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TECHNICAL REPORT

Wash Efficiency Tests

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WASH EFFICIENCY TESTS

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ABSTRACT

Residual thiosulfate in processed film can be detected by precipitation as colored silver sulfide. From the measured density of this precipitate, the quantity of thiosulfate can be determined and correlated with the expected storage life of the film.

A number of film products from the Precision and Motion Picture Laboratories have been tested for thiosulfate by this method.

The silver sulfide stain test, results from it, and the significance of these results are discussed in this report.

SECTION I

INTRODUCTION

A number of factors need to be determined in order to ascertain the storage life of processed photographic film. Common causes of deterioration are temperature, humidity, air quality, and residual chemicals in the film. It is this last cause over which we have some control. The effected components are the film base, the gelatin, and the silver image (or dye image for color film).

Keeping quality for black and white film is often associated with the quantity of fixer which remains after washing. This is because the first sign of aging is often the brown stain of silver sulfide. Many guidelines are available to assist in forecasting the effects of long storage, but since the process of deterioration is so gradual and has so many variables there is no decisive criteria of keeping quality.

To make some assessment, films are first divided into classes principally by silver halide grain size. Each class must contain less than a given level of thiosulfate to be considered archival. The term archival means indefinite or a long time, and should be at least 100 years.

The finest grain films, such as microfilm (grain size about .05μ), are Class I. For archival keeping these films should contain less than 5 micrograms of thiosulfate per square inch.

Class II films are represented by medium grain (0.5 to 1.0μ grain diameter), for instance aerial film. Archival keeping requires less than 20 micrograms of thiosulfate per square inch.

For internal purposes Eastman Kodak uses the term "commercial quality" and this refers to films with less than 100 micrograms of thiosulfate per square inch. This is taken to mean 5 to 15 years keeping.

The relationships discussed above are plotted in Figure 1. This graph should not be considered as authoratative since it only attempts to show roughly how residual fixer content relates to keeping quality.

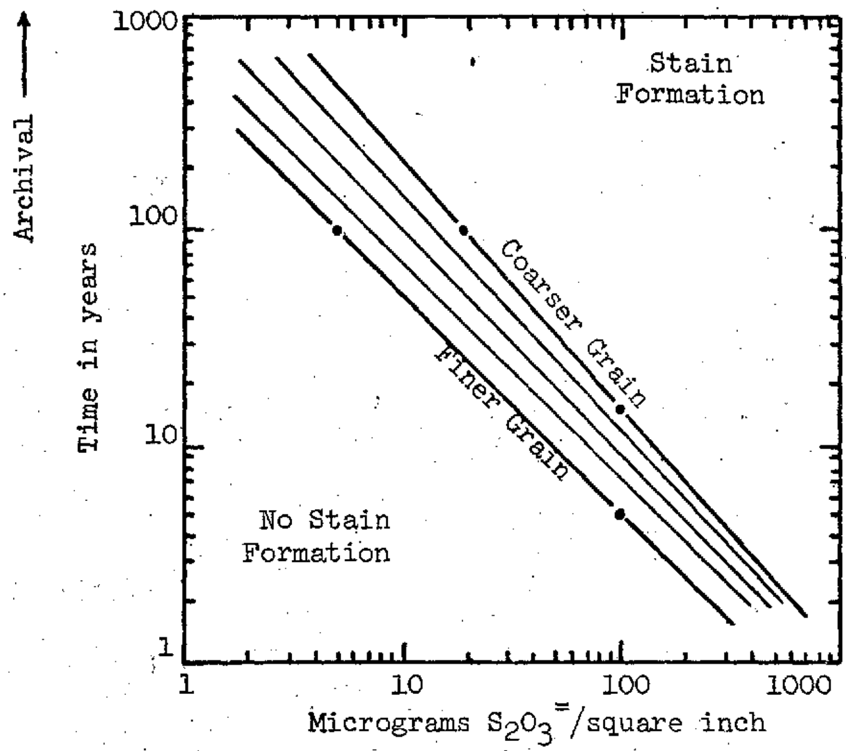

FIGURE 1. Relationship between Thiosulfate content and storage time relative to silver sulfide stain in black and white photographic film.

SECTION II

TEST PROCEDURES

THIOSULFATE DETERMINATION

The test used to determine residual fixing chemicals in the film was adapted from Mattey and Henn.[1]

Several minor modifications were made to make better use of the equipment available and to streamline the procedure.

One of these modifications was that dye backings were not bleached, principally because strong blue absorbing dyes were not encountered in any of the products tested. Although a different procedure for thiosulfate determination has been adopted as a standard test (American Standard Association, PH 4.8 - 1958), the Mattey and Henn method is simpler, more inclusive, and reportedly more sensitive.

