

Deinking Potential of Dye Based Lithographic Inks

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Introduction

The United States, and the world, is facing the problem of handling waste products. Landfills begin to close, fill-up, or both. Landfill sites are no longer being approved, it is estimated that 80% of all U.S. landfill sites will be closed in less than 20 years. It is also estimated that about 11% of the total paper-waste stream is recovered for recycling, 13% is incinerated, and 76% is sent to landfills (Eric O. Edelman, Jan. 1992). Approximately 36-38% of total waste accounts with paper and paper products (J.H.Tomlinson, Aug. 1990).

According to American Paper Institute, the consumption of waste paper in the United States is expected to rise by 1 million tons per year, which means the consumption of waste paper will increase at the rate of 1.5 times more than the increase in virgin fiber usage. There are about 600 paper, pulp, paper board, or related products mills in the U.S. More than 500 of these mills utilize atleast some waste paper and 200 of them depend entirely on recycled paper for their fiber supply (J.H.Tomlinson, Aug. 1990).

The U.S. paper industry is committed to major expansion of paper recycling. The API announced that the paper industry is committed to reach the level of 40% of total paper consumed by waste paper recycling by the end of 1995 (Norman P. Black, May 1990). All these factors make recycling very important.

During the recycling of paper, the paper is converted into pulp. Production of white (colorless) pulp for paper requires the removal of the ink from the printed paper to be recycled. Most printing inks use pigments as the coloring material, which is very difficult to dissolve, so the pigments must be physically removed from the paper during recycling. During this process the paper fiber is scrubbed and light weighted pigments are separated on top of the floatation cells. It is almost impossible to remove pigments without any loss of fiber during the process. Approximately 15% of the fiber is lost during recycling. Moreover, not all of the pigments can be removed from the fibers, which results in an approximate 10% loss of optical properties in the recycled paper (Bill Forester, May 1991).

As an alternative to pigments, dyes may be used as coloring material. By definition, dyes can be dissolved in a reducing or oxidizing agent. Theoretically, paper printed with dye inks can be bleached while recycling, making it possible to have higher yields approaching 100% and no loss in optical properties.

Typically, dyes have not been used a great deal in printing inks. Presently, dyes are used in inks with pigments as toners to provide color strength. The problems associated with using dyes independently include: they are not light-fast to the same degree as pigments; dye inks tend to have problems with migration and water resistance; many dyes are expensive when compared with pigments (Rodger L. Gamblin, May 1985); because dyes do not have any particle, there is a possibility of strike-through in less dense paper such as newsprint (Yuri Berri, Jan. 1992).

Because of their limitations when used independently, dyes are not considered suitable colorants for most printing inks. However, some of these limitations can be compensated for making dye inks suitable for certain products. For example, because the life of a newspaper is not long it is not necessary that inks for newspapers have high degree of light-fastness (Rodger L. Gamblin, May 1985). Non wetting agents can be used so that the ink does not penetrate into the paper, and possibly some fillers may be used to help hold ink out on the surface (Yuri Berri, Jan. 1992).

The author has contacted 4 scientists in ink industry and 3 researchers in paper industry. They suggested that a very little or no research has been done on the recycling of dye printed material, and confirmed the need to have more research in this area. The dyes are available, if research is done, so inks can be formulated to give satisfactory results (Jack Hruzewicz, Jan. 1992).

Objectives

The objectives of this study are to: 1) compare the printability of dye based ink with the conventional pigment ink, and 2) recycle and bleach both dye ink and pigment ink printed papers with hydrogen peroxide and sodium hydrosulfite, comparing the optical properties of recycled papers. During this study a commercially available, uncoated offset paper was printed with a conventional pigment ink and a dye ink. Because paper coating consists of Calcium Carbonate and/or Titanium Dioxide pigments, uncoated paper was selected to avoid the effects of coating pigments during the study.

Procedure

To conduct this study, conventional pigment and dye inks were made in the identical laboratory conditions. The uncoated offset paper was printed with both the inks. The dye ink did not yield satisfactory results during printing which suggested that the dye ink manufacture needs extra attention. Therefore, to continue the study a leading ink manufacturer was asked to provide commercially made dye and pigment inks. A process blue and blue dye ink were made available by the ink manufacturer.

