Article: An Examination of the Effectiveness of Various Toning Solutions on Black and White Silver Halide Emulsions
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An Examination of the Effectiveness of Various Toning Solutions on Black and White Silver Halide Emulsions

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ABSTRACT - The effectiveness of various toning solutions on silver halide emulsions has been investigated. The particular effectiveness of Kodak Brown Toner was noted. Procedures included the use of a test chamber designed by The Image Permanence Institute for hydrogen peroxide fuming. The simplicity and consistency of the apparatus was noted.

INTRODUCTION - "Deterioration is far more frequently the result of defective or careless working than an inherent weakness of the process."[1]

Written in the 1911 edition of Cassell's Cyclopaedia of Photography, these words have been the focus for the photographic technician in attempting to achieve the permanence of negative materials. Continuing further, the same heading reads, "A properly fixed and washed negative should be permanent..."[2]

One need only read the title of Ellen McCrady's History of Consternation Over Redox Blemishes,[3] written in April 1983, to realize other elements are at work in the deterioration of silver images. The problem of redox blemishes, overall discoloration, and image fading all still seem to be with us despite the best efforts of the concerned photographic worker.

Turning again to the world of 1911, under the heading "Fading, Causes Of," Cassell notes, "Everyone knows how prone silver in the form of spoons and forks or ornaments, is to tarnish...it can be well understood how much more readily the metal in a finely divided state can be attacked."[4]

Silver, "in a finely divided state," is one description of film, and its susceptibility to tarnish. For one of the causes of this tarnishing reaction under the section "Deterioration," Cassell adds, "...everyone knows that the minute quantities of

sulphur contained in a London fog will tarnish silver articles..."[5] Here then, stated 78 years ago as common knowledge, are problems regarding the fragility of the silver image, and a source of attack to that image other than improper washing or fixation. That other source is atmospheric pollutants.

The increased presence of pollutants in the environment has accelerated the need to look for solutions for use in the protective treatment of silver images. Such treatments are also needed for already existing images to enhance their resistance to these pollutants.

In their paper Review of the Effects of Processing on the Image Stability of Black and White Silver Materials, Lee and Drago recommended the use of a toner treatment to, "increase the stability of the silver image towards most forms of degradation."[6] It is interesting that in a sense their recommendation returns us to the recommendations of the past.

Once again under "Permanency" The Cyclopaedia of Photography states, "A sulphide toned bromide print should be as enduring as any photographic print, silver sulphide being a most stable substance."[7] Here is also seen the use of toners as a means of permanency, and in particular the use of a sulfide toner for maximum stability. It should be noted that the recommendation given here is for prints not negatives. The objection to sulfide toning of a negative would be then, as now, a change in its color and density.

In 1984, Fuji Photo Film Co., Ltd. introduced a new toner product called Fuji Ag-Guard. This was a sulphur based toner claimed to produce excellent image stability with no change in image color or contrast. In 1986, Jim Wallace, Director of the Smithsonian's Office of Printing and Photographic Services tested Fuji Ag-Guard toner compared to the effectiveness of selenium toner on a variety of photographic materials. In his conclusions Wallace stated, "Ag-Guard shows promising potential for extending the life of some photographic products. Because of the variance of results obtained, however, the usefulness of the product is believed to be heavily product dependent."[8] He also goes on to say, "It should be noted, however, that at present there is no standard hydrogen peroxide fuming procedure."[9] It was also noted that various manufacturers' test procedures had yielded differing results.

Peroxide fuming and the exposure of photographic materials to oxidizing gases has been carried on since the 1850's as a means of observing the effects of these gasses, but no standard technique has been developed. Eastman Kodak and other

manufacturers have been seeking such a standardized test. In July 1987, the Image Permanence Institute (IPI), working under a grant from the New York State Library Preservation Grant Program, began research which had as one of its goals "to develop an improved hydrogen peroxide accelerated test for image oxidation..."[10] By May 1988, IPI was able to announce that this objective had been, "met in full."

It was the development of their test procedures and associated test equipment, as well as conclusions relating to the effectiveness of sulfiding treatments, which led the Smithsonian to re-evaluate and expand the Ag-Guard testing using the IPI test chamber and procedure. Also included in this new testing was an additional sulfide toner treatment, Kodak Brown Toner.

EXPERIMENTAL

A series of experiments were designed to test a variety of films using Ag-Guard, Selenium, and Kodak Brown Toner treatments. Together with untoned samples, the test film was hydrogen peroxide fumed using the IPI test chamber and recommended procedure.

Films Tested were Kodak Tmax 100 and Kodak Professional B/W Direct Duplicating Film. Both films were exposed using a Kodak Step Tablet 1A (11 step) and processed in a Hope 134 B&W processor. Six strips were exposed, processed, toned and fumed for each test.

Toning Solutions used, their preparation, and the treatment procedures were:

Ag-Guard - In consultation with IPI, two dilutions of Ag-Guard were tested, 80 ml of concentrate in 1 liter of water, and 240 ml to a liter of water. The recommended treatment was for two minutes at 70 F, with no wash.

Selenium - The solution tested was prepared 1 part Kodak Rapid Selenium Toner to 19 parts water. Treatment was for two minutes, followed by a two minute wash at 70F.

Kodak Brown Toner - The solution tested was prepared 1 part Brown Toner to 200 parts water. Treatment was for two minutes followed by a two minute wash.

Hydrogen Peroxide Treatment following toning was accomplished using the test chamber designed by IPI. Two of the IPI test chambers were purchased by the Smithsonian for use in these tests and future projects. The fuming procedure, as recommended by IPI, called for exposure for a period of 18 hours at 50C and approximately 81% RH. Relative humidity was maintained through the use of a saturated Potassium Chloride solution. Temperature was maintained in a Hotpack Model 434304 chamber. More complete details of the IPI procedure are contained in Appendex 12.

EVALUATIONS

Evaluation of the results were performed both visually and through densitometer readings.

Visual Reference was performed by observing the presence of spots or blemishes which had formed during the fuming process. These observations were made using a Wild M3Z microscope at a magnification of 10X.

Densitometer Readings were made from each of the 11 steps of all six strips used in each test. The results were then averaged and those values used to create the attached graphs. A complete series of readings were made after the film was processed, after toning, and again after fuming. In each case, readings were made using a Macbeth TD504 densitometer, through the Status "A" red filter.

Readings were also made of D-Min, D-Mid, and D-Max values using Status "A" Visual Density (green), and Blue Density filters.

Procedures - The post-fuming samples obtained from the IPI test chambers showed even distribution of exposure to the hydrogen peroxide gas, and good consistency of results.

CONCLUSIONS

Selenium showed some protection to the TMax film, but some red spots and discoloration were present. Selenium showed almost complete protection when used with the Direct Duplicating Film.

