific questions, thickness and density measurements were made on Ilford nuclear track emulsions before and after processing. Measurements were made as equilibrium was approached under various conditions of ambient relative humidity. Thickness measurements were made with a modified dial micrometer. Volume measurements were made by weighing plates immersed in carbon tetrachloride. A special study of plates stored in a vacuum was carried out. The washing time was found to have an important effect on the shrinkage factor. The data obtained are presented in a number of tables and graphs. The theory of water diffusion in emulsion has been appended by W. H. Barkas, and the emulsion constants evaluated from the experimental data. Attention is directed to the very long characteristic diffusion times implied for thick emulsions.

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I. INTRODUCTION

The interpretation of measurements on nuclear emulsion tracks in precision experiments requires information concerning the effects of the variable moisture content. For example, published information leaves unanswered certain questions which arise when allowance is being made for the shrinkage of processed and unprocessed Ilford emulsion on glass accompanying a reduction in relative humidity.

During 1951 and 1952 measurements[1] were made in this laboratory on plates manufactured no later than the first half of 1952. The measurements consisted mostly of thickness changes and more recently of volume changes produced by changes in moisture content. Water content was changed by changing relative humidity and by pumping in a vacuum, and, in addition, a few measurements were made on volume changes produced by changes in temperature at constant relative humidity. The study was directed toward obtaining answers to the following questions:

(a) How may the volume and volume changes of the emulsion be measured accurately?

(b) Is the reduction of volume equal to the volume of water lost by the emulsion?

(c) How do the weight and volume of emulsion approach equilibrium with the ambient humidity; in particular, how do the weight and volume vary with time when the emulsion is kept at zero humidity in a vacuum?

(d) Do different processing methods affect the processing shrinkage experienced by the emulsion?

(e) How does the thickness of processed emulsion depend on the ambient humidity?

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1 Abstracts of a portion of this paper have been published: A. Oliver and Walter H. Barkas, Phys. Rev. 85, 756 (1952); A. Oliver, Bull. Amer. Phys. Soc. 27 No. 6, 16 (1952).

(f) What conditions affect the "shrinkage factor"?

II. THICKNESS, VOLUME, AND WEIGHT MEASUREMENTS

The data taken represent adsorption starting up from 50 percent relative humidity and desorption down from 50 percent and may differ somewhat from measurements made under different conditions because of hysteresis. The plates measured were exclusively those manufactured by Ilford, Ltd., on glass backing.

Thickness measurements were made using a dial indicating micrometer gauge (Starrett). This was mounted employing a one-point plate support, with an arrangement to hold the plate against this support, and a windlass for allowing the plunger to contact the surface of the emulsion repeatedly without distorting it. After sufficient thickness data were obtained, a procedure was developed for accurate volume measurement by weighing displaced carbon tetrachloride. Tests indicated that the carbon tetrachloride neither penetrated the emulsion a detectable amount nor dissolved it during the lengths of time required for the weighing. Volume measurement by displacement, with length and width measurements using micrometers, yield precise measurements of average thickness.

Figure 1 is a photograph of the dial indicator as it was mounted for use in making thickness measurements on 1 in. x 3 in. plates. The mounting was designed to make possible the measurement of thickness at reproducible points on a plate. The points are along the major axis and are located with one at the center and two others each an inch away from the center. One-point support for the plate being measured was built in, since the plates warp with extreme drying, and provision was made to insure that the plunger may travel with its axis normal to the emulsion. A steel spring inside the case of the indicator, intended to provide a force to return the plunger to zero, was disconnected so as to reduce the pressure of the plunger against the emulsion. Another modification of the dial indicator was to fasten a thread to the top of the plunger. This, by means of a windlass, permitted one to retract the plunger and to lower it carefully to the emulsion without distorting the soft surface. With zero checks between readings on plates, it was possible to obtain individual readings reproducible to within 5×10^{-5} inches. By taking average readings, measurements containing errors of only about 10^{-5} inches were obtainable.

This dial indicator arrangement was used for thickness measurements on unprocessed plates in a safelighted darkroom, plates on which the emulsion thickness was changed by storing in atmospheres of different relative humidities, and plates which had spent different amounts of time in a vacuum. Thickness measurements were made with this device on processed emulsion, some of which before the processing had been brought to equilibrium with 50 percent relative humidity and measured in thickness. Other processed plates were measured after they were brought to equilibrium with 50 percent and then other humidities. Emulsion thickness, of course, is the calculated difference between the plate thickness and the glass thickness measured after the emulsion has been washed away.