The procedure of this test, as it was used, was to cut two adjoining film samples of about 4 to 8 square inches. Fingerprints are to be avoided, since they may interfere with density readings. One sample is labeled with film type and "test" and the other with film type and "reference". The

[1] D. A. Mattey & R. W. Henn, Photo. Science & Eng., 10, 202 (1966).

time the test is made after processing has been shown not to be a variable for this test, as have the time intervals between steps. Treatment times in each of the chemicals must meet a certain minimum but are otherwise non-critical.

The test sample is first immersed in silver nitrate-acetic acid solution. The reference sample is immersed at the same time in a blank solution of acetic acid. Both tray and tank immersion are practical. The silver stain will appear quickly, within about 5 seconds, and the reaction will go to completion in 2 minutes. Minimum time for all samples is considered 2.5 minutes. We generally used 5 minutes.

In the second step, each specimen is briefly dipped in water (optional) and then put into sodium chloride for 5 minutes. The purpose of the sodium chloride is to precipitate unreacted silver. Reaction time is approximately the same as for the silver nitrate solution, but a minimum time of 5 minutes was observed for simplicity.

After another optional water dip the samples were put into a solution of sodium thiosulfate. This third step should convert all silver to a soluble complex. Stated minimum time is 2½ minutes, and again a 5 minute minimum was observed for convenience.

The third solution was followed by a 5 minute wash. The samples are then dipped in photo-flo and dried. Temperatures of these operations are not critical and solutions were at room temperature.

Nothing is said about solution life or exhaustion and there are certain precautions to observe. Silver nitrate should be kept in brown bottles and may be checked by pouring a few drops into tap water or some sodium chloride solution. When a cloudy precipitate forms the solution is OK. Sodium chloride should last indefinitely. Thiosulfate will slowly disproportionate and also become saturated with silver ions. Thus the optional dip in water to prevent too much carry-over will help lengthen solution life.

The composition of each solution is as follows:

Solution A (test)

Water	750.0cc
Acetic Acid (Glacial)	30.0cc
Silver Nitrate	10.0gm
Water to Make	1.0 liter

Solution A (reference)

Water	970 cc
Acetic Acid	30 cc

Solution B

Water	750.0cc
Sodium Chloride	45.0gm
Water to Make	1.0 liter

Solution C

Water	750.0cc
Sodium Sulfite (anhydrous)	15.0gm
Sodium Thiosulfate (crystalline)	45.0gm
Water to Make	1.0 liter

In one test of the useful life of the silver nitrate solution, four samples were prepared in an old solution and then in a fresh solution. The results are below.

TABLE 1

SILVER SULFIDE STAIN TEST FOR RESIDUAL FIXER

	Hypo Concentration in micrograms/sq. inch	
Film Type	1 Month Old $AgNO_3$	Fresh $AgNO_3$
7302	21	23
7234 (7/7)	72	69

Film Type	1 Month Old $AgNO_3$	Fresh $AgNO_3$
7234 (6/15, 7/10)	15	14
IIa-0 129771	30	31

NOTE: Parenthesis refer to the date the film was received after processing. One film was processed twice. The first processing yielded a result of 416 micrograms of hypo per square inch. The second processing considerably reduced the level of residual hypo. The conclusion of the above test is that the silver nitrate solution retains its stain forming capability very well.

Dried samples were cut into no more than eight appropriately sized pieces. The use of tweezers at this point is strongly suggested. The size of the pieces is governed by what can conveniently be held under the densitometer. For 16mm three frames is adequate or a sample 1" x ½".

There are several methods which may be used to relate the intensity of the stain to the concentration of residual hypo. One of these is by use of a spectrometer. Since we had a Beckman DK-2A available and Mattey and Henn provided a calibration curve, this was one of the instruments used. From the calibration curve two wavelengths, 350 and 400mm, were selected and the absorbances for the sample containing

160μ gm hypo/square inch were measured. On an absorbance versus micrograms of hypo/square inch graph, these two points were extended to the 0,0 coordinates. The resulting graph is shown in Figure 2.

Test and reference sample values for absorbance were measured in the Beckman for several thicknesses. Either the whole curve could be plotted or values at these wavelengths measured one at a time. For some samples one thickness would produce a net absorption over 1.0, and for other samples all eight thicknesses would produce almost no net absorption.

Results for this method are given beside densitometer results on the following pages. Generally, both methods are compatible and of equivalent accuracy, although a good calibration below 25 micrograms was not available for the spectrometer. In operation the Beckman was less convenient for routine use, and since it provided no additional information, its use was not continued.

