6-1980

The Effects of Fillers on the Deinkability of Printed Paper

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THE EFFECTS OF FILLERS ON THE DEINKABILITY OF PRINTED PAPER

by

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A Thesis submitted
in partial fulfillment of
the course requirements for
The Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
June 18, 1980

This report covers the effect of fillers on the deinkability of a printed sheet of paper. Paper was produced with varying amounts of titanium dioxide and clay retained as fillers. This paper was then cut into 8½ X 11 inch sheets. The top half of each sheet was printed and cut away from the bottom unprinted half. Both of these portions were repulped by identical methods and brightness measurements were made from this recycled pulp. Differences in these brightnesses were ploted against percent ash in the sheet. It was found that at low levels of addition the filler increases the deinkability and at higher levels it decreases the deinkability of the paper. It was also found that there were only small differences between the effects of titanium dioxide and clay.

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INTRODUCTION

There are many factors that affect the deinkability of a printed sheet of paper. Sheet composition will affect the deinkability and factors such as whether the sheet is coated or uncoated. One question which has not been answered is the effects that filler have on printed paper. This study will deal with clay and titanium dioxide as fillers and the effects they have on deinking the printed paper.

There are three areas which must be investigated in order to examine the effects of filler on deinking. First, the furnish used to produce the paper. Secondly, the printing process and ink used to print the paper. Finally, the process used to repulp and deink the printed paper. It must be kept in mind that there are limitless combinations of furnish types, printing inks, and methods of repulping and deinking. This study will be directed toward only one of these combinations.

Paper Furnish

As stated in the introduction this study will concentrate on the furnish components which were used to produce the paper for this study.

Clay and titanium dioxide are normally used as fillers in the production of printing grade papers. Clay is used for increasing opacity and printing smoothness of the paper.(3) Kaolin clay is is also used as filler because it is inexpensive, soft, and non--abrasive.(3) Kaolins which are used as fillers vary in brightness from 75 to 85 with the GE brightnessmeter.(15) Brightness of kaolin is determined by the amount of iron and trace TiO_2 present in the clay deposite.(15) In nature kaolin clay exists as stacks of plate-like structures.(3) What application clay is used for will depend on how well these stacks are broken down into individual plates. The breaking down of these stacks is called delamination.(15) Coating clays are well delaminated and have a uniform particle size. Filler clays have more stacks with less uniform particle size and they are coarser. Particle sizes for kaolin clay range from 1 to 5 microns.(3)

Titanium dioxide is generally used because it increases brightness and opacity and is very affective in only small additions.(14) There are two types of titanium dioxide which are anatase and rutile.(4) The major differences are within the refractive indexes. Anatase has the lower refractive index and is the major one used as filler.(4) Titanium Dioxide has a crystalline structure which gives it superior light scattering ability. Also it has a very high refractive index and uniform particle size of .25 microns.(4) Titanium dioxide is very high in cost and is only used when it cannot be replaced by other types of filler. Many papers such as high grade bond have as much as 15% titanium dioxide retained in them.(4)

Kaolin clay and titanium dioxide are both inert to the deinking process and cause no adverse affects to this process. Little work and experimentation has been done with paper that has these fillers retained in them. Experiments have been done by adding filler to waste paper when it was being repulped and it has been found to be effective in aiding ink removal and controlling hot melt re-agglomeration.(7) Bentonite, talc, and coating clay have been used in this manner and they were found to be effective in hot melt and sticky control.(7) A Bulgarian study showed that bentonite was impartical as filler because of its coarseness and high abrasiveness.(9) This caused increased equipment wear and was detrimental to the smoothness and other physical strength properties of the sheet.(9)

Internal and external size are non-fibrous materials found in printing paper and both become shrinkage components in the deinking process.(1) Internal size is used to make paper resistant to wetting and penetration.(6) A good internal size will make the surface of the fiber hydrophobic, causing the contact angle of a liquid usually water or aqueous solution to be high.(6) Internal size is done to keep printing inks from wicking during printing. This type of size is used in other areas where some resistance to water penetration is necessary. Rosin size is one of the most common internal sizes used in the paper industry. It is cost effective and is reliable.

The major problem with rosin size is that it only works in a acid system at a pH of about 4.5.(6) This has been found to be one of the problems involved in the ageing of paper. Many mills producing book and document paper are now using alkaline size because of the acidic condition with rosin size.