It was not felt that the average of the thicknesses measured at three points was a sufficiently accurate average thickness of the emulsion on the plate. Therefore, when it was desired to measure emulsion densities, a different method for measuring the volume was chosen. Figure 2 is a photograph of an analytical balance used for measuring the weights of plates. The volume of the plate was found by displacement, or from calculation made from weight measurement of the plate as it was suspended immersed in clean carbon tetrachloride. The temperature of this liquid was held to 25.0°C until the moment the plate was immersed in it. The magnetic damping helped in allowing an accurate weight reading to be obtained within a minute or less of the time when the temperature control was discontinued. Temperature readings were taken to the nearest 0.01°C, and corrections were applied for the time required for obtaining balance while the liquid cooled by evaporation (momentarily being away from heat and without agitation). The temperatures calculated were applied to the equation for density to be found for carbon tetrachloride in the "International Critical Tables". The accuracy of reproducing measurements of volume was about 0.3 mm^3.

The early measurements in this experiment were on plates which had been stored in cells in which the humidity was under the control of various salt solutions which, near ordinary laboratory room temperatures, maintain certain humidities. These data were obtained from the "International Critical Tables". The humidity maintained, however, varies with the temperature, and lack of good temperature control resulted in poor humidity control. It was fortunate, therefore, that a means was found for accurate humidity control using glycerine solutions at 25°C. The data for this comprise Table I.

The test tubes to be seen in the background in Figure 2 are some of those in a constant temperature (25°C) water bath. In each of these tubes are 60 ml of the water solution of glycerine desired for the particular humidities, and a wire in each is bent so as to support a plate above the solution. The tubes are closed with rubber stoppers.

III. BEHAVIOR OF UNPROCESSED EMULSION

The thickness vs. relative humidity data measured with the smallest uncertainties are those calculated from volume measurements on C. 2 emulsion. This information is given in Table II.

These changes provide an indication of what is to be expected, even when humidity control and measurement are not carried out. However, pumping on an emulsion in a vacuum is another matter. In order to study how emulsion behaves in a vacuum, sets of plates were first brought to equilibrium with a controlled humidity and then pumped down, with the vacuum interrupted briefly for the thickness measurement to be made. Table III is a tabulation of some of these measurements.

Another aspect of the variation of moisture content is the consequent variation of density with relative humidity. Measurements of weight and volume on plates of the same batch (Z5333) used for thickness measurements were made, and in Figure 3 the densities are plotted. To go from density change to thickness change, for the same moisture content change, an assumption must be made as to the relationship between weight of water change and volume of emulsion change. Our measurements appear to indicate that adding moisture from equilibrium with 50 percent relative humidity swells the emulsion one cubic centimeter per gram. Data on dehydrating a plate by reducing the humidity from a normal 50 percent to the subnormal 30 percent or 20 percent, allowing several days for a 200μ emulsion to reach equilibrium, seem to imply that for each gram of water lost the average emulsion shrinkage for this interval is about eight tenths of one cubic centimeter. The change from 50 percent relative humidity to 10 percent relative humidity reduced the volume of another plate 0.87 ± 0.07 cc/g.

The investigation of the unprocessed emulsion concluded with measurements on the rate at which equilibrium of moisture content with relative humidity is approached. From measurements on 200μ plates repeated at

intervals of days and weeks, we decided equilibrium had been reached if readings taken at any time after three days were reproduced at least two days later. In order to magnify the effect and to measure the evaporation accurately, we chose to weigh a 1000μ emulsion at intervals as it approached equilibrium with 50 percent relative humidity, and then to pump it down in a vacuum and to measure its weight at intervals over as long a period as possible. Figure 4 is a photograph of this plate at the conclusion of the experiment, before the chipped glass was removed and weighed. The fracturing began on about the fourth day of pumping. Figure 5 is a plot of the changes of weight measured at the times dehydration in the vacuum was interrupted for measurement. The record of weight changes for this plate as it had approached equilibrium with 50 percent relative humidity is tabulated in Table IV. It is evident that even after 18 days, complete equilibrium had not been reached. According to the diffusion theory appended to this article by W. H. Barkas, a characteristic diffusion time exists which is the thickness squared divided by the diffusion constant. The long interval required for a 1000μ plate to reach equilibrium is therefore understandable. However, variation of moisture content affects the composition which in turn affects the value of the diffusion constant.

There remain a number of other questions of less importance to be answered. One of these is: How sensitive is the moisture content to temperature, ambient relative humidity held constant? A partial answer to this is in an unrepeated set of measurements with plates of batch Z5333 (200μ, C-2). At approximately 50 percent relative humidity (held by a solution of $Mg(NO_3)_2 6H_2O$) we measured a change from a density of 3.88 at $3^{\circ}C$ to 3.94 at $35^{\circ}C$, or a change in density of 0.01 for a temperature change of about $4.5^{\circ}C$.