Printing

The two inks were printed in the Western Michigan University's offset pressroom on Heidelberg Kord press under identical conditions. Process blue (pigment ink) was printed first. To compare the print quality, the ink set-up was kept same for the both print trials. Samples were taken and evaluated for density, dot-gain, resolution, and subjective printability observation. The data for printing materials/conditions is listed below.

Materials/Conditions

Plate

Manufacturer: Viking PS plates.
Exposure: 30 seconds.
Processing: Automatic plate processor.

Paper

Type: Maker's Matte text 74 GSM
(commercially available).

Press

Heidelberg Kord single-color sheet-fed offset press.

Ink

Type: 1. Process offset blue
(commercially available).
 2. Dye based blue
(commercially available).

Fountain Solution

Make: Lith 147 (Varn).

Process blue (pigment) ink trial

pH before printing: 4.6
pH after printing: 4.5
Conductivity before printing: 1200
Conductivity after printing: 1300
Number of sheets printed: 700

Dye based ink trial

pH before printing: 5.1
pH after printing: 5.2
Conductivity before printing: 1300
Conductivity after printing: 1400
Number of sheets printed: 900

Bleaching

In a substance elements are bound together with electronic bonds and form molecules. Every element has affinity for another element (except inert gases), the degree of affinity varies depending upon the distribution of electrons in different energy orbits. Reduction of electrons from the surface of a molecule causing fundamental change in chemical properties is called Oxidizing. Reducing is a process of adding electrons to the surface of a molecule causing fundamental change in chemical properties. Most colors are consists of Hydro-Carbon molecules with different molecular structure. The coloring properties of the colors can be changed by oxidizing or reducing.

Previously Sodium hypochlorite, similar to common laundry bleach, was used to remove colors in secondary fiber. Chlorine bleach

generate a chlorinated organic commonly termed as dioxin. The toxic impacts of dioxin are questionable, therefore, the use of elemental chlorine and chlorine containing materials is waning in the U.S. paper industry (Bill Forester, May 1991). Hydrogen Peroxide is an environmentally safe material, but it is a weak oxidizing agent and lacks the oxidizing power of hypochlorite. Many colors and dyes, however, can be removed by reducing while they are in oxidized state. In this study the paper samples were oxidized with Hydrogen Peroxide. Samples were collected and were further reduced by Sodium Hydrosulfite. Hand-sheets were made from both samples for evaluation. The laboratory procedure for bleaching is listed below.

Laboratory Procedure

Step

1. Fill the Morden Slushmaker with 8 gallons of tap water (66.67#)
2. Heat water to 140 degree F.
3. Add 3% Sodium Silicate N (155 grams)
4. Adjust the pH to 10.5 with NaOH, record addition.
5. Add 2% Hydrogen Peroxide (104 grams, 30% concentration).
6. Add paper 4# paper, start slushmaker.
7. Stop slushmaker after 10 minutes, measure and record pH.
8. Re-adjust pH to 10.5, record addition of NaOH.
9. Re start slushmaker, run for an additional 20 minutes.
10. Stop slushmaker, let stand 30 minutes.
11. Collect 4 liters of stock from slushmaker, measure and record pH and temperature, label all samples (sample number H2O2).
12. Start slushmaker, adjust pH to 6.0 with Sulfuric Acid, record addition.

13. Add 2% Sodium Hydrosulfite (32 grams).
14. Run slushmaker for 2 minutes, stop slushmaker, let stand for one hour.
15. Collect 4 liters of stock, measure and record temperature and pH, label all collected samples (sample number, Hydro).
16. Discard remainder of stock.
17. Make hand sheets for evaluation, use recycled water to collect any filtering of pigments.