External sizing or surface sizing is done to improve the surface of the sheet. External size controls receptivity, erasure, porosity, and it imparts some stiffness to the sheet.(5) Starch size is the most common and economical surface sizing used; it is used at the size press to give the sheet a smooth printable surface.(5) Both rosin size and starch cause no adverse effects in the deinking process, although rosin size may be benifical because it forms a rosin soap.(1)

PRINTING INKS AND THE OFFSET LITHOGRAPHY PROCESS

There is a very large and diverse range of inks available. It must be stressed that this alone will affect the end result of a study of this type. This paper will give a general overview of inks and their components.

Printing inks are made up of several components, the major ones being pigments and dyes in combination with vehicles and binders.(13)(12) Other added ingredients are solvents, driers, wetting agents, and waxes which give the desired end characteristics.(12)(13) These characteristics must fit the type of printing process and substrate on which the ink will be used.(13)(10) Important properties that are considered when producing ink are press stability, flow properties, drying time on paper, printability, ink film thickness, material to be printed, and printing equipment.(12) Pigments and dyes can cause trouble in the deinking process and it is important to know the composition of these pigments and dyes. A common pigment found in black ink is carbon black which is obtained by burning oil or natural gas in a limited oxygen supply.(13) Carbon blacks have a very small particle size ranging from 10nm too 200nm.(12) Experimentation indicates that the ease of carbon removal increases in the deinking process as the particle size increases.(11) Pigments wash out quite well in the deinking process.(1) Toner dyes are also present in most black inks, and they do not wash out like pigments and add to color in the reclaimed fiber.(1) Toner dyes are used in black inks to give them a rich dense look when printed on white paper. These dyes are generally blue in color and some common ones are bronze blue, reflex blue, and fanal violet.(13) Bronze blue is the most common and it is used because it is cost effective.(13) Vehicles make up the rest of the ink and consists of oils, resins, solvents, plasticisers, and dryers which will not be covered in detail.(12)

The basic methods of drying ink is by absorption, oxidation, polymerisation, evaporation, and precipitation.(12) The offset lithography process uses inks which dry mainly by oxidation, polymerisation, and absorption.(12) This study will be concerned with the offset lithography process and the demands that this process places on the paper.

The planographic method is used in the offset lithography process.(2) The printing plate is made by photographic methods. It is made of a thin metallic sheet with a light sensitive coating applied to the surface. (Refer to appendix B for an example of a printing plate.) Through a series of photographic procedures an image is produced on the plate. The plate is designed so that the image areas on the plate will accept ink and the non-image areas will except a thin film of water.(2) This plate is mounted on the press and it is attached to a metal cylinder which rotates. This causes the photographic plate to come in contact with the water solution and wet the non-image areas of the plate. This water film prevents ink from being applied to the non-image areas. Then the cylinder continues to rotate and a ink film is applied to the image areas.(2) This ink film is transfered to a rubber covered cylinder (called a blanket).(2) As paper is feed through the printing press it is compressed between the rubber blanket and an impression cylinder.(2) This causes an image to be transferred to the paper.(2)

The offset lithography process demands a sheet which has high pick resistance because of the tacky inks used with this process. When the sheet is printed it will make complete contact with the printing blanket then it will be quickly pulled away this demands high surface strength. Papers should also be able to withstand some wetting from the water solution used in this process. Good stiffness is benifical in aiding the release of the sheet from the blanket. In general a more durable sheet of paper is needed for the offset process as opposed to any other printing process.(3)

The preceding information was given as an indication of the type of paper that was produced for this study. Also at this point it can be seen that there is an infinite number of ways that a sheet can be produced and printed.

REPULPING AND DEINKING

The following is as account of the basic areas of interest when repulping low groundwood waste paper. It is being reviewed as a reminder of some of the procedures that must be followed when repulping low groundwood waste paper.

The process of recycling waste paper consists of defibering and dispersing ink with proper chemicals, temperature, consistancy, and agitation.(1) The pulp slurry is then deinked and cleaned by one of several methods, but the major ones are flotation and side-hill washing.