Ag-Guard at the dilution of 240ml to 1 liter, offered approximately equal protection to TMax film as that found with Selenium. At the weaker dilution of 80ml to 1 liter, noticeably

less protection was observed. Ag-Guard used at the 240ml dilution on Direct Duplicating Film showed less discoloration than the 80ml dilution, however, both samples showed heavy red spots.

Brown Toner provided almost complete protection to TMax film. Results showed almost no discoloration or red spot formation. Brown Toner when used with the Direct Duplicating Film prevented the formation of red spots, however, some noticeably overall discoloration of the film was observed.

The IPI test chambers and the accompanying recommended procedures were able to be used with a minimum of training. Good consistency of results and even fuming were especially notable. The use of two chambers operating in the Hotpack unit creates many possibilities for flexible future testing.

ACKNOWLEDGMENTS - The author gratefully thanks Dr. Peter Krause for his generous assistance in the preparation of this paper.

Thanks are also due to Jim Reilly and the staff of IPI for their help in familiarizing me with the peroxide fuming procedures using the IPI test chamber.

I would also like to thank Jim Wallace of the Smithsonian for his encouragement in this project.

NOTES

1. Bernard Edward Jones, Editor, Cassell's Cyclopedia of Photography, Cassell Publishers, 1911, London, New York.

2. ibid.

3. Ellen McCrady, "History of Consternation Over Redox Blemishes", unpublished manuscript, April, 1983.

4. op. cit., Cassell

5. op. cit., Cassell

6. Drago and Lee, "Review of the Effects of Processing on the Image Stability Stability of Black and White Materials", given at Public Archives of Canada, Aug. 25-28, 1985, Ottawa, Ont. Canada, pg 63.

7. op. cit., Cassell

8. Jim Wallace, "An Examination of the Effectiveness of Ag-Guard Protecting Silver Halide Photographic Emulsions", presented Feb 7, 1987, AIC/PMG Seventh Annual Winter Meeting, New Orleans, La.

9. ibid.

10. Reilly, Nishimura, Cupriks, and Adelstein, "Stability of Black and White Photographic Images With Special Reference To Microfilm", presented to Conservations In Archives Symposium, National Archives of Canada, May 1988, Ottawa, Ont. Canada.

ATTACHMENTS

1. Observations of Samples of TMax and 4168 Direct Duplicating Films After 18 Hr. Hydrogen Peroxide Fuming.

2. Graph, TMax 100, Untreated.

3. Graph, TMax 100, Selenium 1:19.

4. Graph, TMax 100, Brown Toner, 1:200.

5. Graph, TMAX 100, Ag-Guard 80ml/1L.

6. Graph, TMax 100, Ag-Guard 240ml/1L.

7. Graph, 4168, Untreated.

8. Graph, 4168, Selenium 1:19.

9. Graph, 4168, Brown Toner, 1:200.

10. Graph, 4168, Ag-Guard, 80ml/1L.

11. Graph, 4168, Ag-Guard, 240ml/1L.

12. IPI "Procedures for Peroxide Testing", 2pp.

Figure 1

VISUAL OBSERVATIONS OF SAMPLES
TMAX 100 & 4168 DIRECT DUPLICATING FILM
AFTER 18 HOURS HYDROGEN PEROXIDE FUMING

Untreated		
	TMax 100	Yellowish discoloration, Microspots.
	4168 Direct Dupe	Yellow/orange discoloration, microspots, Loss of density.
Brown Toner		
	TMax 100	No color change, No microspots.
	4168 Direct Dupe	Slight brownish color change, No microspots.
Selenium Toner 1:19		
	TMax 100	Brownish discoloration, few microspots.
	4168 Direct Dupe	Elimination of original "greenish" tint. No further color change, No microspots.
Ag-Guard 80ml/1L		
	TMax 100	Brownish Discoloration, No microspots.
	4168 Direct Dupe	Brownish discoloration begins at third step. Microspots heavy as density increases.
Ag-Guard 240ml/1L		
	TMax 100	Slight purplish discoloration. No microspots.
	4168 Direct Dupe	Less discoloration than 80ml/1L. Microspots still heavy as density increases.

Note: Ag-Guard samples had "scummy" appearance. In some samples scummy area coincided with a plus density.

