TESTING AERIAL PHOTOGRAPHIC NEGATIVES FOR RESIDUAL SODIUM THIOSULPHATE

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THE Aerial Photographic Laboratory has custody of aerial film negatives totaling, in value, more than $4,000,000. While optimum storage conditions are maintained with our present equipment, any factor which might endanger the life of this film must be thoroughly examined and controlled to eliminate possible costly loss of such valuable material. Ordinary visual inspection of film which has just been processed does not reveal certain chemicals which might be residing in the film emulsion in quantities sufficient to ruin the image in several months. The image contrasts are altered (faded) by hypo or other sulphur-containing compounds remaining in the emulsion which combine with the black silver grains to form brown silver sulphide.

Quoting from a paper by Hickman and Spencer, *Brit. J. Phot.*, vol. 69, p. 387 (1922), the reaction of hypo (sodium thiosulphate) and silver proceeds along the following lines:

"Assuming a photograph to be perfectly fixed, and the absence of silver thiosulphate in the film, the process of fading might be explained as follows, the upper arrows showing the direction in which the equilibrium sets:

(1) $2Ag+Na_2S_2O_3 \rightleftarrows Ag_2S+Na_2SO_3$.
(2) $2Na_2SO_3+O_2 \rightleftarrows 2Na_2SO_4$.
(3) $Na_2SO_4+Ag_2S \rightleftarrows Na_2S+Ag_2SO_4$.
(4) $Na_2S+CO_2+H_2O \rightleftarrows Na_2CO_3+H_2S$.
(5) $Na_2S_2O_3+2O_2+H_2O=Na_2SO_4+H_2SO_4$.

"Equations (1), (2), and (5) show that there is a tendency for the formation of silver sulphide and an excess of sodium sulphate. All reactions being strictly reversible, minute quantities of sodium sulphide and silver sulphate will be formed as in (3), and the sodium sulphide will be decomposed by atmospheric gases (4). As hydrogen sulphide precipitates silver sulphide quantitatively from sulphate solutions, it will require a large excess of sulphate, and complete removal of H_2S, to reverse the action. These conditions exist, however, in a photographic film containing sodium sulphate and sulphuric acid, from which the gas is freely permitted to escape."

The chief factors governing fading may be listed as follows:

1. The quantity of hypo or other sulphur-containing compounds retained in the image.
2. The size of grains which comprise the image.
3. The relative acidity or alkalinity of the gelatin film containing the image.
4. The temperature and humidity of the air during storage.
5. The presence of sulphur-containing gases during storage.

While the composition of film bases and emulsion grain sizes are of importance, the efficiency of washing remains as the factor most subject to observation and improvement at this time. Therefore, the chemical testing of aerial negatives was initiated to help insure against possible fading due to sodium thiosulphate remaining in the film as a result of improper washing.

Residual hypo is measured by the National Bureau of Standards, and a leading commercial company, by means of the Ross-Crabteee mercuric chloride test. This test consists of immersing a small sample of the film in a solution of mer-

curic chloride and potassium bromide. Any sodium thiosulphate present in the emulsion will react with the solution to form mercurous bromide and a turbidity is thus set up in the normally clear test solution.

Since an increase in the hypo content of the negative emulsion increases the turbidity of the test solution, it follows that a measure of the turbidity of the test solution is an indication of the quantity of sodium thiosulphate remaining within the emulsion.

The general practice has been to make measurements of this turbidity visually by comparing the test solutions with standard solutions of known hypo content. The comparison is best made in a darkened room, using a mercury vapor lamp.

Several other tests for residual hypo were considered and the Ross-Crabtree mercuric chloride method was found to be the most accurate and best suited to testing aerial film negatives. The reasons for choosing this test are as follows:

1. Only 1/10 square inch of film is required for testing.
2. The test is capable of being adapted to practical photoelectric turbidity determinations of the test solution, which permits tests to be made at the rate of 30 per hour.
3. The test is extremely delicate and capable of detecting the presence of .005 milligram hypo[1] per square inch.

It has been observed, as a result of a large group of tests that the visual method of comparative determination is generally subject to a considerable variation in reproducibility for a definite known turbidity quantity. It was in recognition of this fact that the photoelectric principle[2] was adopted as a means of measurement to this test.

This method involves the use of an apparatus similar to one used in tests by Mr. Brooks A. Brice, Senior Physicist of the Bureau of Agricultural Chemistry and Engineering, and explained by him in a report of August 1937, titled, "A Compensating Circuit for Blocking-Layer Photoelectric Cells."