Choice of chemicals and cooking conditions are determined by the type of waste paper being repulped. Waste paper low in lignin is cooked at higher temperatures and with harsher alkalies then papers high in lignin.(1) The amount of lignin in the waste paper is determined by the amount of groundwood present in the waste paper.(1) The bleaching method is also determined by the amount of groundwood present in the waste paper. For waste papers with less then 50% groundwood deinking is generally done with caustic soda. This is done at 5-8% consistancy and at temperatures between 180 and 210^{o}F.(1) Most cooking of waste paper is done at a consistancy of 5-7% and the normal cooking time is about 45 minutes.(1) The most widely used chemicals for deinking are caustic soda and soda ash. Caustic soda is the most widely used.(1) Chemical use is based on percent weight of waste paper and chemical additions range from 2 to 10%.(1) As the consistency of repulping goes up the amount of chemical addition will go down to give the same effective deinking.(1) So when deinking at high consistencys less chemical is necessary.(1)

Agitation is very important in deinking because it helps cooking liquor to penetrate into the paper and helps maintain chemical contact at all times. This also helps distribute the heat evenly which results in a uniform cook and reduced cooking time.(1)

Consistency has an important effect on the end result and proper consistency will give savings in heat and chemicals. Proper consistency will improve ink removal and pulp quality. With increased consistency defibering is much more effective because of increased shear develope from colliding action. Consistency of repulped waste paper is based on the fiber only, and not on fillers and other non-fibrous materials. These materials have little affect on the behavior of the repulped slurry. They take in little or no water and contribute little to the reology of the slurry.(1)

Sidehill and flotation deinking are two methods of removing ink carbon particles from the pulp slurry. Both processes make use of the same pre-deinking stages of pulping waste paper. The method picked for removing ink is dependent on the end product that is being obtained. Washing removes a large amount of fillers and flotation retains all materials but the ink.(8)

The sidehill washing process uses an inclined screen, showers wash the pulp as the pulp rolls down the sidehill screen. In this fashion the pulp is physically washed with large amounts of water.

Also the fillers that are removed from this pulp reduces yield, and the amount of reduction is related to the amount of filler originally in the paper.(8) Paper washed by this process is superior in strength compared to floatation deinking because of the removal of these fillers.(8)

It is the nature of this thesis to see if the removal of fillers help the deinking process. It will be based on the removal of these fillers so the sidehill washing process will be used.

Experimental Design

This project is designed to find the effects of fillers on the ability to remove ink from a sheet that has been printed by the offset lithography process. Deinkability will be based on the amount of carbon left in the sheet after deinking as determined by brightness. This project will be broken down into four areas listed below.

1. Production of a printable sheet with increasing levels of Klondyke clay and titanium dioxide retained as filler in the sheet.
2. Printing of the sheet by the offset lithography process using black inks without toner dyes.
3. Repulping and deinking of these printed sheets.
4. Tabulating the brightness test data.

1. A printable 50 pound sheet (24X36-500 ream size) was produced on the Western Michigan University pilot plant Fourdrinier paper machine. This paper machine trims out at about 24 inches and has a production rate of 120 pounds per hour.

Weyerhaeuser bleached kraft hardwood and Rayonier bleached kraft softwood were used in a 50/50 blend. This pulp was defibered in a hollander type beater and then Clafined to 375 CSF. All of the paper production was done with softened water which was adjusted to a standard hardness of 100ppm with $CaCl_2$. $CaCl_2$ was added at the beater after refining was completed. Softwater was used because Kalamazoo city water had a high degree of varying hardness. A look at appendix D will show this in more detail. Paper production was done in a rosin size acid system at a pH of 4.5. The rosin size used was Hercules Pexol. Rosin size was metered in at the wet end of the paper machine at 1.5% based on bone dry production rate. A 6% starch solution was applied at the size press with 30 pounds of nip pressure. Then the sheet was given three nips at the calendar stack with 30 pounds of nip pressure.

Titanium dioxide and Klondyke clay were used as fillers. Titanium dioxide was used alone and in combination with Klondyke clay. The combinations and amounts of filler attemped to be retained at the wire are listed in the table below. The combinations of clay and titanium dioxide were premixed at 25% solids and metered in

TiO_2/Clay	100/00	75/25	50/50	25/75
Attempted	10%	10%	10%	10%
Attempted	15%	15%	15%	15%
Attempted	20%	20%	20%	20%
Attempted	25%	25%	25%	25%
Attempted	30%	30%	30%	30%

according to appendix A at the wetend of the papermachine. Reten 210 (Hercules Retention Aid) was used and metered in at .05% based on bone dry production rate. All materials used are listed in appendix A.