Bleaching

The data corresponding to laboratory procedures is listed below.

| <u>Process blue (pigment) ink trial</u> | |
|---|---|
| Step # | |
| 4. | Beginning |
| | Temperature: 140 degree F. |
| | Add NaOH: 12 grams. |
| | pH: 10.57 |
| 7. | After 10 minutes |
| | Temperature: 140 degree F. |
| | pH: 10.52 |
| 10. | 30 minutes after the slushmaker run |
| | Temperature: 135 degree F. |
| | pH: 10.42 |
| 12. | Sodium Hydrosulfite run |
| | Sulfuric Acid: 152 grams (66 degree Be) |
| | pH: 6.0 |
| 15. | After two hours wait |
| | Temperature: 117 degree F. |

| <u>Dye based ink trial</u> | |
|----------------------------|----------------------------|
| 4. | Beginning |
| | Temperature: 140 degree F. |
| | Add NaOH: 25 grams |
| | pH: 10.55 |
| 7. | After 10 minutes |
| | Temperature: 140 degree F. |

- pH: 10.08
Add NaOH: 10 grams
Corrected pH: 10.50
10. 30 minutes after the slushmaker run
Temperature: 130 degree F.
pH: 10.52
12. Sodium Hydrosulfite run
Sulfuric Acid: 140 grams (66 degree Be)
pH: 6.01
15. After 1.5 hours wait
Temperature: 120 degree F.
pH: 6.28

Observations

The printed samples were observed and density and dot gains were recorded. Density was recorded on the solid bar at the tail edge of the printed sheet. Densities were very low in the dye printed paper (Table 1 and 2). Dot gain/loss is the percentage change in the area of a printed dot from the original (negative or plate). The dot gain is different at different size dots. Therefore, dot gain was recorded at 25% and 50% dots for 133, 110, and 85 lines per square inch screens (Table 1 and 2). The paper printed with pigment ink had higher dot gain as compared to the paper printed with dye ink (Graph 1 and 2).

Brightness is the measure of reflectance of incident light from a surface. The brightness of the recycled papers was measured and recorded. The brightness of the recycled paper from the paper printed with dye ink was higher than the recycled paper from the paper printed with pigment ink (Table 3 and 4). It was also observed the brightness was higher and more consistent in the case of paper bleached with Sodium Hydrosulfite as compared to paper bleached with Hydrogen Peroxide (Graph 3 and 4).

Brightness is a representation of reflectance from the surface of paper which does not represent the coloring characteristics of the paper. Therefore, the recycled paper color was tested with a Gretag Spectrophotometer and L a b values were recorded (Table 5 and 6). Representation of L a b values as follows:

L Measure of lightness, higher the number lighter the coloring strength of the substrate (100 maximum).

+a represents redness in the substrate.

-a represent green color in the substrate.

+b represent yellow color in the substrate.

-b represent blue color in the substrate.

The recycled paper printed with dye ink and bleached with Sodium Hydrosulfite had highest lightness, about 0 a values and little -ve b values (Graph 5, 6, and 7). The paper printed with dye ink and bleached with Hydrogen Peroxide had little red color (Graph 6). The recycled paper printed with pigment ink had high blue and green color values.

Results

Printability of dye ink was as good as pigment ink. It had very good and smooth lay. Densities were very low in dye printed paper. Dot gains were less in dye ink as compared to pigment ink. No color bleeding in fountain solution, or scumming, was observed while printing with dye ink.

Paper printed with dye ink, and recycled, had higher brightness as opposed to recycled paper printed with pigment ink. Moreover, paper bleached with Sodium Hydrosulfite had higher brightness as compared to paper bleached with Hydrogen Peroxide.

Spectrophotometric measurement of recycled papers showed that paper printed with dye ink had higher Lightness values and neutral to other colors. While paper printed with pigment ink had Blue and Green color and lower Lightness values.

Limitations

The color strength of dye ink was very low, which makes the results questionable. It is recommended to revise the study to address the density of the prints, attempting to print the inks at equal densities rather than that at similar press conditions, as in this study. Also further study is necessary using Black, Red, and Yellow inks.