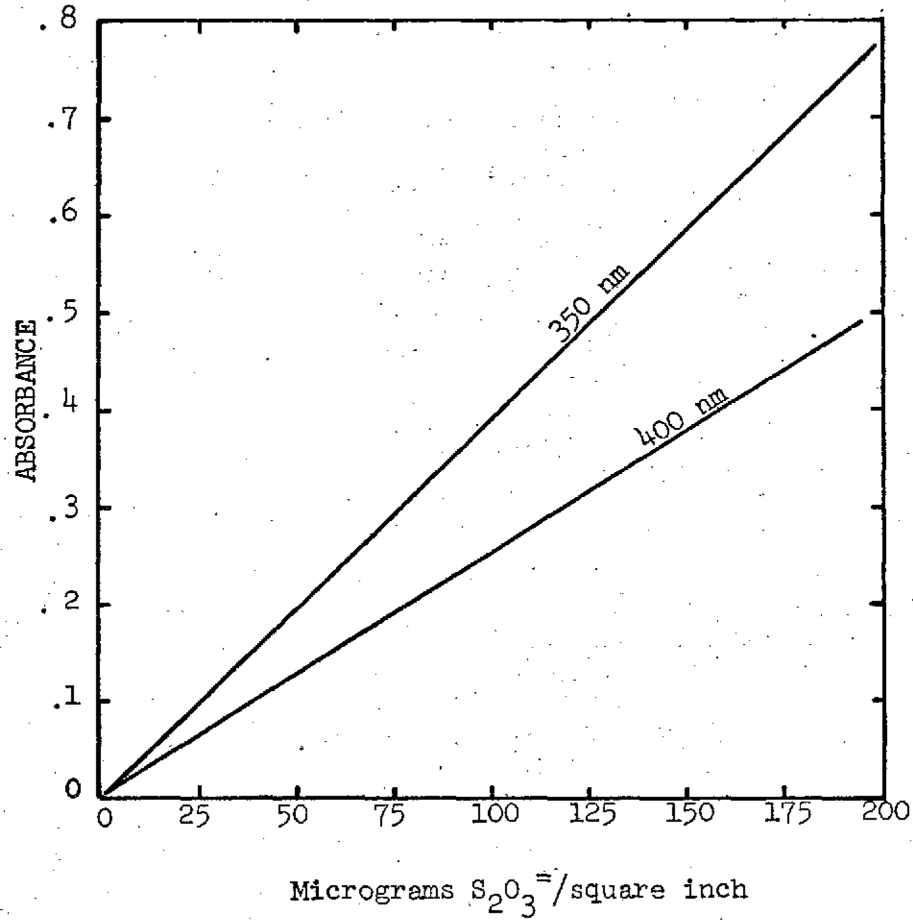

FIGURE 2. Absorbance versus thiosulfate content at 350 and 400 nm for silver sulfide stain test for processed black and white film.

Another method for stain density measurement described at length by Mattey and Henn is by the use of a blue filter in the densitometer. Since the stain is brown, it has some modest red and green absorption, and then attenuates strongly into the blue becoming opaque without reaching any maximum. The Kodak Status A blue densitometer filter in the MacBeth has a transmission maximum at 440 to 450 nm and measures the stain absorption quite reliably. Calibration curves for four thicknesses of film read through the blue densitometer filter are given in Figures 3 and 4. These curves were published by Mattey and Henn and were adopted without further calibration.

Actual data for two samples are presented below. Results of this data are given in the appropriate table in the text which follows.

TABLE 2

Film Type SO-212 READ THRU KODAK STATUS A BLUE DENSITOMETER FILTER ON THE MACBETH DENSITOMETER.

No. Thicknesses	Optical Density Reference	Test	Net Difference	Difference Per Thickness
1	0.14	0.13	-.01	-.010
2	0.24	0.24	.00	.00
3	0.33	0.34	.01	.003
4	0.42	0.44	.02	.005

No. Thicknesses	Optical Density Reference	Test	Net Difference	Difference Per Thickness
5	0.54	0.55	.01	.002
6	0.64	0.66	.20	.003
7	0.78	0.76	-.02	-.003
8	0.89	0.86	-.03	-.004
			average	-.004

The conclusion is that the level of thiosulfate in the film is below the limit of detectability by this test.