In the device utilized by Mr. Brice, the sensitivity of the instrument depends upon the brilliancy of the exciter lamp in the circuit. This apparatus utilizes an inexpensive galvanometer and dispenses with the necessity of using batteries in the exciter lamp circuit.

Briefly, two matched photronic cells are connected, with reversed poles, to a galvanometer in such manner that light thrown upon them from a single alternating current exciter lamp source will pass equalizing currents through the galvanometer, thus avoiding the two sources of possible fluctuation—the alternations of the light circuit and the peak load rise and fall natural to such a circuit. In practice, the galvanometer indicator is found to remain steady at a zero point in the center of the scale, unless either of the beams of light from the common exciter lamp source is partially or completely interrupted.

Thus, any decrease in light because of a turbidity in the test solution will lessen the output of the measuring photocell which will cause a deflection of the galvanometer mirror by the compensating photocell. By reducing the output of the compensating cell by a shunt slide wire potentiometer, a reading is obtained on the potentiometer dial. This reading is reproducible by the introduction of a standard solution containing an equivalent hypo concentration. Since the test reading obtained has previously been duplicated by the introduction of a stand-

[1] Anhydrous sodium thiosulphate.

[2] The use of photoelectric turbidity determination for the hypo test solutions was initiated by the Engineering Sub-Unit staff, Aerial Photographic Laboratory.

ard solution of known hypo concentration and that reading recorded with hundreds of others on a conversion table, it may be concluded that the dial reading may be used to designate the hypo content of the specimen solution.

As the quantity of hypo produced by 1/10 square inch of film in 1 cc. of test solution is now known, it is possible to state the hypo content of the film in milligrams per square inch.

While other qualities of the film are being checked in the film inspection room, two punchings 2.52 inch in diameter are taken near the leaders at both ends of each section. These two punchings, making up a 1/10 square inch area,

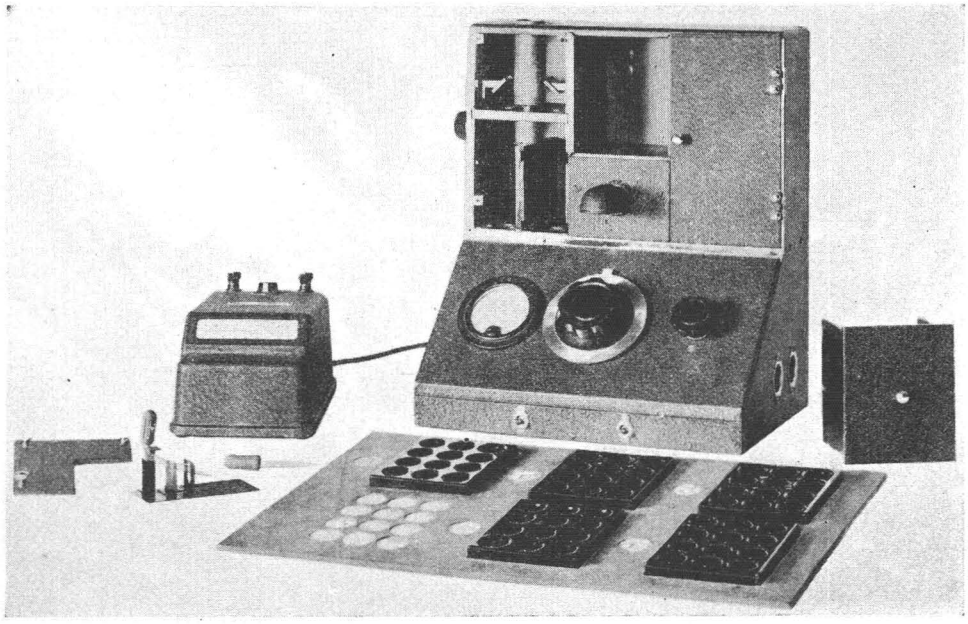

FIG. 1. Turbidimeter.

are put in marked envelopes and sent to the Engineering Sub-Unit for chemical testing.

The punchings are immersed, emulsion side up, in a black porcelain spot plate containing 1 cc. $HgCl_2$ test solution[3] where they remain for 15 minutes, which is sufficient time to allow diffusion of hypo out of the emulsion into the test solution.

The test solution is then picked up by a dropper type absorption cell and introduced into the light beam energizing the measuring photocell. A dial reading is thus obtained which gives the hypo content per square inch of film.