Table 1

PAPER PRINTED WITH DYES

| DOT GAIN AT SCREEN LINES SOLID DENSITY | 25% | | | 50% | | |
|--|----------|-------|-------|----------|-------|-------|
| | 133 | 110 | 85 | 133 | 110 | 85 |
| | DOT GAIN | | | DOT GAIN | | |
| 51.00 | 18.00 | 13.00 | 12.00 | 38.00 | 29.00 | 25.00 |
| 53.00 | 17.00 | 12.00 | 11.00 | 36.00 | 28.00 | 23.00 |
| 53.00 | 17.00 | 12.00 | 12.00 | 36.00 | 29.00 | 24.00 |
| 53.00 | 18.00 | 13.00 | 13.00 | 36.00 | 28.00 | 24.00 |
| 52.00 | 18.00 | 12.00 | 11.00 | 36.00 | 28.00 | 24.00 |
| 53.00 | 17.00 | 12.00 | 12.00 | 37.00 | 28.00 | 24.00 |
| 53.00 | 17.00 | 12.00 | 12.00 | 37.00 | 28.00 | 25.00 |
| 52.00 | 18.00 | 13.00 | 12.00 | 38.00 | 29.00 | 24.00 |
| 52.00 | 17.00 | 12.00 | 11.00 | 37.00 | 29.00 | 23.00 |
| 53.00 | 17.00 | 13.00 | 12.00 | 36.00 | 28.00 | 24.00 |
| 52.50 | 17.40 | 12.40 | 11.80 | 36.70 | 28.40 | 24.00 |

Table 2

PAPER PRINTED WITH PIGMENT

| DOT GAIN AT SCREEN LINES SOLID DENSITY | 25% | | | 50% | | |
|--|----------|-------|-------|----------|-------|-------|
| | 133 | 110 | 85 | 133 | 110 | 85 |
| | DOT GAIN | | | DOT GAIN | | |
| 118.00 | 13.00 | 11.00 | 19.00 | 39.00 | 34.00 | 31.00 |
| 116.00 | 27.00 | 20.00 | 21.00 | 40.00 | 34.00 | 30.00 |
| 118.00 | 27.00 | 21.00 | 20.00 | 38.00 | 33.00 | 30.00 |
| 115.00 | 28.00 | 21.00 | 21.00 | 39.00 | 34.00 | 30.00 |
| 117.00 | 27.00 | 21.00 | 21.00 | 38.00 | 33.00 | 30.00 |
| 118.00 | 27.00 | 20.00 | 20.00 | 38.00 | 34.00 | 30.00 |
| 115.00 | 27.00 | 20.00 | 20.00 | 38.00 | 34.00 | 29.00 |
| 115.00 | 27.00 | 20.00 | 20.00 | 37.00 | 34.00 | 29.00 |
| 115.00 | 18.00 | 17.00 | 17.00 | 38.00 | 34.00 | 30.00 |
| 114.00 | 26.00 | 20.00 | 20.00 | 38.00 | 33.00 | 29.00 |
| 116.10 | 24.70 | 19.10 | 19.90 | 38.30 | 33.70 | 29.80 |

Table 3

BRIGHTNESS (RECYCLED PAPER)

Paper Printed with Dye Ink

| No. | Hydrogen Peroxide Bleached | | | | Sodium Hydrosulfite Bleached | | | |
|-----|----------------------------|-------|-------|-------|------------------------------|-------|-------|-------|
| | A | B | C | AVE | A | B | C | AVE |
| 1 | 82.90 | 81.70 | 81.80 | 82.13 | 82.90 | 82.90 | 83.30 | 83.03 |
| 2 | 82.70 | 83.40 | 82.80 | 82.97 | 83.80 | 83.70 | 83.90 | 83.80 |
| 3 | 83.10 | 82.90 | 83.60 | 83.20 | 83.70 | 84.30 | 84.00 | 84.00 |
| 4 | 83.40 | 82.60 | 83.80 | 83.27 | 84.90 | 84.00 | 85.70 | 84.87 |
| 5 | 82.70 | 82.20 | 83.20 | 82.70 | 85.30 | 85.40 | 84.00 | 84.90 |