IV. BEHAVIOR OF PROCESSED EMULSION AND THE SHRINKAGE FACTOR

The moisture content of the unprocessed emulsion is of interest because it affects the emulsion density and emulsion thickness at the time of exposure. This thickness upon exposure differs from plate to plate and is often found by multiplying the thickness measured after processing by a shrinkage factor, which for the same composition of emulsion and equivalent handling should be a constant. At the outset of this experiment, unprocessed plates were brought to equilibrium with 50 percent relative humidity, measured, processed, again

brought to equilibrium with 50 percent relative humidity and measured, and shrinkage factors were obtained after the glass backings were measured. Not all plates were processed together, and one processing was the same as the next only in that developing times and temperatures were the same. Fixing and hardening, along with washing, were not always identical.

Significantly different shrinkage factors were obtained for plates fixed and washed differently; therefore, controlled experiments were performed and repeated. Successful processing may be accomplished in widely different ways, but it was found that amounts of shrinkage were different with different times for fixing and washing. Without making measurements of the composition of emulsion, it was concluded that what is important is the variation in the glycerine content of the plates processed for different lengths of time. Glycerine may freely be added, and it must be assumed that it also may be subtracted by soaking in water solutions. The composition quoted for unprocessed Ilford emulsion includes 9.3 percent glycerine (by volume). Glycerine is hygroscopic, and by itself, at least, can exhibit a moisture content vs. relative humidity curve which is significantly different from that of gelatin, falling to zero at zero humidity and rising steeply at high humidities.

In Table V are listed shrinkage factors resulting from different treatments, all at the same temperature and humidity, using the same batch of plates and identical development. Plates fixed identically were washed different lengths of time, and the plates washed longer became thinner at 50 percent relative humidity than plates washed barely enough. Plates washed the same lengths of time but fixed for widely different times were also somewhat affected. Each treatment produced emulsions which were satisfactory for study of tracks. As for following the washing or drying with a soaking in glycerine solution (to prevent peeling at low humidities), the difference between six hours and 24 hours of soaking seemed to be insignificant. As expected, plates soaked in less concentrated glycerine became thinner at 50 percent relative humidity than plates soaked in more concentrated glycerine.

If the processed emulsion is not brought to equilibrium with 50 percent relative humidity, adjustment of the shrinkage factor to 50 percent relative humidity may be made by consideration of the relationship between thickness of the processed emulsion and relative humidity implied by the data listed in Table VI.

V. ACKNOWLEDGMENTS

Acknowledgments are due Dr. Walter H. Barkas for suggesting that measurements such as these would fill a need and for his generous help in preparing this report for publication.