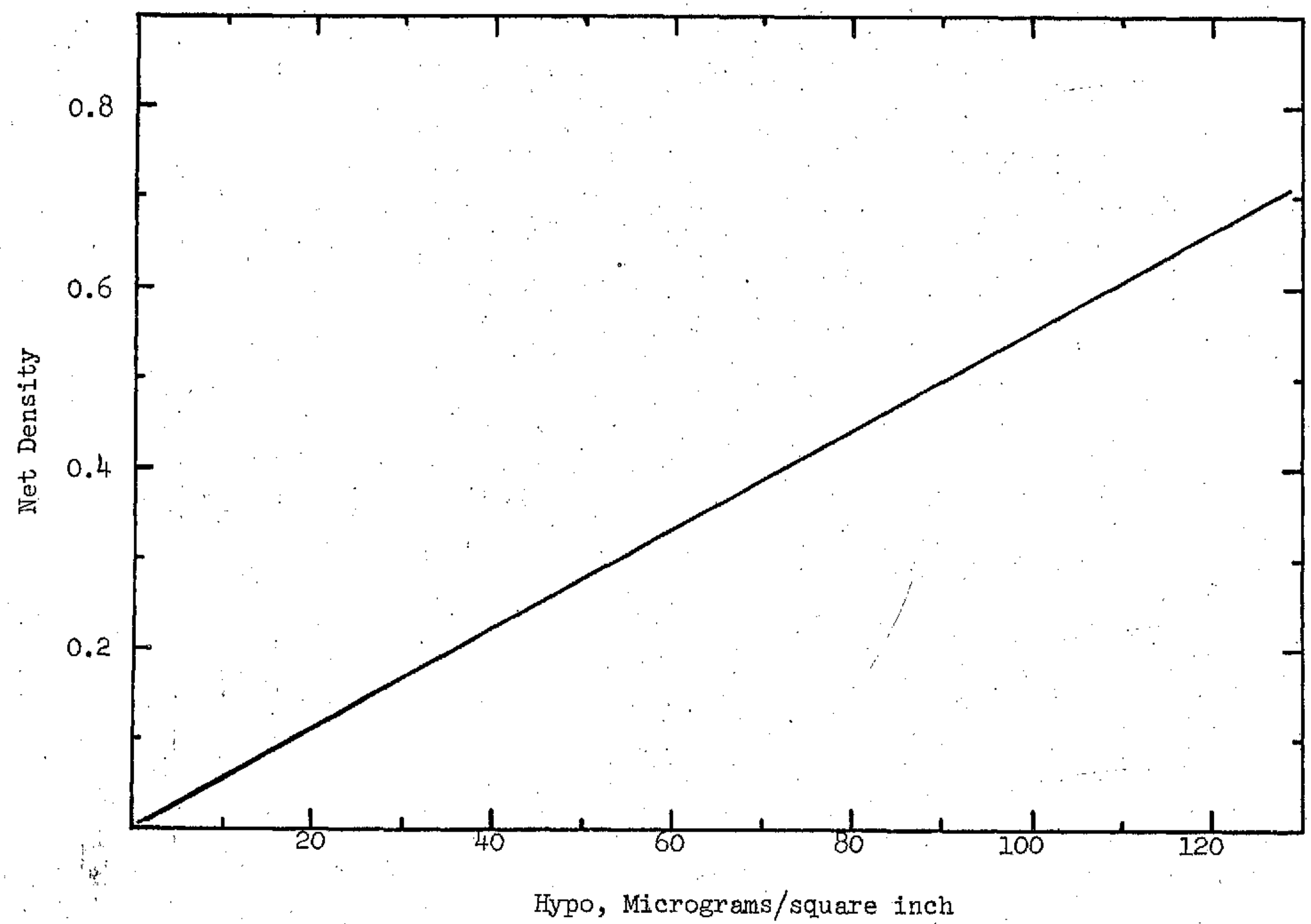

FIGURE 3. Relationship between hypo and net density for 4 thicknesses of film read thru Kodak Status A blue densitometer filter.