Table 4

BRIGHTNESS (RECYCLED PAPER)

Paper Printed with Pigment Ink

| No. | Hydrogen Peroxide Bleached | | | | Sodium Hydrosulfite Bleached | | | |
|-----|----------------------------|-------|-------|-------|------------------------------|-------|-------|-------|
| | A | B | C | AVE | A | B | C | AVE |
| 1 | 82.00 | 83.00 | 82.60 | 82.53 | 78.10 | 76.70 | 78.30 | 77.70 |
| 2 | 81.60 | 82.40 | 82.30 | 82.10 | 78.60 | 78.50 | 78.80 | 78.63 |
| 3 | 82.60 | 81.80 | 82.50 | 82.30 | 77.30 | 78.50 | 77.30 | 77.70 |
| 4 | 82.60 | 81.80 | 82.80 | 82.40 | 78.20 | 77.10 | 77.70 | 77.67 |
| 5 | 82.50 | 82.50 | 82.60 | 82.53 | 77.90 | 77.90 | 77.00 | 77.60 |

Table 5

SPECTROPHOTOMETRIC READINGS OF RECYCLED PAPERS

Paper Printed with Dye Ink

| No. | Hydrogen Peroxide Bleached | | | Sodium Hydrosulfite Bleached | | |
|-----|----------------------------|-------|--------|------------------------------|-------|-------|
| | L | a | b | L | a | b |
| 1 | 94.94 | 2.18 | -3.18 | 95.41 | -0.07 | -4.08 |
| 2 | 95.17 | 2.16 | -3.25 | 95.24 | 0.04 | -4.14 |
| 3 | 94.94 | 2.09 | -3.33 | 95.29 | 0.11 | -4 |
| 4 | 94.63 | 2 | -3.41 | 95.1 | 0.16 | -3.12 |
| 5 | 94.7 | 2.2 | -3.22 | 95.05 | -0.16 | -4.31 |
| Ave | 94.876 | 2.126 | -3.278 | 95.218 | 0.016 | -3.93 |