Figure 2

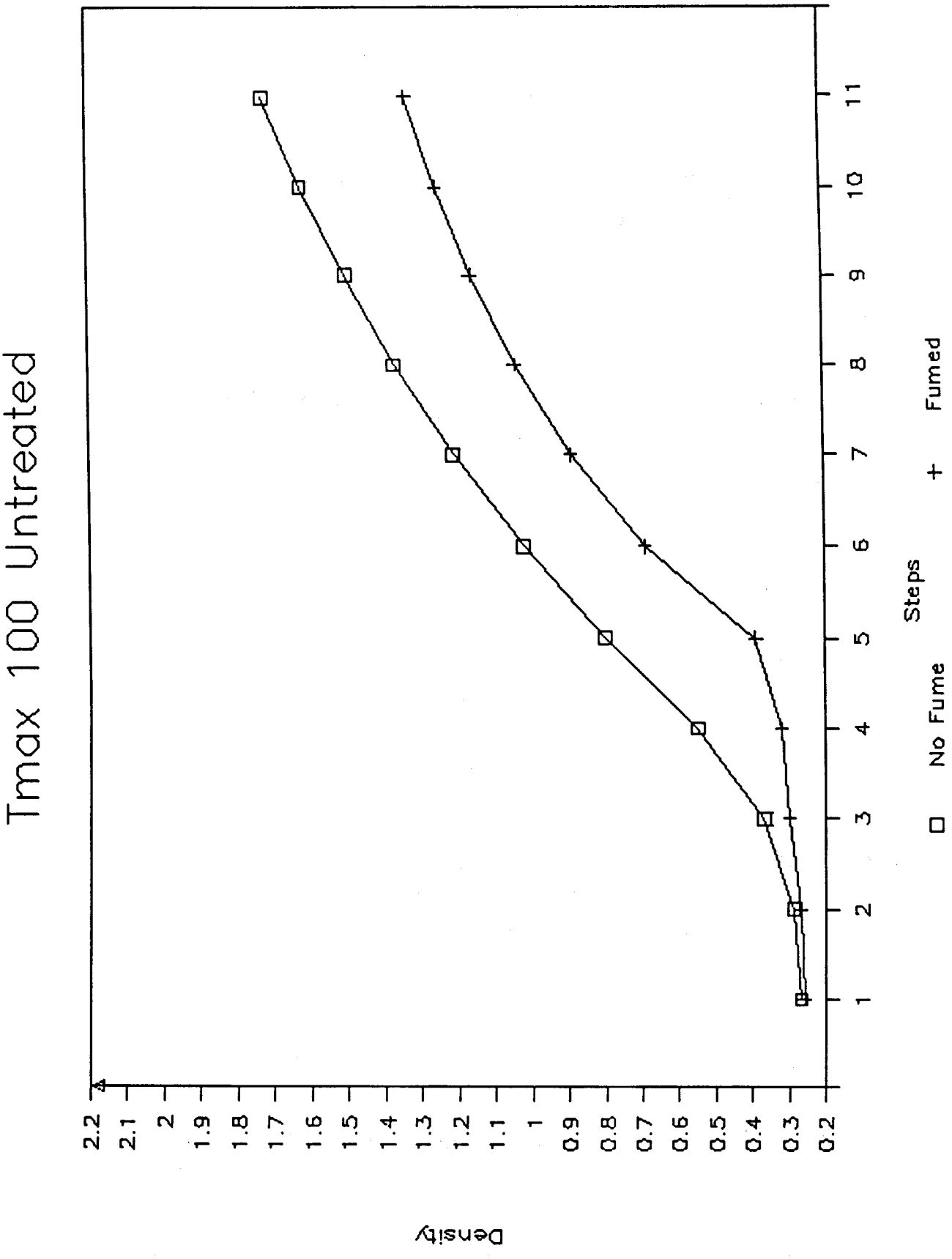

Tmax 100 Untreated
Density
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
1
2
3
4
5
6
7
8
9
10
11
Steps
No Fume
Fumed

Figure 3

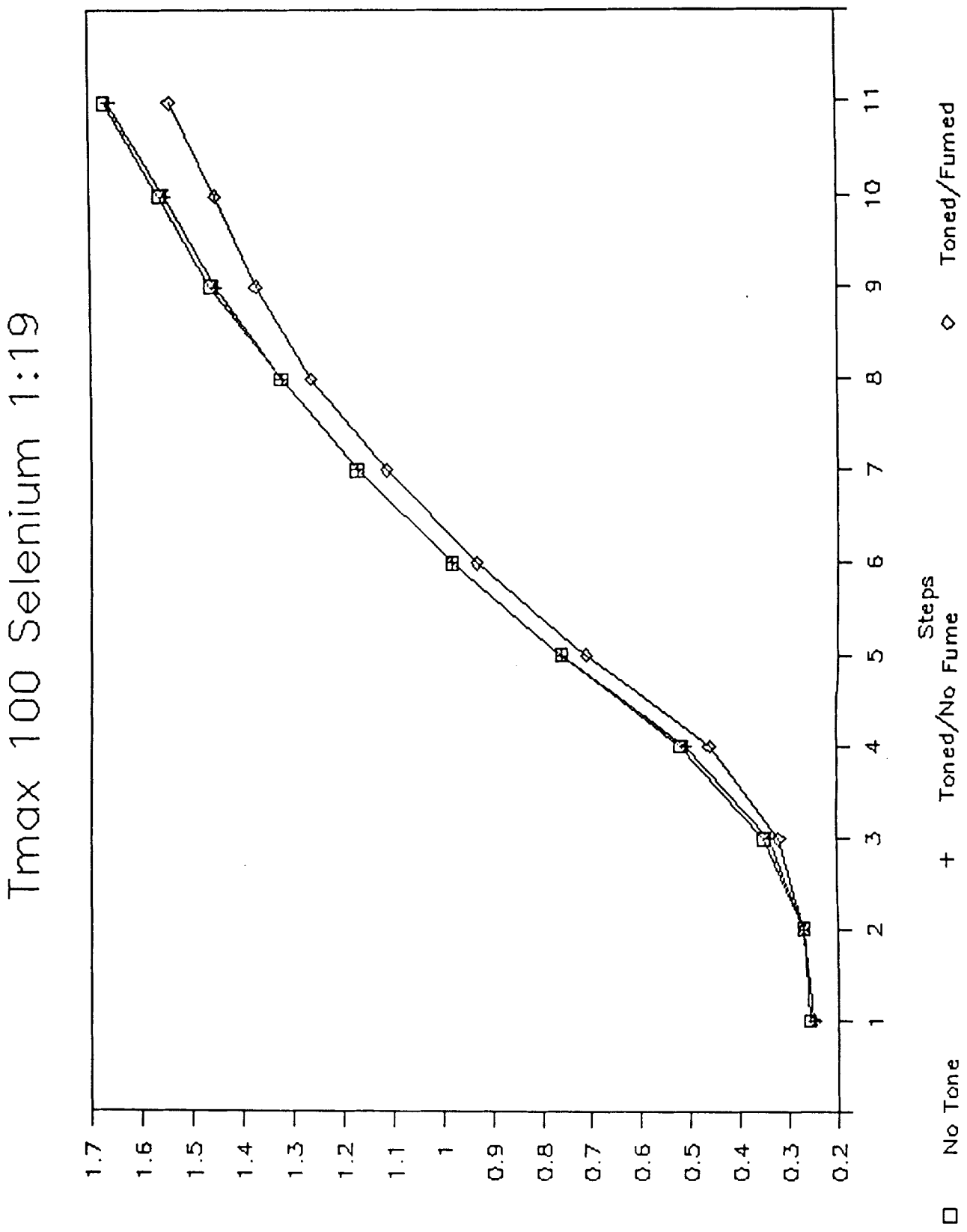

Tmax 100 Selenium 1:19
Density
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
1
2
3
4
5
6
7
8
9
10
11
Steps
□ No Tone
+ Toned/No Fume
◇ Toned/Fumed