The hypo content is then listed on the negative inspection reports and is also recorded for contractor comparison charts and for data to be used for definitely establishing a permitted maximum of hypo content for aerial negatives.

Since it is not known exactly how much hypo may be considered as negligible, and until a figure for each emulsion and grain size has been determined as negligible, it would be careless procedure to disregard completely the checking

[3] For this test solution, C.P. chemicals are used: 25 grams $HgCl_2$ (mercuric chloride), 25 grams KBr (potassium bromide) and distilled water to make 1,000 cc. This stock solution must be filtered before using and it should not be kept over 30 days.

of incoming film for hypo remaining in excessive quantities from a too-short or improper washing.

It is obvious that some maximum hypo content should be set for incoming film. Therefore, the question arises as to what figure would be safe and at the same time reasonable from the viewpoint of cooperation with the contractors flying and processing the aerial negatives.

The National Bureau of Standards recommends .005 milligram per square inch of film as a safe maximum residual hypo content for fine-grained micro films for archival storage. Since aerial negatives contain much coarser-grained images which are more resistant to fading than fine-grained film, it is not necessary in this case to set the limit so low as .005 milligram per square inch.

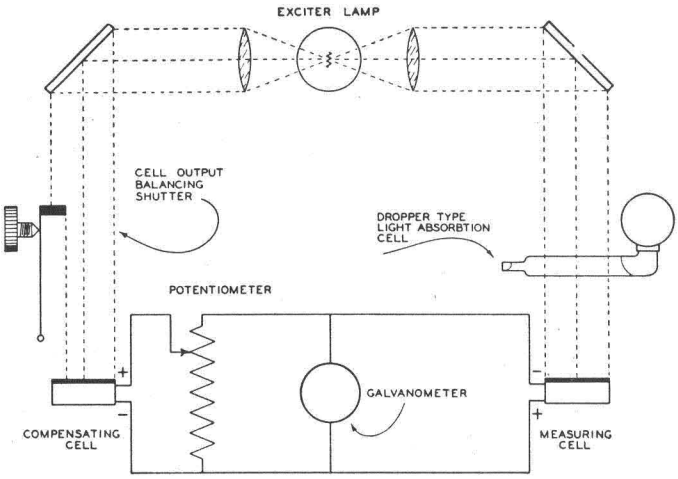

FIG. 2. Schematic Diagram of Wiring and Optical System of Turbidimeter.

Naturally, the required life of the aerial negatives is a factor, and for the purposes of the Aerial Photographic Laboratory, this may generally be accepted as 10 years maximum and 5 years average. As the rate of fading is not known, a time limit only complicates the problem of whether or not aerial negatives will fade during their active service.

The next question which naturally arises is what low hypo content is attainable within reason. A washing time test[4] run with Smith-Fairchild field developing equipment shows that a 1-hour washing of 100-foot rolls with this type of washer, running at a much higher speed than normal, would cut the hypo content to a figure as low as .005 milligram per square inch. Though this test was necessarily run with the water at 80° Fahrenheit, the test is valid, since heat causes the emulsion to swell and hinders the hypo removal.[5] A subsequent examination has revealed no evidence of physical damage to the film.

However, for the present, and in the absence of sufficient information on this subject, a quantity could be arbitrarily assumed which will insure adequate attention to washing and, at the same time, will not require too much from the contractor.

[4] See curve, Figure 3.

[5] From a paper by K. C. D. Hickman entitled "Washing Motion Picture Film," published in *Transactions of the Society of Motion Picture Engineers*, No. 21, Meeting of May 1925 at Schenectady, N. Y., pp. 62–76.

It appears that a limit of 0.10 milligram of hypo per square inch of film should be easily attained and at the same time more nearly insure adequate washing. Experience has indicated that under the present uncontrolled conditions about 24 per cent of the submitted material[6] has exceeded this content of residual hypo.

The Engineering Sub-Unit of the Aerial Photographic Laboratory has developed the test methods and equipment to such an extent that making the tests on aerial film requires but two $\frac{1}{4}$-inch punchings taken during routine inspection.