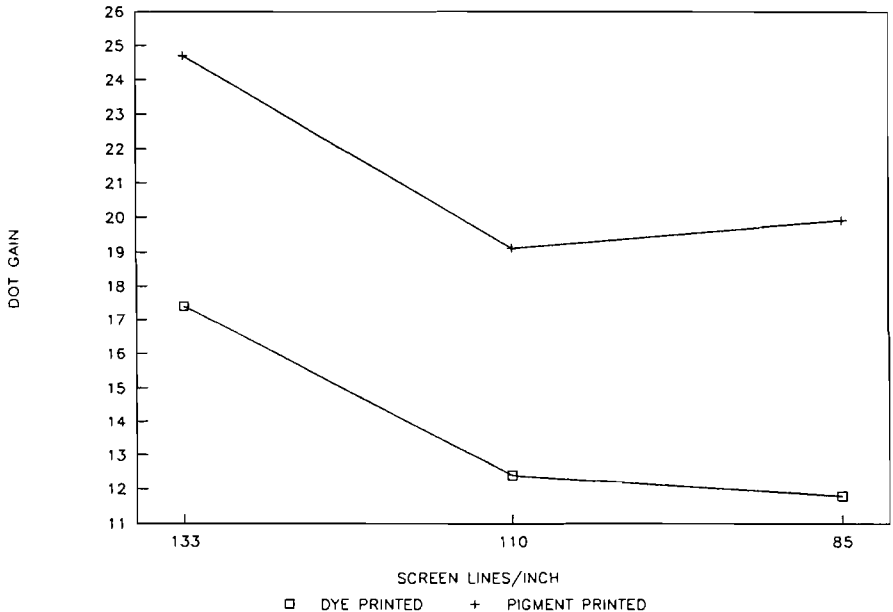
Table 6

Paper Printed with Pigment Ink

| No. | Hydrogen Peroxide Bleached | | | Sodium Hydrosulfite Bleached | | |
|-----|----------------------------|-------|--------|------------------------------|--------|---------|
| | L | a | b | L | a | b |
| | 90.96 | -2.63 | -9.56 | 87.94 | -3.84 | -9.97 |
| | 91.42 | -2.3 | -9.11 | 87.5 | -4.36 | -10.79 |
| | 90.87 | -2.5 | -9.48 | 88.26 | -3.79 | -10.16 |
| | 91.37 | -2.17 | -9.07 | 86.8 | -3.69 | -9.12 |
| | 90.75 | -2.6 | -9.47 | 88.14 | -3.78 | -10.03 |
| Ave | 91.074 | -2.44 | -9.338 | 87.728 | -3.892 | -10.014 |