Figure 4

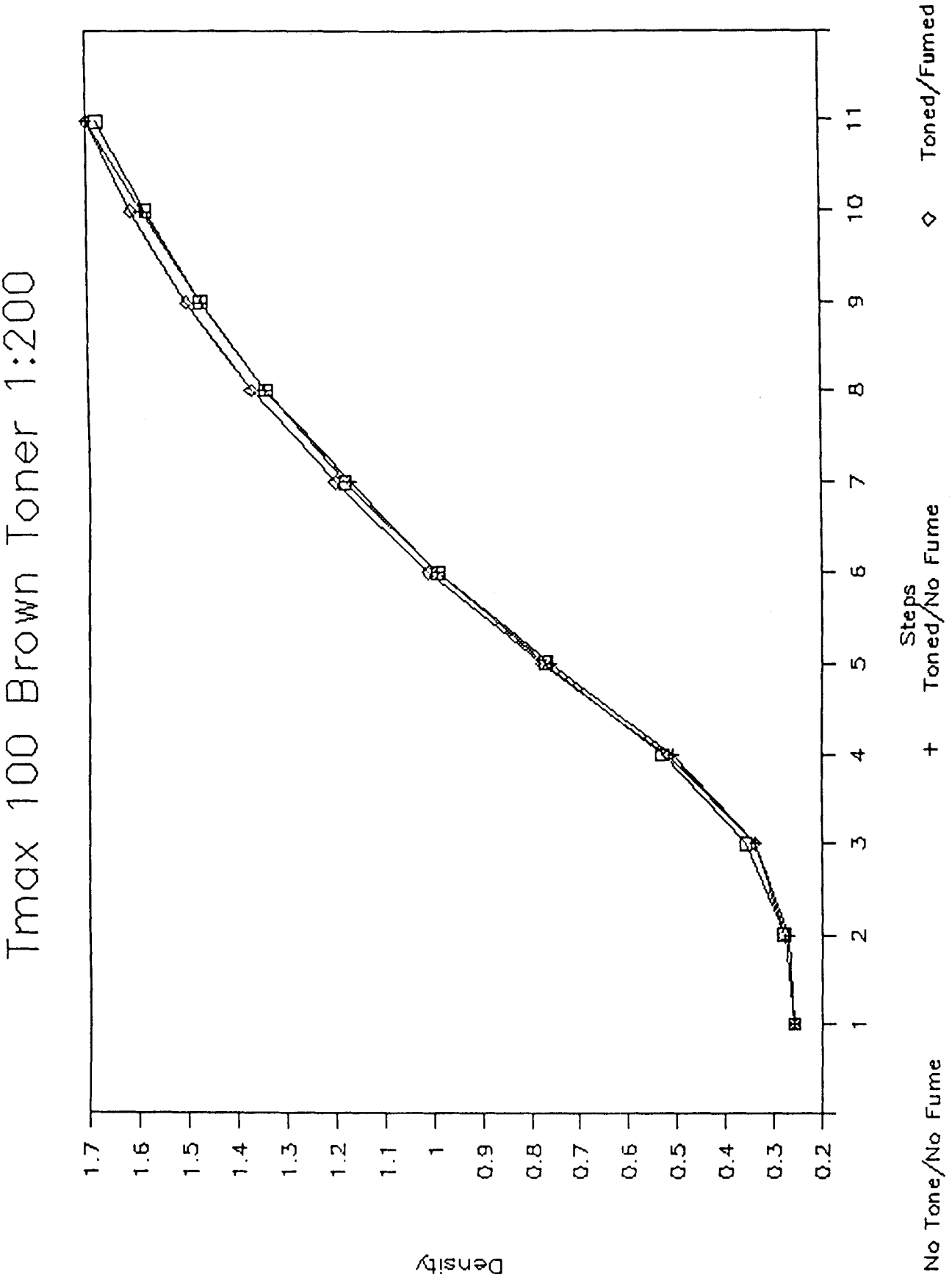

Tmax 100 Brown Toner 1:200
Density
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
1
2
3
4
5
6
7
8
9
10
11
Steps
No Tone/No Fume
+ Toned/No Fume
◇ Toned/Fumed

Figure 5

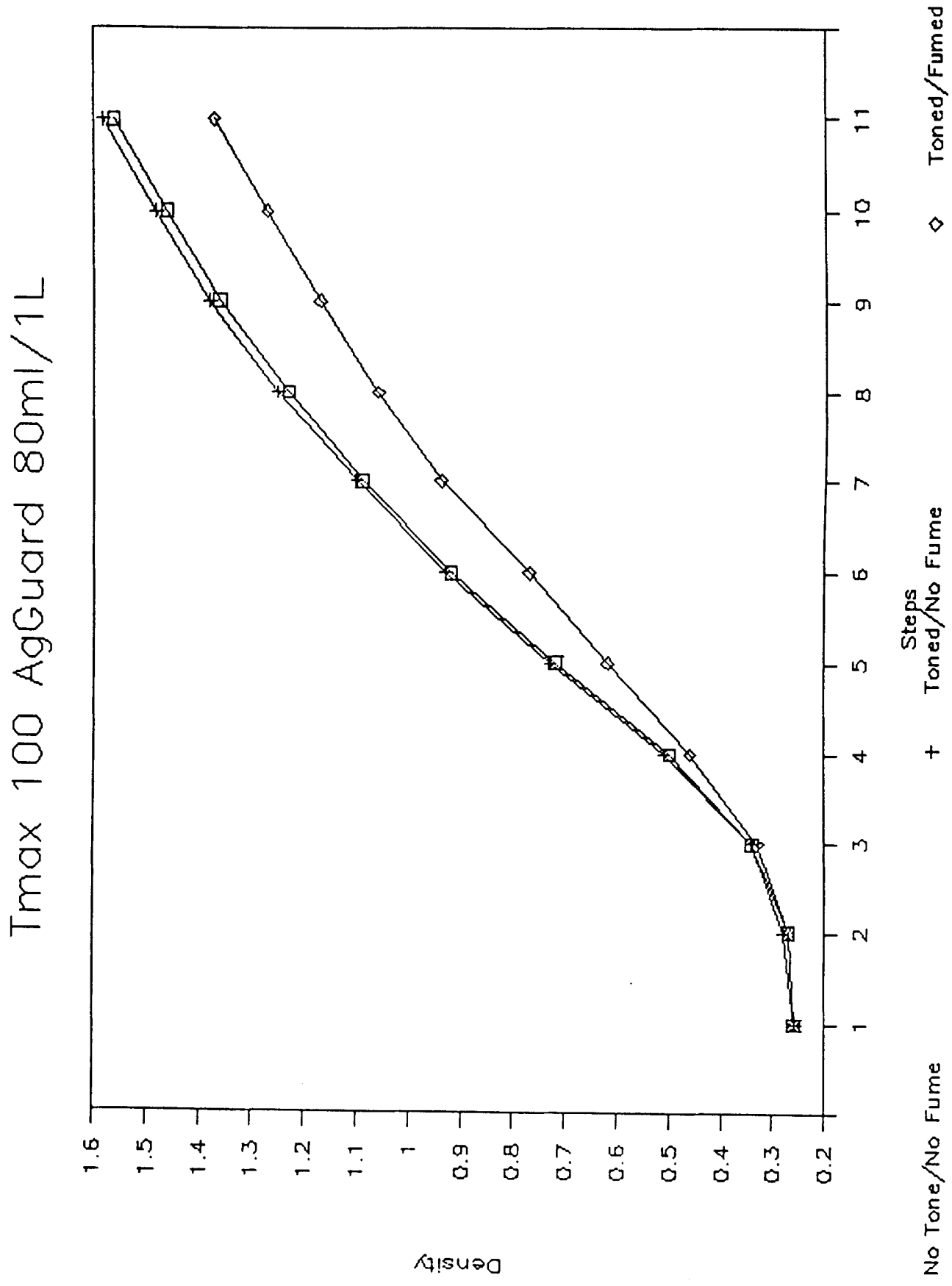

Tmax 100 AgGuard 80ml/1L
Density
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
1
2
3
4
5
6
7
8
9
10
11
Steps
No Tone/No Fume
+ Toned/No Fume
◇ Toned/Fumed