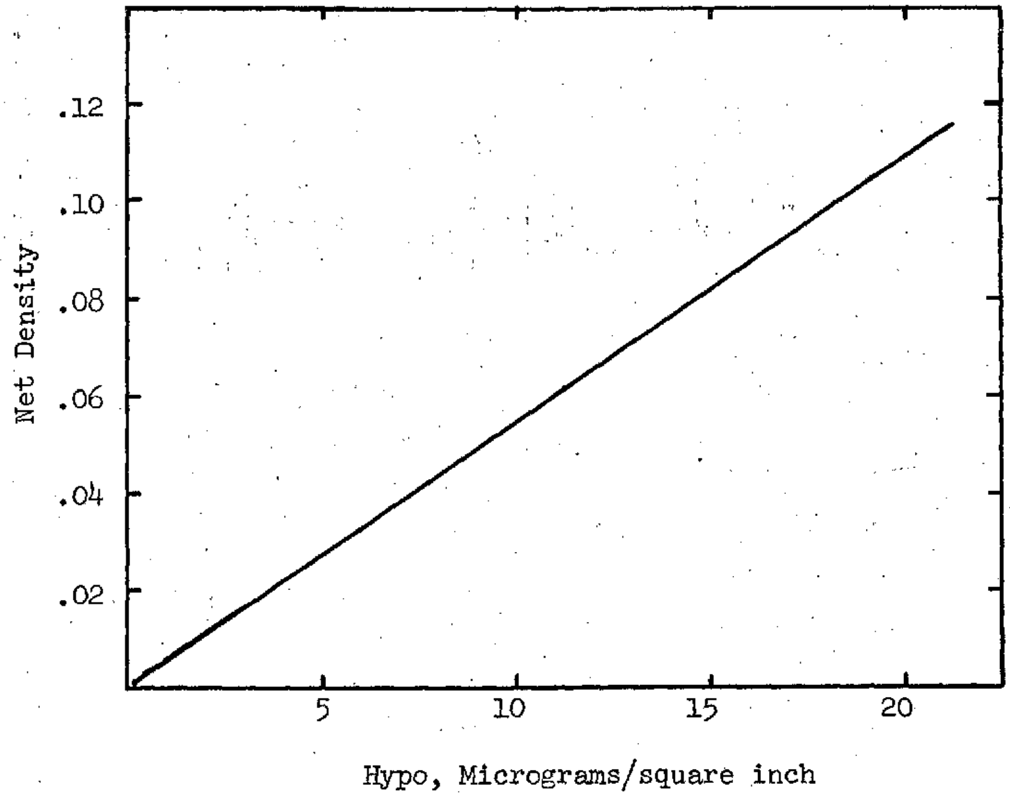

FIGURE 4. Enlarged scale from Figure 3. Relationship between hypo and net density for 4 thicknesses of film read thru Kodak Status A blue densitometer filter.

TABLE 3

FILM TYPE 5302 READ THROUGH KODAK STATUS A

BLUE DENSITOMETER FILTER ON MACBETH DENSITOMETER.

No. Thicknesses	Optical Density Reference	Optical Density Test	Net Difference	Difference Per Thickness
1	0.07	0.17	0.10	0.100
2	0.10	0.29	0.19	0.095
3	0.14	0.42	0.28	0.093
4	0.17	0.56	0.39	0.098
5	0.21	0.71	0.50	0.100
6	0.24	0.83	0.59	0.098
7	0.28	1.03	0.75	0.107
8	0.31	1.12	0.81	0.101
			average	0.099

A plot of the number of thicknesses versus the net difference in optical density is presented in Figure 5. From this figure the net density of four thicknesses, 0.40, corresponds to a hypo concentration of 72 micrograms/square inch. This meets the Kodak commercial keeping quality value of under 100 micrograms per square inch.

The visual appearance of this film sample before and after staining is shown by actual specimens in Figure 6.