Ash tests were done on the sanples according to Tappi Standard T413 ts-66 and duplicated until specified precision had been obtained. This data was then corrected to obtain estimated percent filler. Titanium dioxide was assumed to have 100% ash and data that was obtained from Hercules Corporation showed that Klondyke clay ashed at 86.2%. The percent ash was converted to percent filler by assuming equal retention for clay and titanium dioxide at the wire. Then making the ash correction for clay percent filler was obtained by the equation below.

$$\frac{(\%ASH)}{.862} \times \frac{(\%CLAY \text{ in filler})}{100}\ \frac{TiO_2}{Clay} + (\%ASH) \times \frac{(\%TiO_2 \text{ in filler})}{100}\ \frac{TiO_2}{Clay}$$

The table below is a comparison of filler level attempted and estimated percent filler calculated.

TiO_2/Clay Attempted	Calculated 100/00	Calculated 75/25	Calculated 50/50	Calculated 25/75
10%	11.25%	8.13%	10.38%	10.97%
15%	16.63%	17.09%	16.38%	16.40%
20%	20.93%	21,42%	20.16%	21.55%
25%	25.00%	24.47%	23.87%	26.81%
30%	30.87%	27.63%	27.84%	29.63%

2. Samples were cut into 8½ X 11 inch sheets at the Western Michigan University printing department and then printed with a non-toner dye ink. The ink used was aquamatic rubber base ink (Vanson Pantone Black V5510) that is used in three color processing. This ink is sometimes called a neutral black because of the absence of toner dyes. Inmount Corporation which is an ink manufactureing firm has verified the absence of toner dyes in this ink. It was necessary to eliminate toner dyes from this study because of the changing absorbtivity of the sheet with changing filler retainment. This changing absorbtivity would cause the amount of dye in each sample to be different which would give more variability to the brightness data. So all brightness variability will be based on the carbon left in the sheet.

The printing plate was designed to give visual indication of ink coverage applied to each sheet. Appendix B has a portion of that plate and it can be seen that there are five solid areas on it. These solid areas gave a visual indication of ink coverage on the final printed sheet. A small offset lithography press was used to print the sheets on the felt side. Printing was done only on the top half of the sheet. This was done so that the top half of the sheet could be run as the test sample and the bottom half of the sheet could be run as the control sample. Appendix C has examples of all the sheets that were printed.

3. Printed samples were picked for repulping by visual inspection

for equal ink coverage. The reader is again referred to appendix C for inspection of ink coverage. In the repulping and deinking process, two portions of the same sample were put through the same procedure. For example, a sample which contained 10% filler and a 50/50 ratio of titanium dioxide and clay would be run through the deinking and repulping process, once for the test sample (printed portion) and once for the control sample (unprinted portion). Brightness measurements were then taken from the test and control samples. Differences in these brightnesses were used as an indication of the amount of ink left in the fiber.

Repulping was done in two one gallon Waring blenders. Five percent caustic soda was used to disperse the ink. This addition was based on the weight of air dry sample. The following is a step by step procedure that was used to repulp and deink the samples.

1. Add 1500cc 170 ^{o}F tap water too blender.
2. Add 3 grams 50% caustic soda too blender.
3. Add 30 grams of air dry sample too blender.
4. Agitate blender on low speed for 10 seconds.
5. Retain in blender with no agitation for 18 minutes.
6. Agitate blender for 2 minutes on low speed.
7. Retain in blender with no agitation for 18 minutes.
8. Agitate blender on low speed for two minutes.
9. Sidehill wash with five passes of 160 ^{o}F tap water.
10. Filter washed fiber with Buchner funnel.
11. Press pads with a chrom roll.
12. Dry pads in a constant draft oven at 140 ^{o}F.