Figure 6

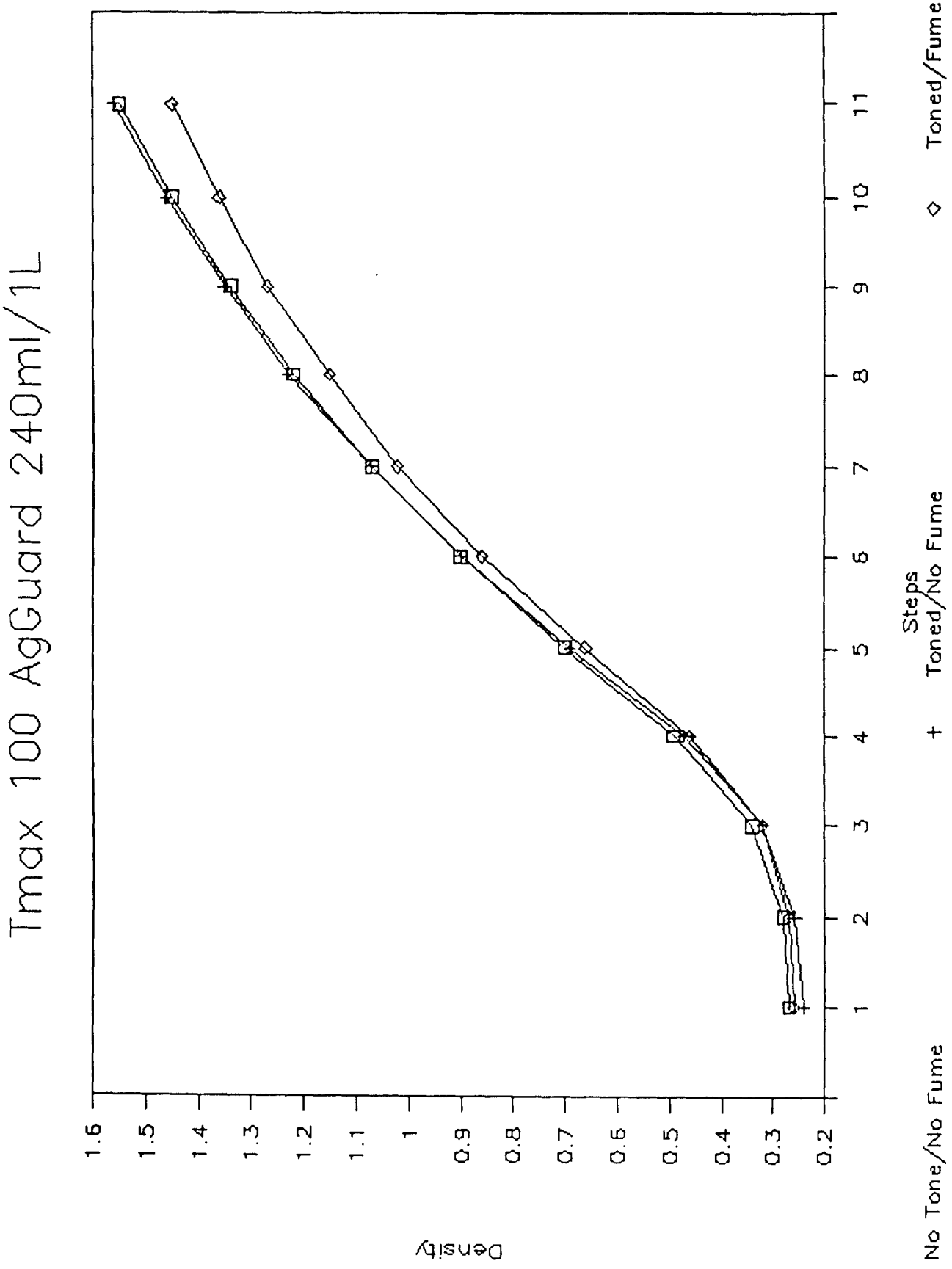
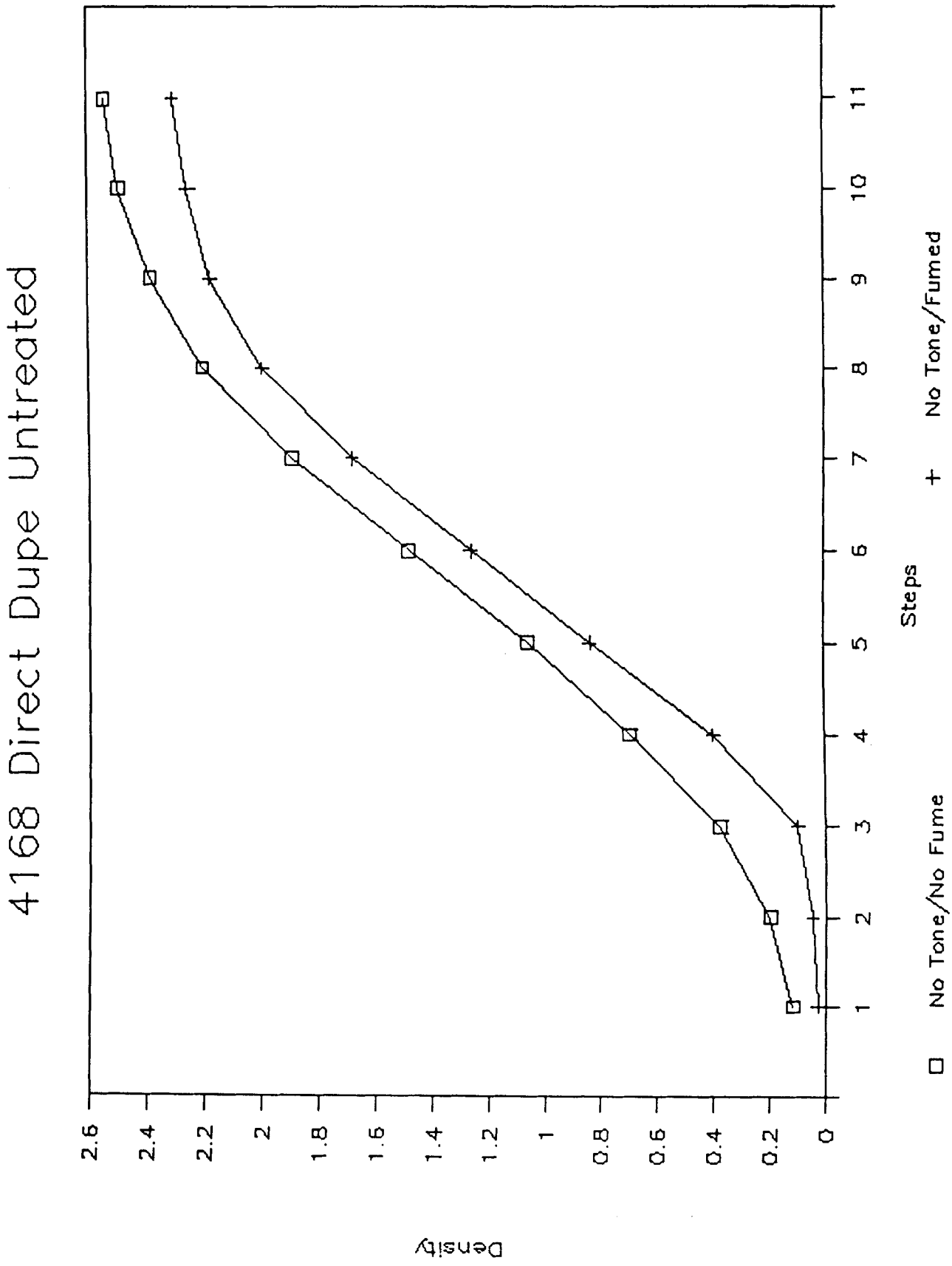