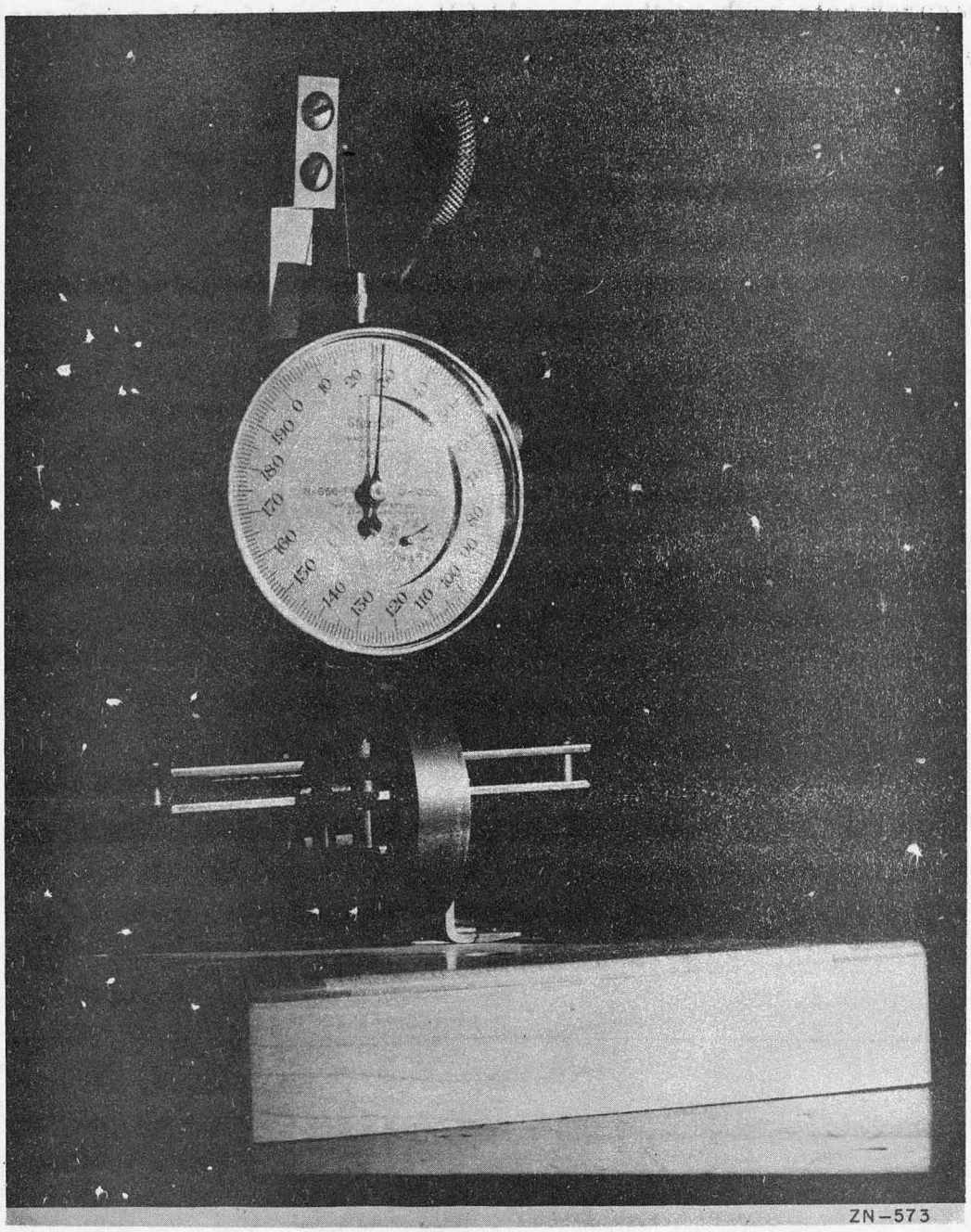

Fig. 1

Photograph of arrangement used to measure plate thicknesses.