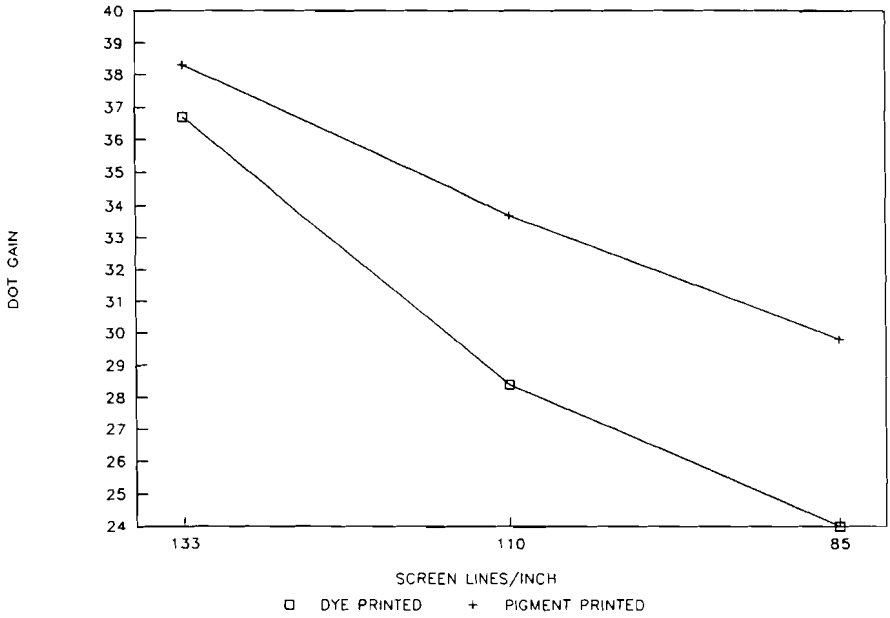
Graph 1

DOT GAIN AT 25% SCREEN



Graph 2

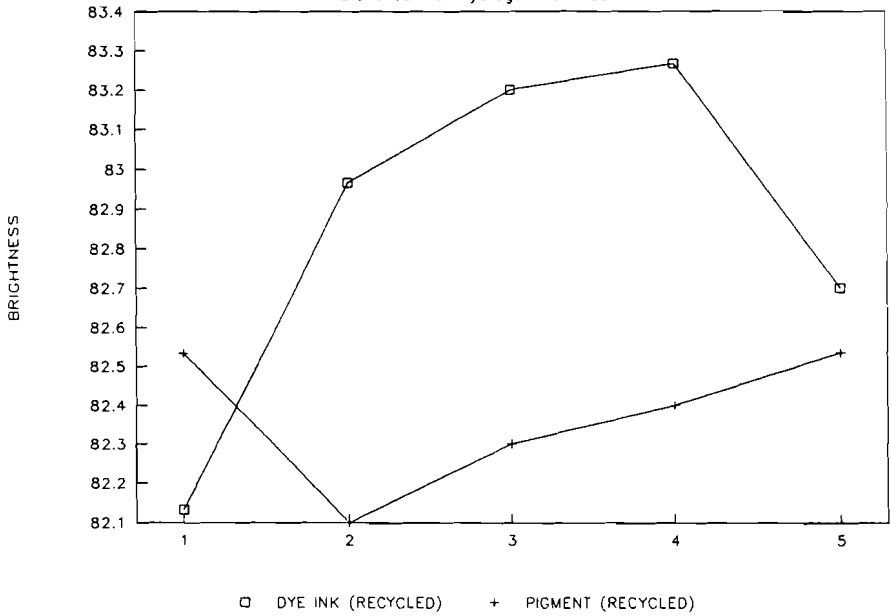
DOT GAIN AT 50% SCREEN



Graph 3

BRIGHTNESS OF RECYCLED PAPERS

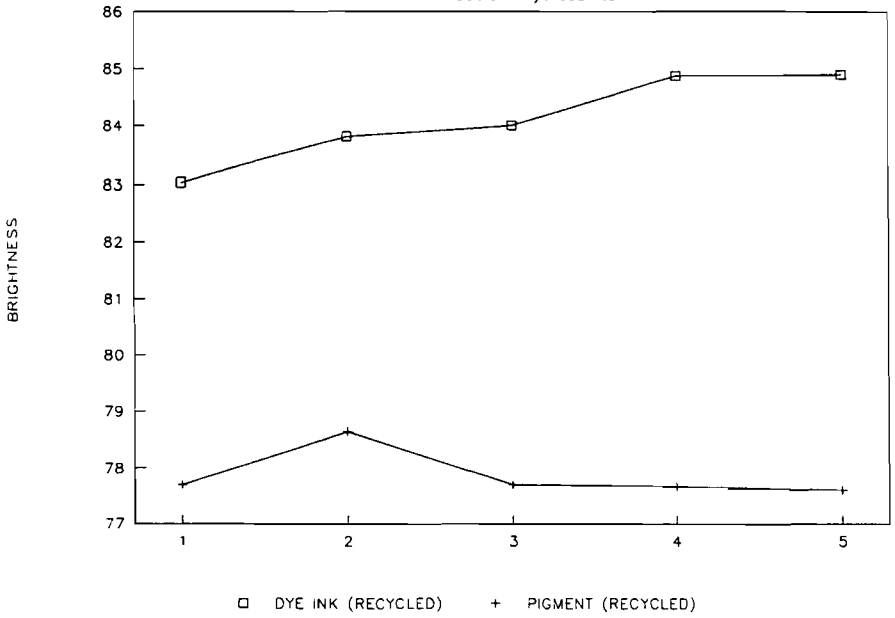
Bleached with Hydrogen Peroxide



Graph 4

BRIGHTNESS OF RECYCLED PAPERS