Tmax 100 AgGuard 240ml/1L
Density
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
1
2
3
4
5
6
7
8
9
10
11
Steps
No Tone/No Fume
+ Toned/No Fume
◇ Toned/Fumed

Figure 7


4168 Direct Dupe Untreated
Density
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
11
Steps
□ No Tone/No Fume
+ No Tone/Fumed

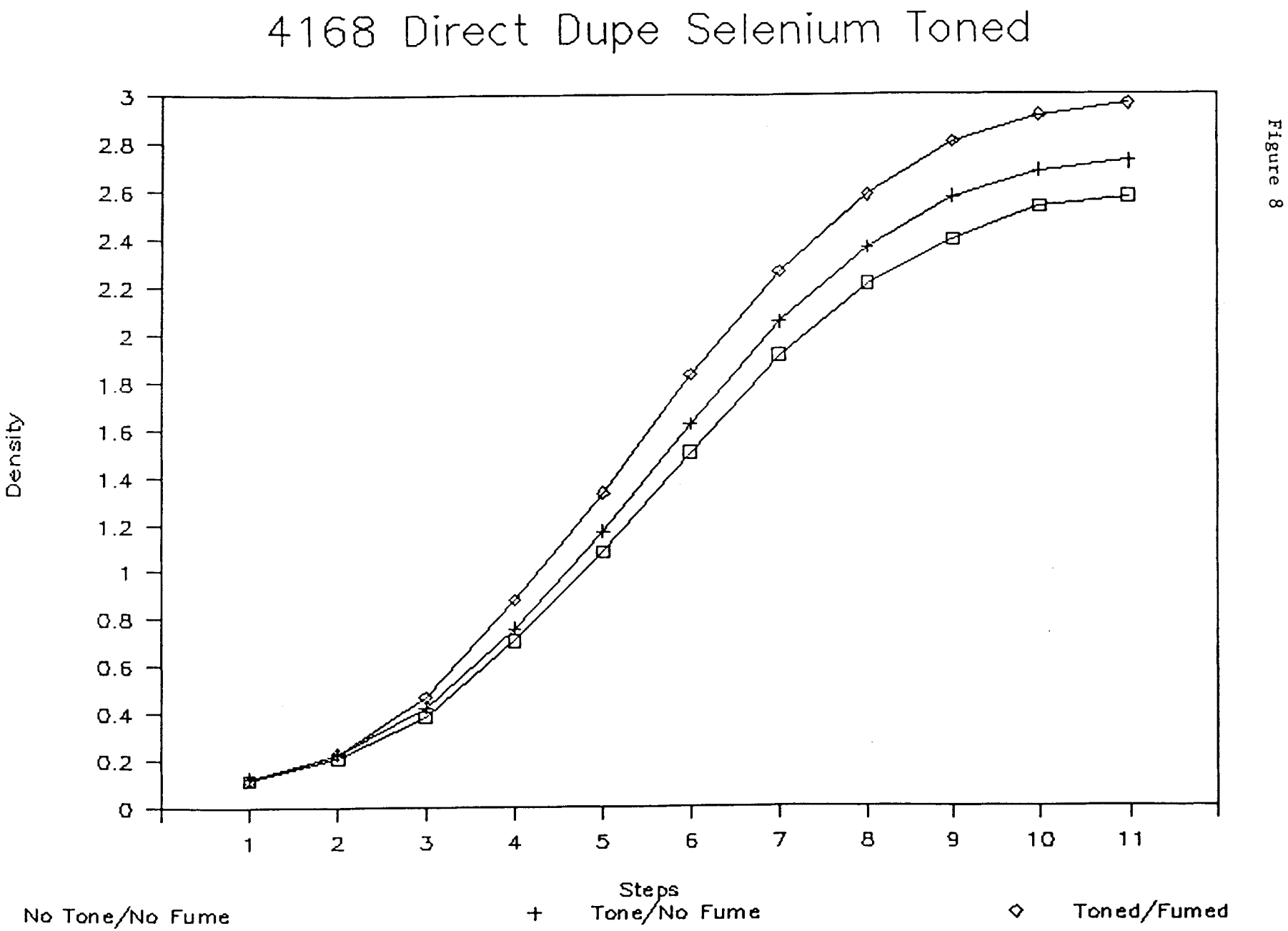

4168 Direct Dupe Selenium Toned
Density
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
11
Steps
No Tone/No Fume
Tone/No Fume
Toned/Fumed