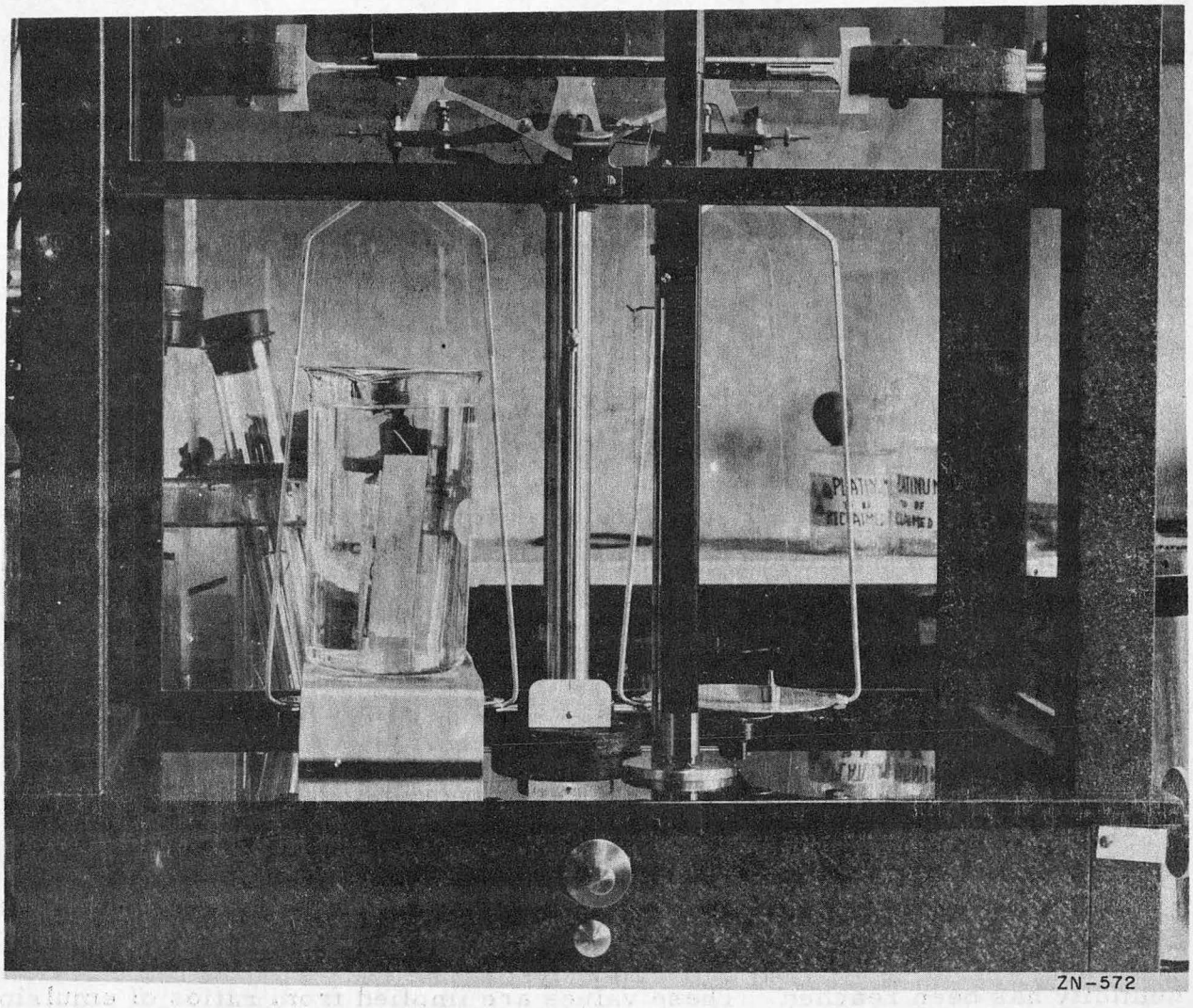

Fig. 2

Photograph of arrangement used for measurements from which plate volumes may be calculated. The plate is held by a wire hook and is suspended by a 3-mil wolfram wire from the beam of the magnetically-damped analytical balance. The plate is shown as it appears when displacing carbon tetrachloride.

TABLE I

Relative Humidity Obtained from Water-Glycerine Mixtures at 25° C.

Relative Humidity	Glycerine (by weight)	Specific Gravity
%	%	
10	95	1.245
20	92	1.237
30	89	1.229
40	84	1.216
50	79	1.203
60	72	1.184
70	64	1.162
80	51	1.127
90	33	1.079

Humidity control using solutions of glycerine, quoted in "Fundamental Techniques for Calibrating Hygrometers", Arnold Wexler and W. G. Brombacher, National Bureau of Standards, "Instrumentation" 5 (25) No. 6.

TABLE II

Unprocessed emulsion thickness vs. relative humidity expressed as ratios of thickness to the thickness obtained when equilibrium with 50% relative humidity has been reached. These values are implied from ratios of emulsion volume, assuming a negligible shrinkage in length and width.

% R. H.	T/T 50% R. H.
10	0.9657 ± .0035
20	0.9720 ± .0011
50	1.0000 ± .0000
60	1.0202 ± .0016
70	1.0466 ± .0004
81	1.1090 ± .0035

TABLE III

Shrinkage in Microns

Hours in Vacuum	from 50% R.H. 200μ	from 50% R.H. 600μ	from 70% R.H. 200μ	from 70% R.H. 600μ
1	1.3	1.3	4.2	----
2	2.0	1.9	6.3	11.7
3	2.4	2.4	7.9	----
4	2.8	2.8	8.8	16.3
5	3.2	3.0	9.4	----
6	3.6	3.4	10.4	18.9
7	4.0	3.6	10.9	----
8	4.1	4.1	11.2	22.3
16	5.8	---	13.5	----
24	6.4	8.2	14.1	31.6
32	7.4	10.9	14.4	33.8
48	8.1	12.0	14.9	----
72	---	13.8	----	40.6
96	---	----	----	42.6

Emulsion shrinkage vs. time in vacuum. Uncertainties are ± .4μ except for the column of shrinkages from 70% R. H. for the 600μ emulsion, which are ± 1.4μ. Any emulsion, after a certain number of hours in vacuum, peels and distorts and becomes impossible to measure. The 200μ plates measured for these data were Ilford type C. 3, and the 600μ plates were type C. 2.

TABLE IV

Weight loss, grams of moisture lost per gram of emulsion at 50% relative humidity, as equilibrium with 50% relative humidity was approached after the 1000μ G. 5 was removed from its package.

Days in 50% R.H.	Wt. Loss grams/gram
1	.00502
4	.00807
5	.00836
11	.00907
15	.00916
18	.00922