The repulping of test and control samples were timed 20 minutes apart. This allowed for washing time as the samples were removed from the two one gallon Waring blenders. Each pass on the sidehill washer was done by adding a repulped 30 gram sample to the top pan of the sidehill washer. This pan was filled with 160^{o}F tap water and dumped down the sidehill screen. (sidehill washer specifications are contained in appendix A) Fiber tumbled down into the bottom pan and wash water drained through the screen. Any fiber that was retained on the screen after each washing was hosed down into the bottom pan and the procedure was repeated four more times. After washing was completed, recovered fiber was de-watered with a Buchner funnel. This formed a pad which was then pressed with a chrom-roll that is normally used to press British Sheet Mold handsheets. Pressing of the pad was done to give more uniform brightness data. The pad was then place in a constant draft oven at 140^{o}F over night. After the pad had dryed ten brightness measurements were made with the Elrepho brightnessmeter on the top side of the pad. The top side of the pad is the side an observer would be looking at when the pad was formed in the Buchner funnel. These brightness measurements were then averaged and recorded along with the standard deviation. Both the test and control sample was done in this manner. For each sample the brightness of the test sample was subtracted from the brightness of the control sample. This difference was used as an indication of the amount of deinking that was taking place in the repulping and washing process. This difference of brightness was used to show the effects of fillers on deinking.

After all of the samples had been repulped and deinked several pairs of pads were selected to determine how comparable the yields were between these pads. This data would show how repeatable the washing was on the sidehill washer. Below is a table of the data obtained from those pad pairs that were weighed. It can be seen

Pad 1	17.0	17.2	18.3	21.1	18.7	21.0	20.9	17.8	17.8
Pad 2	17.1	17.0	18.9	22.0	17.9	21.9	20.1	17.8	17.2
Difference	-.1	.2	-.6	-.9	.8	-.8	.8	0	.6

from this random sample that the repeatability of the sidehill washer is within + or - one gram. This repeatability was exceptionally good.

4. All brightness data is tabulated in the following tables. It should be noted that brightness of the base stock was measured and recorded before the samples were repulped. The tables below also contain percent ash and calculated percent filler as outlined in section one of the experimental procedure. Standard deviations are recorded in the tables for the ten brightness measurements made on each pad. And most important of all the differences in brightness for the control and test sample are recorded.

100% TiO_2

%Ash	11.25	16.63	20.93	25.00	30.87
* %Filler	11.25	16.63	20.93	25.00	30.87
Base Stock					
Brightness	94.6	95.5	96.0	96.6	96.6
Unprinted					
Control					
Brightness	82.85	79.40	85.73	84.29	83.90
Printed					
Test					
Brightness	82.44	78.33	84.52	83.17	81.80
Differerence	.09	1.07	1.21	1.12	1.37
** SDEV					
Control	.38	.52	.19	.42	.37
** SDEV					
Test	.32	.35	.38	.26	.26

75% TiO_2 25% Clay

%Ash	7.82	16.43	20.62	23.53	26.57
* %Filler	8.13	17.09	21.42	24.47	27.63
Base Stock					
Brightness	90.9	91.7	92.6	92.9	92.9
Unprinted					
Control					
Brightness	80.91	80.57	82.52	82.92	85.01
Printed					
Test					
Brightness	80.21	80.35	81.38	81.57	83.00
Difference	.70	.22	1.14	1.35	2.01
** SDEV					
Control	.25	.29	.25	.40	.15
** SDEV					
Test	.35	.22	.27	.52	.44

50% TiO_2 50% Clay

%Ash	9.61	15.17	18.67	22.10	25.78
* %Filler	10.38	16.38	20.16	23.87	27.84
Base Stock Brightness	89.3	89.3	89.4	89.5	89.8
Unprinted Control Brightness	79.79	81.83	82.98	82.65	84.06
Printed Test Brightness	79.53	81.69	82.35	80.78	82.48
Difference	.26	.14	.63	1.87	1.58
** SDEV Control	.60	.28	.50	.35	.27
** SDEV Test	.22	.20	.50	.06	.72

25% TiO_2 75% Clay

%Ash	9.79	14.64	19.24	23.93	26.45
* %Filler	10.97	16.40	21.55	26.81	29.63
Base Stock Brightness	89.3	89.3	89.3	89.3	89.3
Unprinted Control Brightness	82.85	80.91	81.11	81.10	80.32
Printed Test Brightness	82.38	80.62	79.31	79.66	79.32
Difference	.47	.29	1.80	1.44	1.00
** SDEV Control	.38	.65	.36	.29	.60
** SDEV Test	.15	.26	1.42	.69	.22