Figure 8

Figure 9

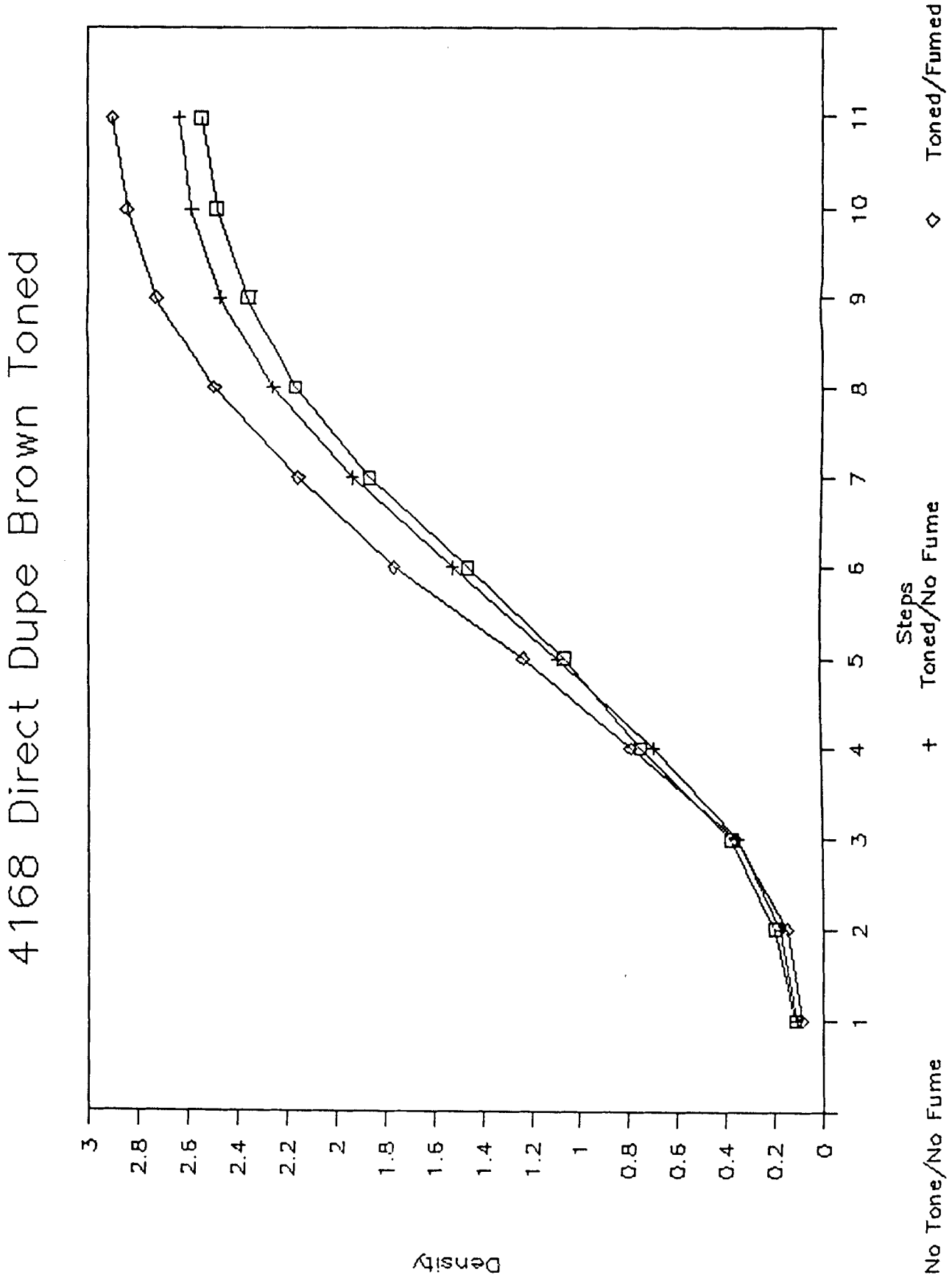

4168 Direct Dupe Brown Toned
Density
Steps
No Tone/No Fume
Toned/No Fume
Toned/Fumed
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
1
2
3
4
5
6
7
8
9
10
11

Figure 10

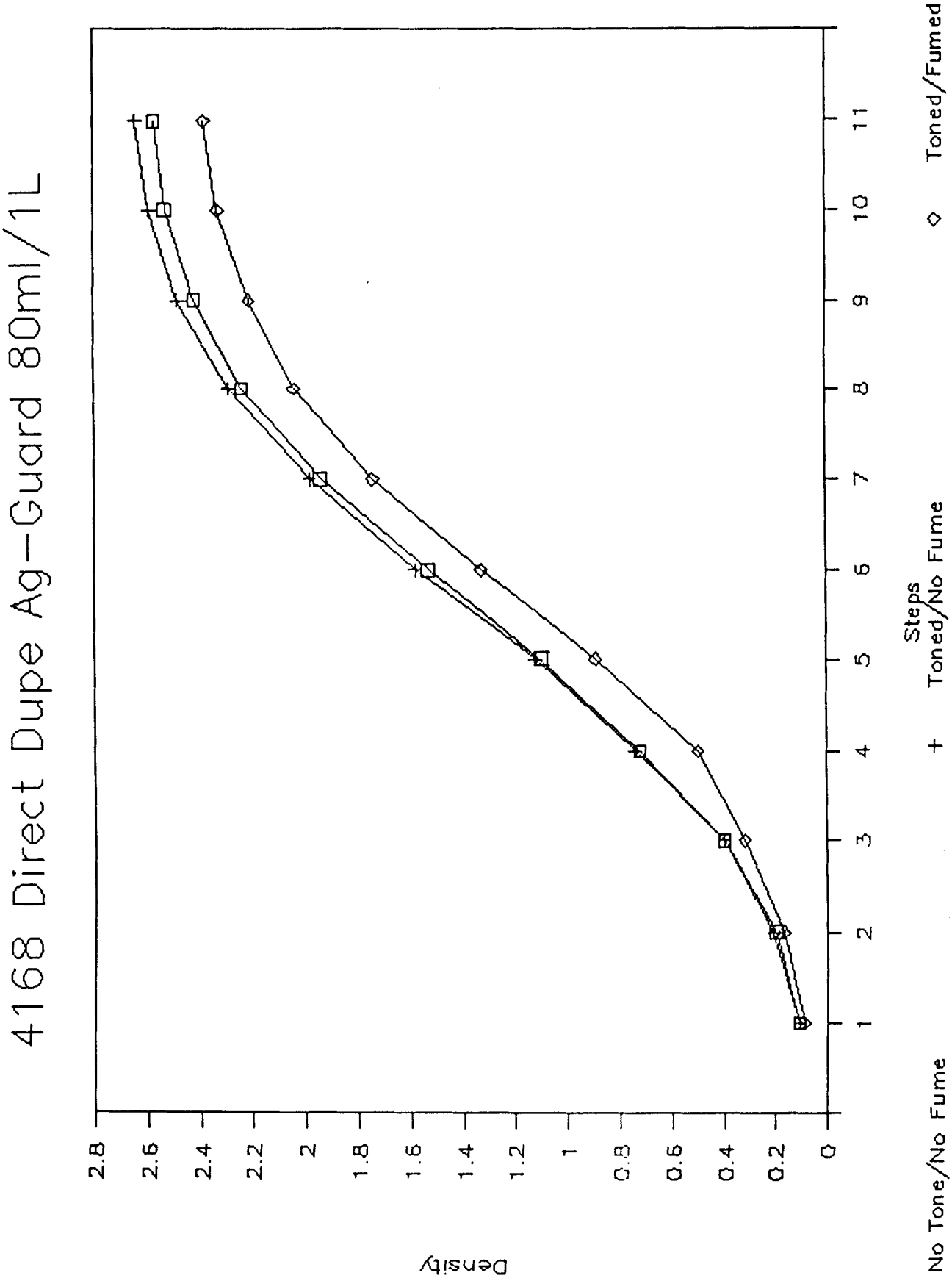

4168 Direct Dupe Ag-Guard 80ml/1L
Density
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
11
Steps
No Tone/No Fume
+ Toned/No Fume
◇ Toned/Fumed