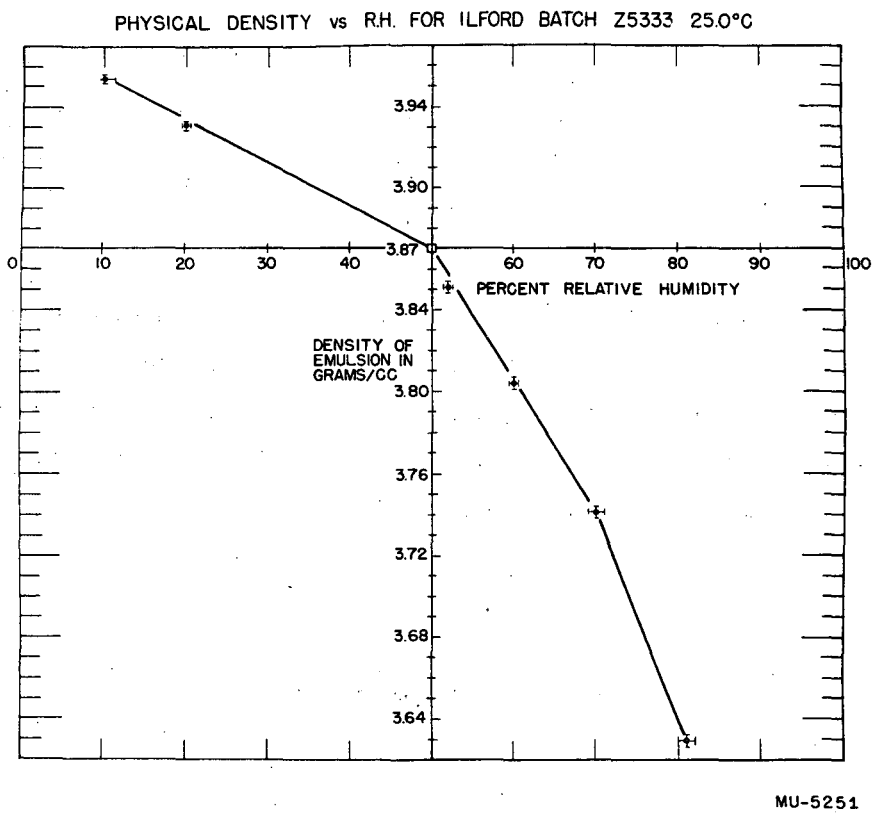

Fig. 3

Emulsion density vs. relative humidity.

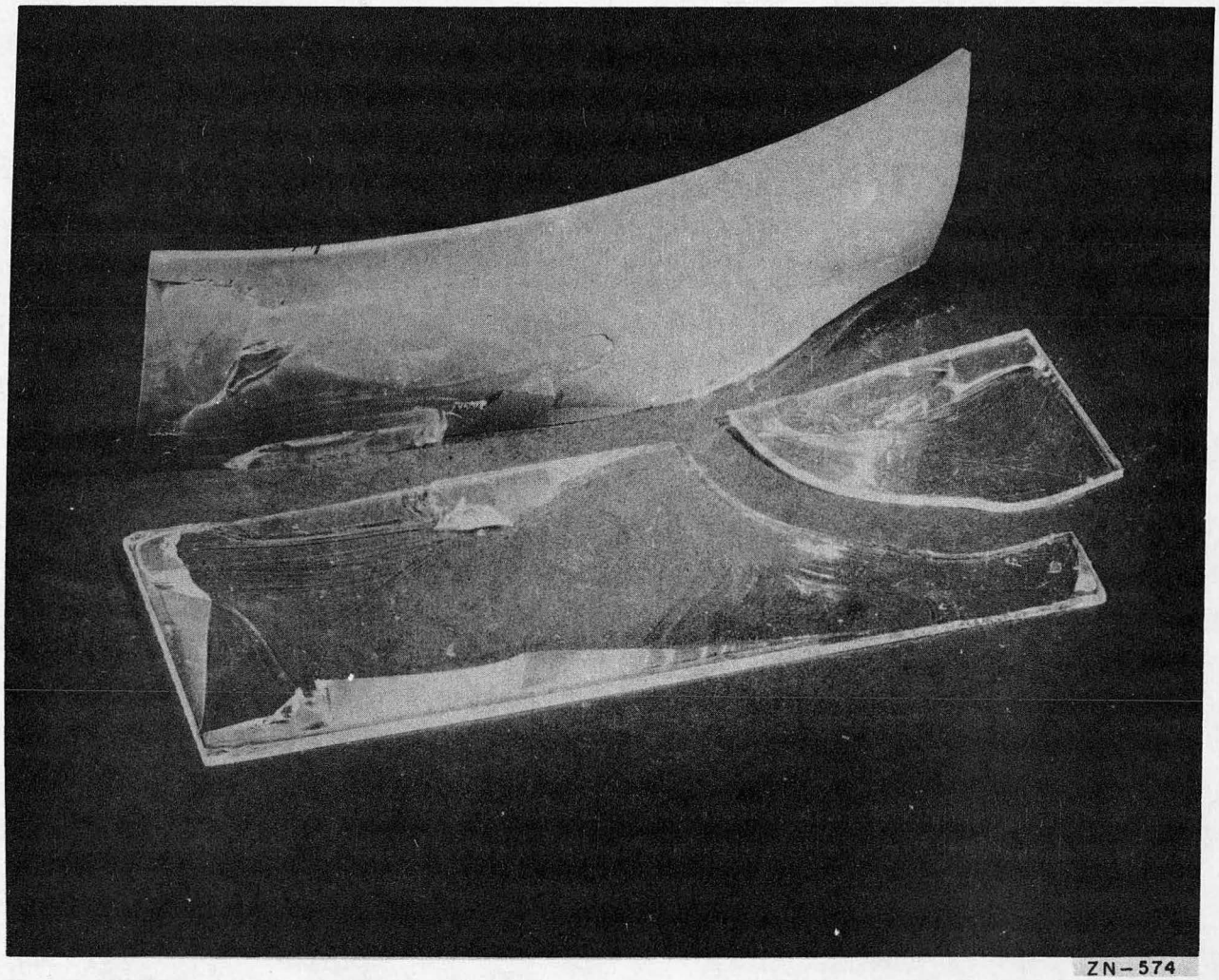

Fig. 4

Photograph of the 1000μ Ilford G. 5 after one month in a vacuum. Accurate measurements of the weight of moisture lost were made until the smallest chips began falling away from the emulsion and could no longer be accounted for.