Unfilled Sample

%Ash	.42
*%filler	.00
Base Stock Brightness	89.6
Unprinted Control Brightness	79.8
Printed Test Brightness	78.77
** SDEV Control	.18
** SDEV Test	.27

* As calculated in procedure
** Standard Deviation

Figure 1

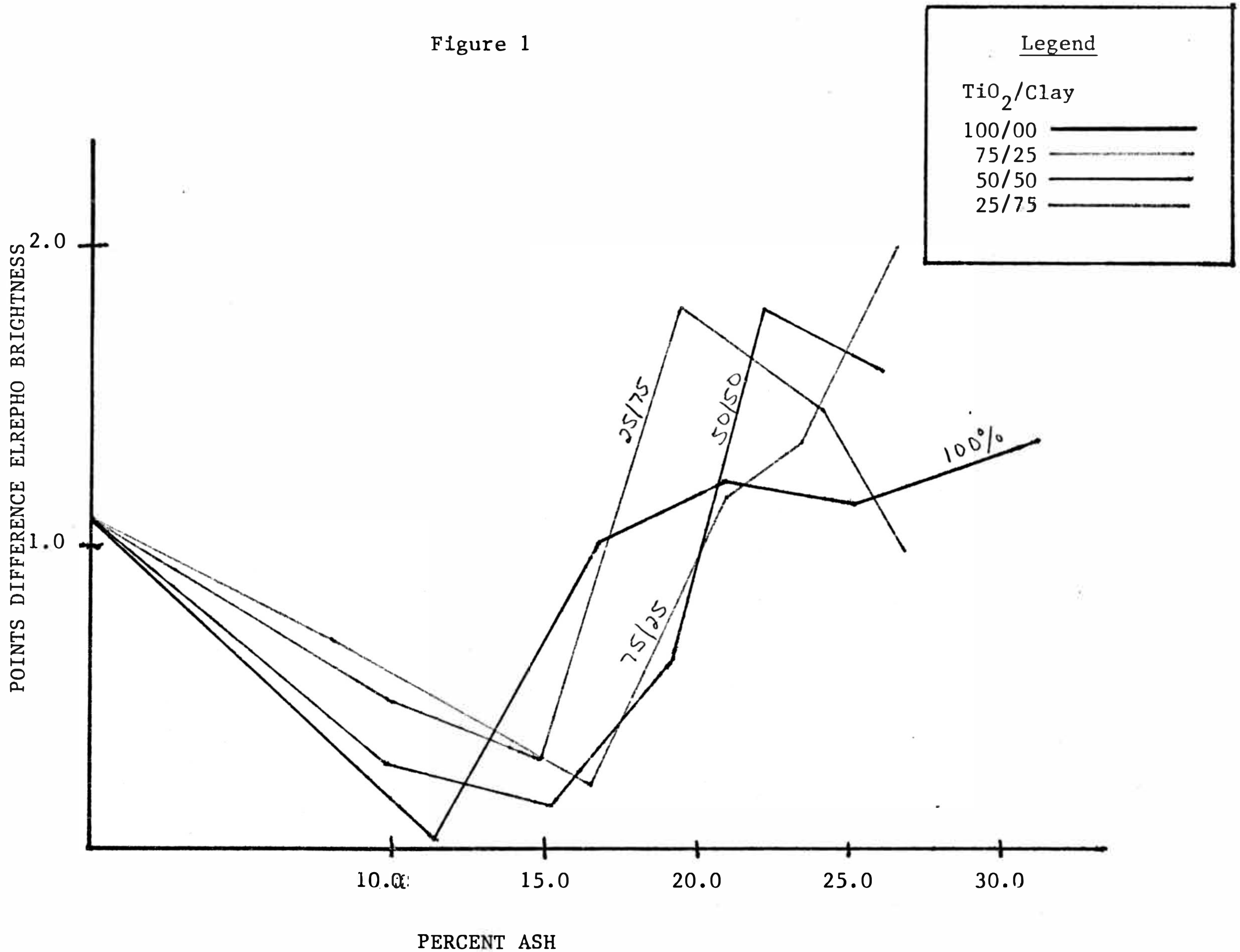
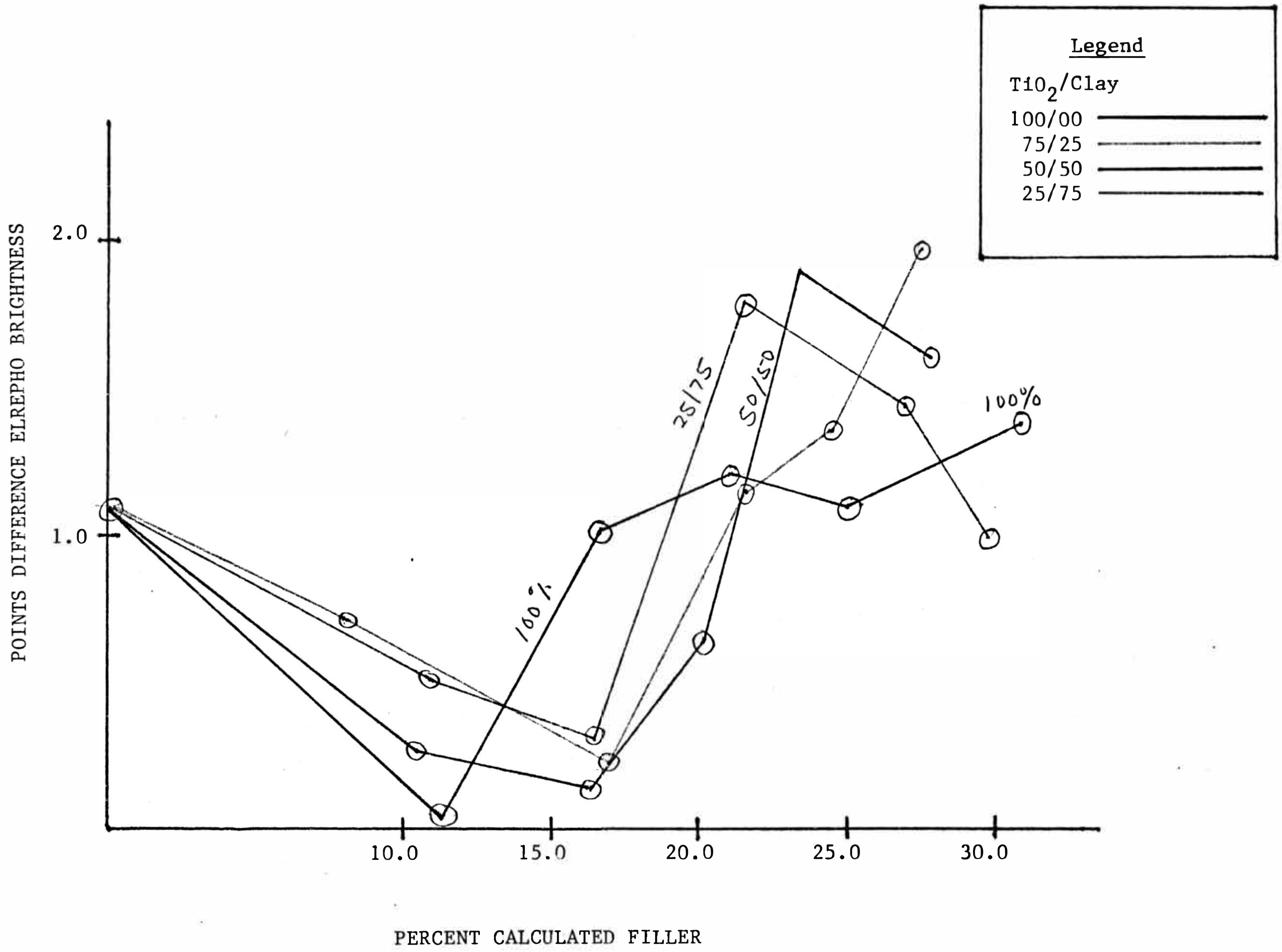