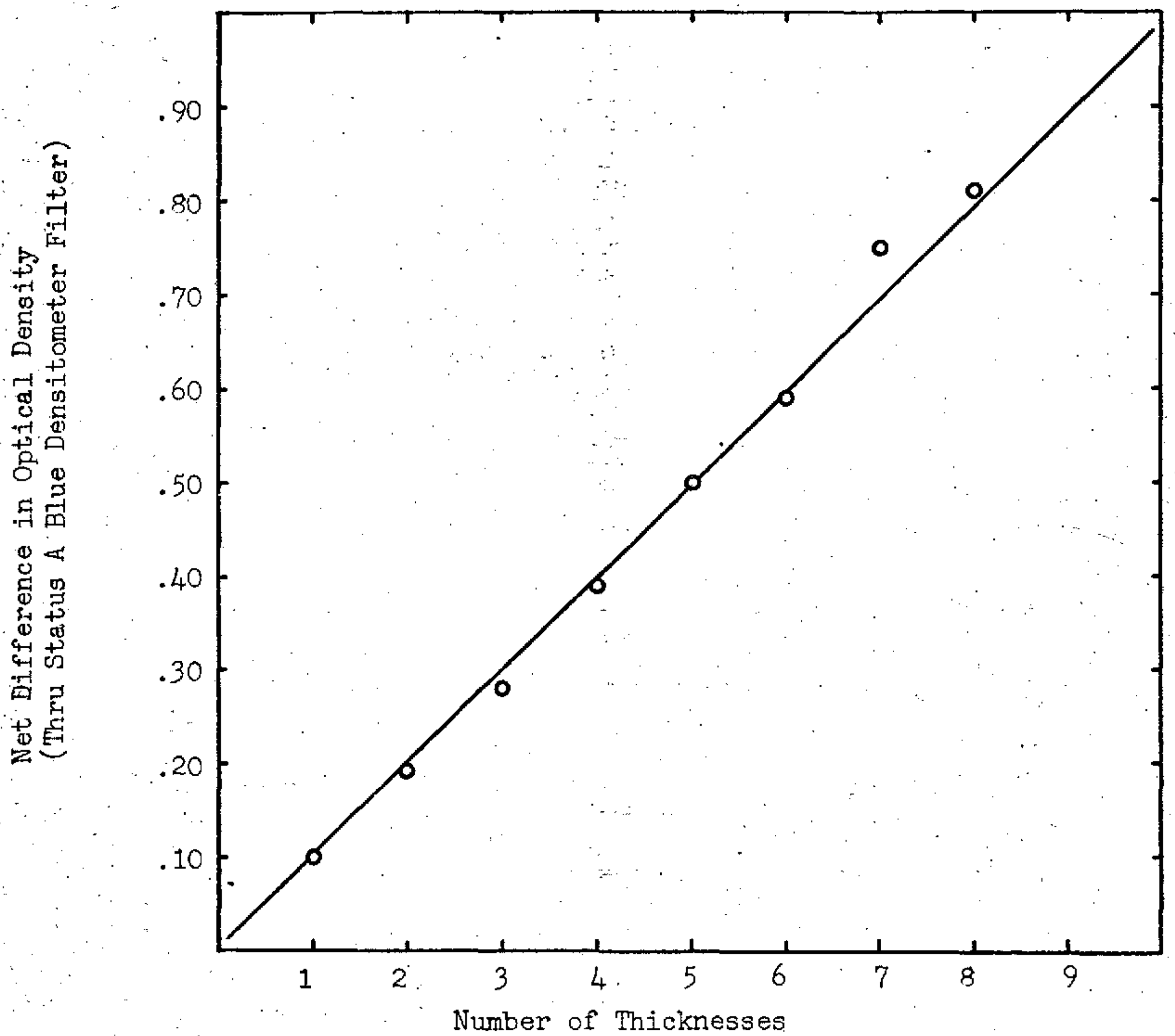

Figure 5. Net optical density versus thickness for Eastman type 5302 fine grain release positive film processed June 29,1972 on the Hi-Speed 35 mm machine. The difference in density is produced by treating a test sample with silver nitrate to form a silver sulfide stain.

SECTION III

RESULTS

Black and White Flight Emulsion Rawstock

Wherever possible the flight emulsion rawstock was processed in the proper machine configuration. No sensitometric strips were run to determine if the machines were in control for the particular emulsion. Data are tabulated in Table 4.

For the IIa-0 (129771) the processing was definitely out of control, but the film was run anyway. The stain test for this sample was done on five different days and the results of 41, 36, 32, 30, and 31 micrograms per square inch were recorded. This is a $\pm$ 14% variation. The other IIa-0 emulsion (163611) was run at the same time and found to have a residual thiosulfate level 39% lower than the average value for the flight emulsion. These two values do not closely correspond. The only other factors remaining are machine fluctuation and batch to batch emulsion differences. It is suggested that a machine, set up and running, will not produce this discrepancy in a few hours, and these are emulsion differences which are appearing in this test. Factors in emulsion manufacture which could cause washing differences would be emulsion thickness and gelatin hardness. Age, hardener level, gelatin batch, and holding times before coating can also contribute to subtle changes in

TABLE 4. Silver Sulfide Test Results for Black & White Mission Film Rawstock

Film Type	Width	Machine - Configuration	Lab	Micrograms of Thiosulfate/Sq. In. MacBeth Densitometer	Micrograms of Thiosulfate/Sq. In. Beckman Spectrometer
2485-107-2	35mm	Hi-Speed Color, D-19, 85°F	MP	≤ 1	≤ 3
NTB-3-088-03-01	35mm	Hi-Speed Color, D-19, 76°F	MP	≤ 1	≤ 3
3401-378-11/1	35mm	Hi-Speed Color, D-19, 68°F	MP	≤ 2	≤ 3
3401-378-6	70mm	Versamat, MX-641, 85°F	Precision	127, 132 (6/2)[1] 101 (7/6)[1]	102-127
3400-252	5"	Fultron, MX-641, 68°F, 55 fpm[2]	Precision	40	12-28
3414-16	5"	Fultron, MX-641, 68°F, 55 fpm[3]	Precision	67	60-70
SO-394-3-1 and SO-397-4-1	70mm	Hi-Speed Color, D-19, 85°F	MP	≤ 1	≤ 3
SO-212-1-1	35mm	Hi-Speed Color, D-19, 75°F	MP	≤ 1	
IIa-0-129771	70mm	Hi-Speed Color, D-76, 76°F	MP	41, 36, 32, 30, 31	
IIa-0-163611[4]	70mm	Hi-Speed Color, D-76, 76°F	MP	22	

[1]Date the processed film was received from the laboratory.