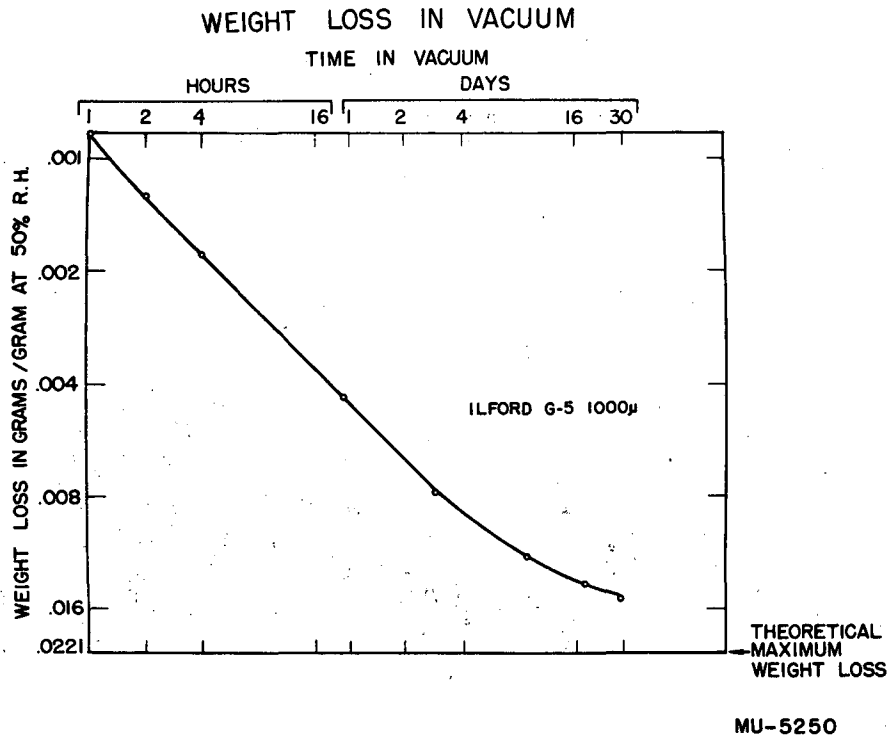

Fig. 5

Weight loss in vacuum, plotted as grams of moisture lost per gram of emulsion in equilibrium with 50 percent relative humidity; the plate was a 1 in. x 3 in. x 1000μ Ilford G. 5.

TABLE V

A distribution of shrinkage factors obtainable through varying the processing procedure.

Shrinkage Factors

50% rel. hum. before and after processing
Ilford C. 2, 200μ, Z5333

Fix	Wash	Glyc.	T/t
16 hrs	1-1/2 hrs	10 %	1.75 ± .05
16 hrs	1-1/2 hrs	3 %	1.95 ± .05
22 hrs	1 hr	0	2.17 ± .02
6 hrs	1-1/2 hrs	0	2.20 ± .01
5-1/2 hrs	1 hr	0	2.21 ± .02
22 hrs	17 hrs	0	2.26 ± .02
6 hrs	16 hrs	0	2.30 ± .02
5-1/2 hrs	17 hrs	0	2.31 ± .02

Development: 1/2 hr, 20°C, 6:1 D-19
Fixed in Kodak Acid Fixer

TABLE VI

Processed emulsion thickness vs. relative humidity. Ratios of thickness at specified humidities to thickness at 50% relative humidity. C. 2 200μ plates.

Plasticized after processing, 3 days in 10% glycerine

% R.H.	
10	0.904 ± .006
20	0.920 ± .006
76	1.088 ± .006

Plasticized after processing, 3% glycerine

% R.H.	
10	0.930 ± .003
20	0.944 ± .003
35	0.968 ± .003
76	1.06 ± .01

Not glycerated; fixed 5-1/2 hours and washed 1-1/2 hours

% R.H.	
21	0.975 ± .002
32	0.983 ± .002
63	1.015 ± .002
73	1.037 ± .004

APPENDIX

Note on the Theory of Water Diffusion in Emulsion

Walter H. Barkas

One of the studies Mr. Oliver has made is the weight versus time relation for emulsion kept in vacuo. He found that after weeks in vacuum, a 1000 micron layer of emulsion originally at 50 percent R.H. was still continuing to lose weight, whereas 200 micron emulsion came nearly to equilibrium in a few days. It appears necessary to emphasize this observation for it has important practical consequences. Because of the long time involved, equilibrium is usually never attained in thick emulsions. Consequently, it is difficult to know well the stopping power, the scattering factor, the shrinkage factor, and especially the hydrogen content of thick layers of emulsion, and it may often happen that the water concentration varies in an important manner with depth in the emulsion.