Figure 11

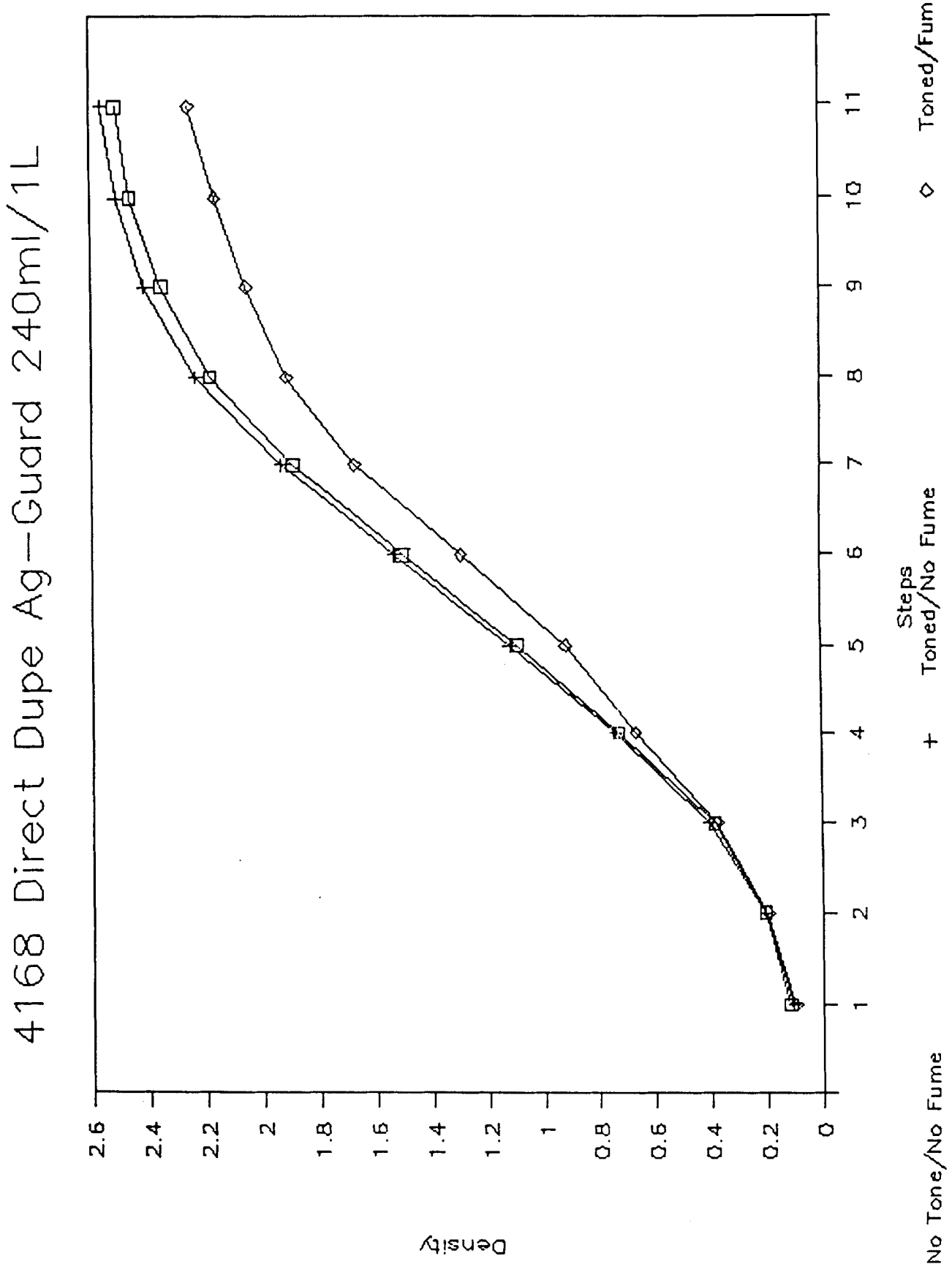

4168 Direct Dupe Ag-Guard 240ml/1L
Density
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
11
Steps
No Tone/No Fume
+ Toned/No Fume
◇ Toned/Fumed

Figure 12 IMAGE PERMANENCE INSTITUTE 4/88

PROCEDURES FOR PEROXIDE TESTING

1. Affix test samples to the inside surface of the plexiglas collar with Filmoplast linen tape, making sure that the samples are snug against the surface with no sags, ridges, bends, buckles, or protruding edges which might disturb air circulation.

2. Pour 20 ml. of 30% peroxide stock solution into a small beaker, to be drawn as needed. Pippetting from the beaker eliminates the risk of contamination in the stock container.

   With a 100 ml volumetric flask, prepare a 2% peroxide solution by adding 6.66 ml of 30% H_2O_2 concentrate to approximately 70 ml of distilled water; add distilled water to bring volume to the 100 ml line. Cap and shake vigorously

   Peroxide concentration in parts per million (ppm) is related to the quantity of 2% solution used to inoculate the paper source disk. At this concentration, .24 ml of solution yields 2000 ppm H_2O_2,
   .18 " " " 1500 " ,
   .12 " " " 1000 "
   Because the absorption capacity of the paper is limited, it is recommended that the total liquid dispensed not exceed .30 ml. And because amounts of less than .10 ml are very difficult to control, peroxide concentrations of less than 1000 ppm require weaker working solutions, such as 1% or 0.5%. A 1% solution, made using half the concentrate, yields 1000 ppm from .24 ml of solution. A 0.5% yields 500, and so forth.

3. Make sure that a sufficient quantity of saturated KCl solution is on hand. This is easily prepared by adding KCl salt to water at 60C until no more salt can go into solution and collects as sediment on the bottom of the jar. The cooled liquid is the working saturated solution.

   Put approximately 10 grams (1 slightly rounded teaspoon) of the dry KCl salt in a petri dish and, using a pipette, add 4 ml of saturated KCl solution. In a small, enclosed environment such as a sealed dessicator jar, this amount of salt and solution will maintain relative humidity at approx. 81% R.H. Place the petri dish in the bottom center of the dessicator jar.

4. Wire a 4 cm circle of chromatography paper to the mesh platform with a small strand of stainless steel wire, passing the wire through two central points on the paper disk and twisting it upon itself underneath the platform.

5. Using a 1 ml pipette and aspirator, apply the desired amount of peroxide solution directly onto the chromatography paper, making sure that no liquid runs or drips off. Place this assembly directly over the petri dish so that is clears by 1/2 to 3/4". Slightly splay the 4 legs of the platform so that there will be some resistance to strong clockwise air circulation which might upend the platform.

. Insert the sample collar into the jar and make sure it is evenly seated on the glass ledge. Cover the jar quickly with the ground glass lid and check that the glass stops are flush against the jar lip. Inspect the tabs on the bottom of the motor housing to ensure that they provide correct perpendicular alignment of the motor shaft through the center hole.

. Place the prepared jar into a dry oven which has been preheated to 50C and connect the power source wires to the motor. Run the motor at full speed (2500rpm) for 30 minutes and then turn it off. A timer is very convenient for this operation. The samples should remain in incubation for another 18 hours, which gives the oxidi-dation/reduction reactions sufficient time for completion.

. After the samples have been incubated and removed from the jar, redevelop them for about 30", using the developer in which they were originally processed. This makes the oxidative effects of the peroxide easier to see by reducing the remaining ionic silver to a colloidal form. Wash the samples thoroughly and air dry.

IOTE: The amount of peroxide required will vary with the quantity and nature of the materials tested, but the following conditions have proved useful for the evaluation of microfilm:

1) 50C, 500 parts per million H2O2 (.12 ml 1% solution)

2) 24C, 1000 " " " " (.12 ml 2% solution)

3) 50C, 2000 " " " " (.24 ml 2% solution)