[2]Flight Configuration is MX-819, 80°F, 7 fpm.

[3]Flight Configuration is MX-819, 90°F, 20 fpm.

[4]Not flight emulsion. Run same day as IIa-0-129771.

gelatin hardness and emulsion thickness. The point is that there are many factors which could each permit some small variation in the wash efficiency, and the emulsion batch is likely one of these.

The Type 3400 and 3414 emulsions were processed at a much higher speed than flight configuration. It is expected (but not proven) that flight configuration speeds would produce negatives suitable for archival storage.

The Versamat processing of Type 3401 film produced an unusually high thiosulfate level when processed on two different days. It was not determined if the machine was in control but the processing conditions are a long way from providing archival storage. In addition, on page 33 of Kodak Data For Aerial Photography (Kodak Publication No. M-29), the processing of Kodak Plus-X Aerial Film 3401 in the Versamat at speeds up to and including 15 feet per minute is the guideline for commercial keeping quality. The flight configuration for 3401 is 15 feet per minute and the wash efficiency results for two separate processing runs of short lengths of flight emulsion rawstock are reasonably close together (30% variation), but at or over the 100 microgram level of Kodak commercial quality.

With these exceptions the remaining five flight emulsions, all processed in D-19 on the Hi-Speed color machine, were washed to archivally low levels of residual thiosulfate. If it is true that occasional anomolous operation in flight configuration causes variable wash efficiency (such as seen with the 3401 film), then low values may be as equally questionable as high values. More wash efficiency data are needed.

Black and White Production Films

Production films generally show a higher level of thiosulfate than flight film emulsions. This is indicated in Table 5. The reason for the higher level may be due to the fact that these are production films, and results are measured in terms of footage turned out. When the machines are working well, wash efficiency is fully adequate, probably even archival in some cases. But then a few small things may happen - the flow of wash water may be interrupted for example - and although the film looks fine, the level of thiosulfate remaining has shot up one hundred fold. People operating the machinery, being concerned with other things, have no feeling for the change that has taken place. And, of course, there is no visible evidence.

In a test of rewashing, the film was selected and returned to

TABLE 5. Silver Sulfide Test Results for Various Black & White Production Films

Film Type	Width	Use	Machine	Lab	Micrograms of Thiosulfate/Sq. In* MacBeth Densitometer	Beckman Spectrometer
5234	35mm	Fine Grain Dup.	Hi-Speed 35	MP	29 (6/13) 65 (6/13) 7 (6/30)	25-28 (6/13)
5302	35mm	Fine Grain Rel. Pos.	Hi-Speed 35	MP	60 (6/13) 116 (6/28) 72 (6/30)	45-48 (6/13)
7276	16mm	Plus-X Reversal	Hi-Speed 16	MP	7	7-11
7234	16mm	Fine Grain Dup.	Houston B & W	MP	416 (6/15) 40 (6/28) 67 (6/30) 108 (7/6) 72, 69 (7/7)	414-474 (6/15)
		(7234 from 6/15 reprocessed 7/10)			15, 14 (6/15 & 7/10)	
7302	16mm	Fine Grain Rel. Pos.	Houston B & W	MP	252 (6/15) 2 (6/28) 15 (6/30) 35 (7/6) 23 (7/10)	256 (6/15)
2420	70mm	Aerographic Dup.	Versamat #1	Precision	18	
2420	9½"	Aerographic Dup.	Fultron,55 fpm	Precision	2	
SO-233	9½"	Fine Grain Dup.	Versamat	Precision	21	

* Dates listed are those on which the film was received from the processing laboratory.

the Motion Picture Laboratory for reprocessing. The film was 16mm, Type 7234, which originally contained 416 micrograms of hypo per square inch when delivered to us on June 15. The reprocessing was a complete simulation, including developer and fixer. The film was successfully rewashed to a value of 15 micrograms of hypo per square inch. Thus, it should be possible to rewash films which contain high levels of residual hypo so that better storage life may be obtained.

Various Color Emulsions

The interpretation of this test for color emulsions is open to question. The major keeping factor in all processed color film is generally considered to be dye stability. The presence of residual thiosulfate would be a minor contributor to poor keeping quality.

Also, all color emulsions are bleached, and since there is supposedly no silver present, a secondary test would have to be made to determine unbleached silver. It should be assumed that residual thiosulfate and silver will react with each other and not with any dye mioties, and this could be highly presumptuous.