To understand the effects better, it will be worth while to calculate the behavior of the water concentration in a simple case, making certain idealizations so that the mathematical problem can be handled without undue effort.

Let the glass-emulsion interface be the x, y plane. Then we take the free surface of the emulsion to be the plane $z = z_o$. The diffusion of water through the emulsion is assumed to be described by the partial differential equation:

$$\frac{\partial c}{\partial t} = k \frac{\partial^2 c}{\partial z^2} \tag{1}$$

where $c \equiv c(z, t)$ is the water concentration, z is the coordinate of the layer of emulsion in which the concentration is c, t is the time, and k is the diffusivity.

Suppose that initially the water concentration is c_o, a constant throughout the emulsion, and that at time $t = 0$ the plate is suddenly subjected to evacuation. Since the time for water to diffuse through the emulsion is long compared to the time of evaporation from the surface, the effect of the evacuation can be described by imposing the boundary condition $c(z_o, t) = 0$. Only water which is free to diffuse is considered in the calculation.

The solution of Eq. 1 is found using the method of the Laplace transform. With the above assumptions, the solution is:

$$c/c_o = 1 - \frac{2}{\sqrt{\pi}} \sum_{n=o}^{\infty} (-1)^n \left[\int_{\frac{2n+1-z/z_o}{2\sqrt{t/T}}}^{\infty} e^{-x^2} dx + \int_{\frac{2n+1+z/z_o}{2\sqrt{t/T}}}^{\infty} e^{-x^2} dx \right] \qquad (2)$$

with $T = z_o^2 / k$

In units of the distance z_o and the characteristic time T, this expression for the concentration ratio is universal. As would be expected physically, the drying out proceeds from the surface inward, and a long time is required for the layer nearest the glass to suffer much change in water concentration.

In this approximate calculation, z_o has been assumed constant, but since the emulsion shrinks, this assumption is not strictly true. The diffusion takes place between the crystals of silver halide, which occupy a large fraction of the volume of dry emulsion. Therefore, the diffusivity, which has been assumed constant, will depend on the space available between grains. It will vary, therefore, in an unknown way with the local water concentration. Saturated emulsion which is appreciably swollen will, of course, have a high diffusivity. The effects of these two inexact assumptions tend to cancel each other, so the present calculation probably is not much in error for low water concentrations. In any event, the form of the diffusion equation for the general case indicates that to bring about similar changes in the distribution of water concentration, the time varies with the square of the dry emulsion thickness.

Now, $\phi = -k \left.\frac{\partial c}{\partial z}\right|_{z = z_o}$ is the flux of water through the free surface of the emulsion. From Eq. 2:

$$\left(\frac{\pi t}{k}\right)^{1/2} \frac{\phi}{c_o} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2 \frac{T}{t}} \qquad (3)$$

For the sample of emulsion studied by Oliver (which had a nominal thickness of 1000μ, but actually when measured was found to be 884μ), we find

agreement with his curve if we take:

$$T = 12 \text{ days}$$
$$k = 6.58 \times 10^{-6} \text{ cm}^2/\text{day}$$
$$c_o = 0.0537 \text{ gm/cc}$$

Table A compares the calculated and observed weight losses for this plate. One can now estimate the following characteristics for plates coated with G. 5 emulsion below 50 percent relative humidity:

(a) Characteristic diffusion time: $T = z_o^2/6.5$ days where z_o is expressed in units of one hundred microns.

(b) Diffusible water content at 50 percent relative humidity: 0.0537 gms/cc.

TABLE A

Calculated and Observed Weight Losses

Weight loss calculated from:

$$W = 0.100 \int_o^t \frac{\left(\frac{1}{2} + \sum_{n=1}^{\infty} (-1)^n e^{\frac{-12n^2}{t}}\right)}{\sqrt{t/12}} \left(\frac{dt}{12}\right)$$

t (days)	Obs. Loss gm	Calc. Loss gm
0.0417	0.0055	0.0059
0.0833	0.0081	0.0083
0.1667	0.0117	0.0118
0.941	0.0280	0.0280
2.94	0.0500	0.0490
8.96	0.0743	0.0770
17.96	0.0878	0.0864
27.95	0.0962*	0.0880

* It is believed that this number is erroneous. Some chips of splintered glass were unaccounted for in the weighing.