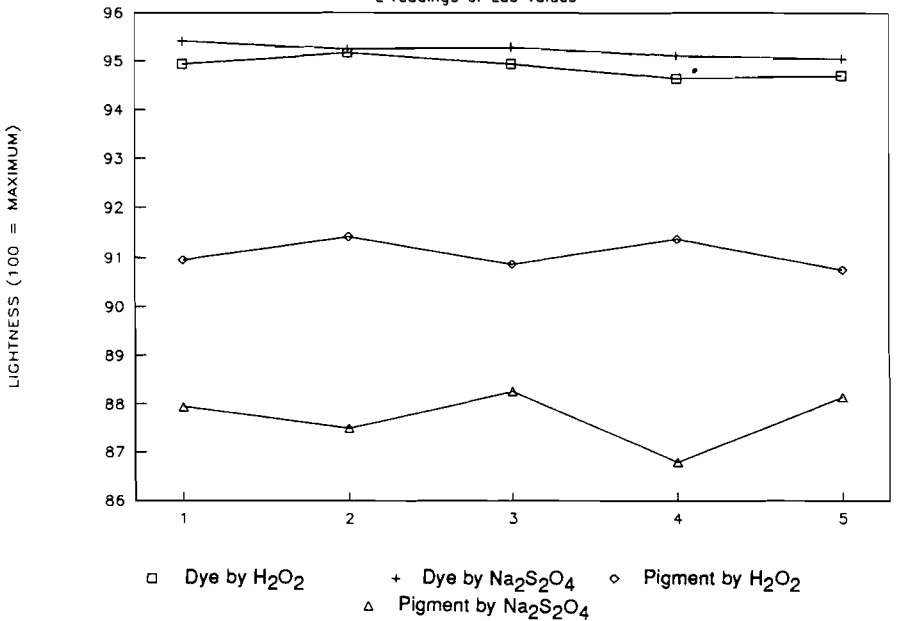
Bleached with Sodium Hydrosulfite



Graph 5

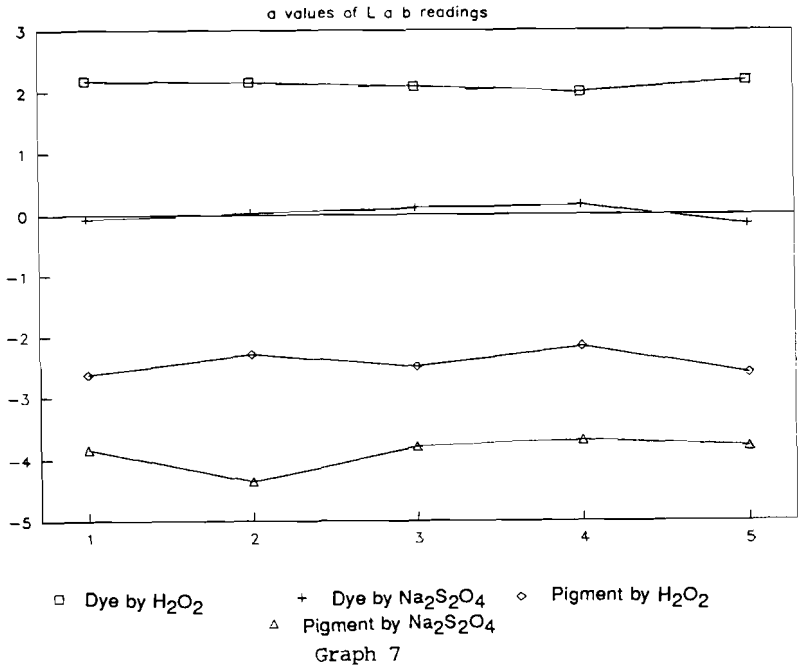
Lightness of Recycled Papers

L readings of Lab values

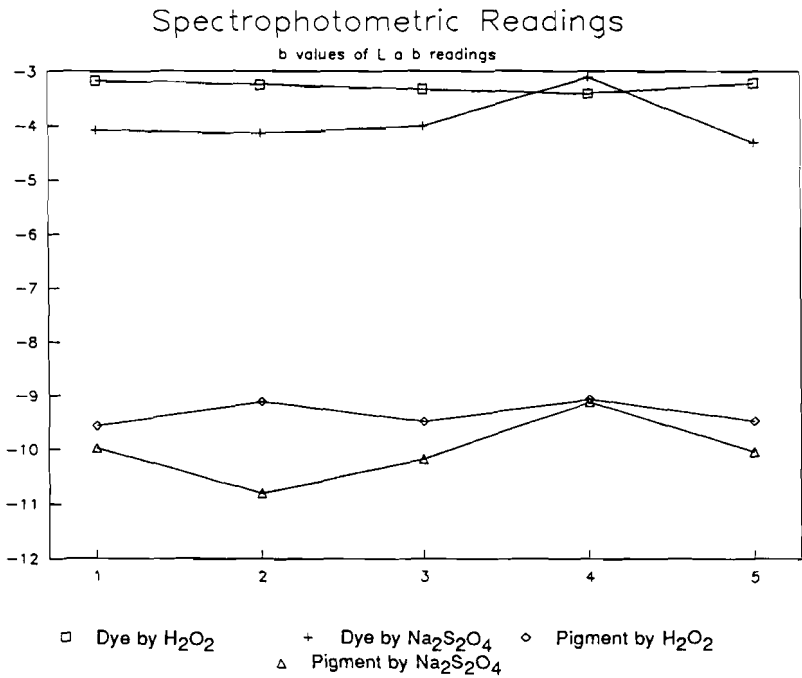


Graph 6

Spectrophotometric Readings



Graph 7



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