In any case, color emulsions should be well washed so that processing variables will not interfere with keeping quality.

Several color films were tested by the silver stain test and the results are listed in Table 6. Two color flight emulsions were tested (SO-168, SO-368) and the results are encouragingly low.

The irregularity of machine processing is shown with SO-360 film and Versamat processing. Hopefully, the two machines should be able to wash the film under what are supposed to be identical processing conditions with less than 100% difference in residual hypo.

TABLE 6. Silver Sulfide Stain Test Results for Various Color Emulsions

Film Type	Width	Machine	Lab	Micrograms of Thiosulfate/Sq. In.* MacBeth Densitometer	Micrograms of Thiosulfate/Sq. In.* Beckman Spectrometer
5389	70mm	Houston Color	MP	80	107-113
7252	16mm	RAM	MP	14-29	
SO-360	9½"	Versamat 1811	Precision		
		#1 (hi Temp)		145 (6/26)	133-150 (6/26)
		#2 (hi Temp)		75 (6/30)	
2445 (neg)	9½"	Versamat 1411 (6.4 fpm)	Precision	51	
SO-168-009-1	70mm	Houston Color	MP	≤ 1	
SO-368-18-32	70mm	Hi-Speed Color	MP	36	

*Dates listed are those on which the film was received from the processing laboratory.

SECTION IV

CONCLUSION

The detection of unwashed thiosulfate in processed film by staining with silver nitrate is a reasonably simple, reliable test. For black and white film the interpretation of the test is quite straight forward. Wash efficiency varies considerably from machine to machine, from day to day, and apparently from one emulsion batch to another.

To make an accurate determination that a film was washed thoroughly, the test strip must come from as close to the actual processing time as practical. Where it is desired to monitor the wash efficiency of a given film used in production, tests on this film must be conducted at regular intervals. To say, as Kodak does in its Aerial Photography booklet, that Plus-X aerial film 3401 should be processed in the Versamat at 5 feet per minute for archival keeping quality and 15 feet per minute for commercial keeping qualtiy, is to offer only broad guidelines for processing.

Guidelines for wash efficiency should be set. As a starting point, black and white production films should meet Kodak commercial quality standards of 100 micrograms of thiosulfate per square inch. Mission original black and white film should meet archival keeping quality guidelines, some-where under 10 micrograms of thiosulfate per square inch. Processing conditions must meet these standards before certification for original film and periodic checks on production films should be made. A single test indicates that rewashing is practical.

The question of color film remains open at this time. I would suggest that mission original color film should be processed to archival keeping quality according to the silver sulfide stain test. The only justification for this is that any future assessment to be made for the keeping quality of color film will be appreciably simplified.

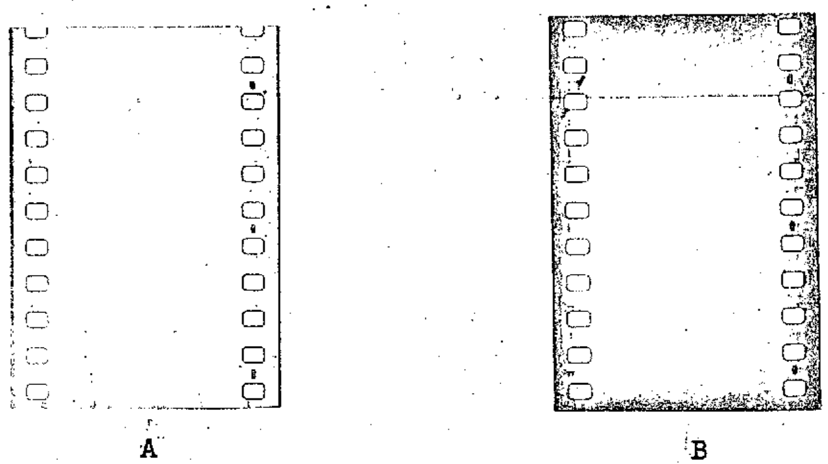

FIGURE 6.

Samples of Eastman film type 5302 fine grain release positive. This film was processed in the Hi-Speed 35mm processor on June 29, 1972. Sample A indicates how the film looks as it comes off the processor. Sample B was treated with silver nitrate to form the silver sulfide stain according to the procedure described in the text. A single thickness of each sample produced optical densities (read with the Kodak Status A blue densitometer filter) of 0.07 and 0.17 for A and B respectively. Four thicknesses resulted in density readings of 0.17 and 0.56 in the same manner. From Figure 4 the net density (0.39) is equivalent to 71 micrograms of hypo per square inch. Considering this to be a finer grained film, the plot in Figure 1 indicates a storage life of about 7 years before natural stain formation.