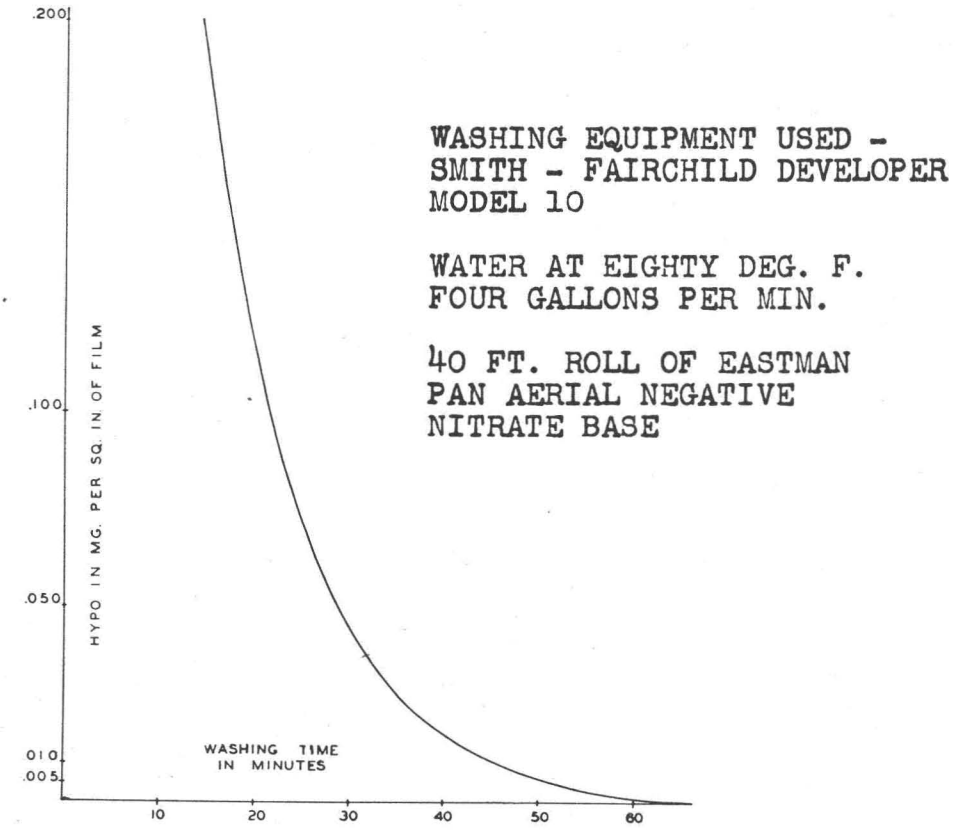

FIG. 3. Results of a Test Correlating Washing Time with Residual Hypo Content.

This quantity of film has not affected in any way the handling of the material on light tables and in cameras. These punchings are tested at the rate of 30 tests per hour, two punchings being required for one test. The cost of making tests by this technique can be considered as negligible when compared with the great loss possible should some film be accepted which was rushed through an improper washing period by oversight or haste on the part of the processor.

Of the one thousand or more tests of aerial negatives considered as typical for comparative purposes in this article, 24 per cent of the film tested contained over 0.1 milligram of hypo per square inch, as stated previously. In one instance a high of 0.5 milligram per square inch was found. Assuming the possibility that out of the 2,000 rolls received by the Sub-Unit this year, ten will contain

[6] See curve, Figure 4.

hypo in quantities sufficient to cause fading in a year or so, we find that the loss, at $200 per roll, would amount to $2,000. Against an average of two tests per roll with each roll containing two sections, or 4,000 tests costing about $400, we have a probable loss of $2,000. A cost of $400 per year for 2,000 rolls amounts to 20 cents per roll to guard against fading for 10 years. The active life expectancy of negatives should not be placed beyond 5 years, and on this basis the cost per year can be placed at 4 cents per roll.

Two contractors out of ten show consistent washing of film to average 0.010 milligram per square inch of hypo. The other eight average 0.100 milligram per square inch. There have been numerous instances where the film from this latter group showed a very low hypo content which apparently indicates that

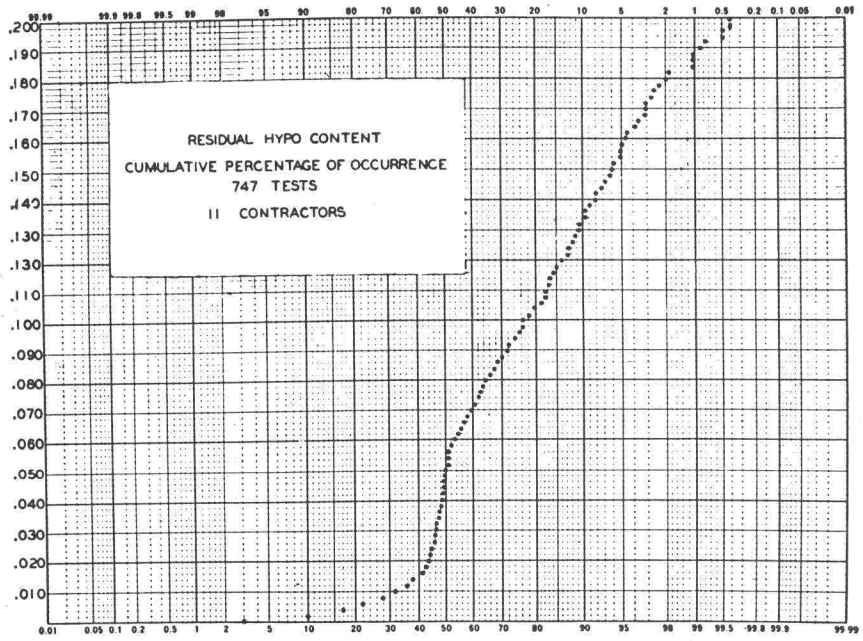

FIG. 4. Hypo Contents Plotted in Relation to the Frequency of Their Occurrence.

with their present equipment they could produce a thorough washing without the harmful effects of overwashing.

Considering the inconsistencies in hypo content of incoming aerial film, since high hypo contents were found in numerous tests, it appears advisable to test all incoming film in order to insure against fading. Furthermore, the standards of our products would be raised by acceptance of only well-washed film.

With reference to the quality of aerial negatives, we quote a portion of an address presented at the Annual Meeting of the American Society of Photogrammetry by Marshall S. Wright, retiring president of that society, at the January 1940 meeting, Washington, D. C.:

"Studies and tests conducted by the photographic laboratories and research divisions of the Department of Agriculture with both processed film and prints delivered under contract show in some cases almost a total disregard for proper exposure of film and development and washing technique.

"A carefully compiled and confidential list of all the aerial contractors who have performed work shows that some companies consistently deliver a far more inferior product than others. This can only be a reflection of improper processing methods in their laboratories. This condition can be corrected by two methods: (1) By contractual compulsion (i.e., specific requirements in specifications); and (2) by education and dissemination of knowledge among the executing agencies. Unquestionably, the latter method is preferred, as certainly no contractor wishes to risk the chance of having his material rejected after he has incurred the expense of procurement."

While other considerations such as flow rates may have their effects, a few facts relative to washing conditions not touched on previously may be of interest.

The wash water should be kept near the same temperature as the rest of the solutions. Increasing the temperature swells the emulsion and counteracts the effects of the quickened diffusion. With heavily hardened emulsions which do not swell in warm solutions, film hardened in strong alum or formalin will wash a little quicker in summer than in winter.

As to the nature of the washing water, the following is an excerpt from *Transactions of the Society of Motion Picture Engineers*, meeting of May 1925:

"Nearly all town water supplies are suitable for washing film. Brackish water, containing common salt, is to be avoided; but lime and magnesia, as carbonate and sulphate, are probably harmless, and the carbonates are perhaps beneficial. Very hard waters merely need more perfect surface removal by pneumatic squeegee before drying. Iron salts occurring in acid and peaty waters may discolor the film, but they are not likely to affect its permanency. Therefore, contrary to accepted belief, the nature of the water supply is not of vital importance."

The important conclusions arrived at as a result of the residual hypo investigations are as follows:

1. The $HgCl_2$ test is apparently the most practical residual hypo test.
2. The photoelectric turbidity determination of test solutions introduced by the Engineering Sub-Unit enables tests to be made more accurately and quickly than by the visual comparison method, thereby reducing the cost to a minimum.
3. The hypo content of over 1,000 rolls of aerial film has been checked, showing inconsistent washing.

Of 747 tests run on one Government contract, a graph accompanying this article shows that 50 per cent of incoming film is likely to fall under 0.05 milligram, while 5 per cent is likely to contain very close to 0.2 milligram of hypo per square inch, which is unnecessarily high.

We may conclude from these results that a few contractors consistently wash film well and some consistently wash film ten times as poorly as the others, while on rare occasions these same latter contractors wash a roll or two very well.

Obviously all contractors could, if they would, wash all aerial negatives well, thereby eliminating any doubt as to whether or not the film would fade under proper storage conditions.

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