Legend
TiO2/Clay
100/00
75/25
50/50
25/75
POINTS DIFFERENCE ELREPHO BRIGHTNESS
2.0
1.0
25/75
50/50
100%
75/25
10.0
15.0
20.0
25.0
30.0
PERCENT ASH

Figure 2


Legend
TiO2/Clay
100/00
75/25
50/50
25/75
2.0
1.0
POINTS DIFFERENCE ELREPHO BRIGHTNESS
100%
25/75
50/50
100%
10.0
15.0
20.0
25.0
30.0
PERCENT CALCULATED FILLER

RESULTS AND CONCLUSIONS

Figure 1 shows a graph of percent ash verses points of differential brightness. It can be seen that all families of curves had the same trend, also it is hard to see differences between clay and titanium dioxide. With additions of filler up to 15% the points of differential brightness became smaller and smaller. This indicated that as the filler level approached 15% the deinkability of the paper was increasing. For values of ash or filler greater then 15% points of differential brightness started to increase. This indicated that the deinkability was decreasing with filler level above 15% for all families. A look at the tabulated data tables show that the base stock brightness stayed fairly constant with increased filler addition. Although there was a small upward trend for titanium dioxide. It can again be seen in the tabulated data tables that the standard deviation of the ten brightness measurements were in most cases less then .5 brightness points. This indicated that the pads were fairly uniform on the surface giving good constant brightness measurements. Figure 2 is a graph of percent calculated filler verses points of differential brightness. This graph is very simular to graph 1. A close look will show that the points tend to be closer together for each filler addition level.

There are two faulty areas in this data that should be discussed. First, all indication of deinkability is based on only two points of differential brightness. This is a very narrow range to base deinkability, because two points of brightness are just about within instrumental error. But the fact still remains that the families of curves all follow the same trend in figures 1 and 2. Secondly, only one run was made with the unfilled stock. This puts a lot of weight on the data point at 0% ash and there could be a lot of unaccounted variation in this point.

Assumming this narrow range on which the experimental data is based is accurate and assuming the 0% filler data point is accurate. Then a conclusion can be made that fillers do increase the deinkability of the paper at low levels of addition and at high levels, the deinkability is decreased.

It appeared when the pads were made from the deinked fiber that the ink was attached to the filler particles. If this is the case it would be supported by the data obtained. At low levels of filler addition with constant washing, there is less filler to be removed. If the ink is part of this filler it has a greater chance of being removed at low filler levels then at high filler levels with constant washing. This would give the kind of curves found in figures 1 and 2.

RECOMENDATIONS

If this type of experiment is ever repeated it is recommended that a more heavily printed sheet be used, and that it be printed on both sides. This would widen the span of points used for differential brightness.

It would also be interesting to see what effect fillers have on toner dyes when paper is being repulped and deinked. Then it may be possible to compare both the effect of filler on carbon and toner dyes together.

APPENDIX A

EQUIPMENT AND MATERIALS

Paper Production

1100 lb Weyerhaeuser Bleached Hardwood Kraft
1100 lb Rayonier Bleached Softwood Kraft
16 lb $CaCl_2$
2.5 liters conc. H_2SO_4
5 water softners
5 50 pound bags Klondyke clay
5 50 pound bags Tri-Pure TiO_2
1.5 lb Hercules Reten 210 (Hercules Retention Aid)
55 lb alum
33 lb Hercules Pexol Rosin Size
100 lb Penford Gum 280 (starch)

Printing Materials

Vanson Pantone Black V5510 (neutral black non-toner dye ink)
samples from above trial
cutter
offset lithography press

Repulping and Deinking

2 Waring blenders
1 Buchner funnel
caustic soda 50% solution
1 thermometer
1 laboratory sidehill washer
1 constant draft oven
1 box filter paper to fit buchner funnel

STOCK PREPARATION AND FLOWRATES TO PAPER MACHINE

Stock Preparation

50% Hardwood 110 lb dry base
50% Softwood 110 lb dry base
100cc H_2SO_4
Clafin to 375 CSF
150cc H_2SO_4
720 grams $CaCl_2$
dilute to 2% with soft water (Culligan water softners Na^+ exchange)
Ajusted to 150ppm
100ppm

APPENDIX A

Filler flowrates to Paper Machine

	100% TiO_2	75% TiO_2 25% Clay	50% TiO_2 50% Clay	25% TiO_2 75% Clay
10%	484	484	484	484
15%	726	726	726	726
20%	968	968	968	968
25%	1210	1210	1210	1210
30%	1453	1453	1453	1453

(Note: table contains flow rates in ml/min metered @ 25% solids)

Other Flowrates to Wetend of Paper Machine

Pexol Rosin Size (6% solids) @ 300ml/min 1.5% based on bone dry fiber

Alum (12% solids) metered @ 250ml/min 2.5% based on bone dry fiber

Reten 210 (.5% solids) metered @ 120ml/min .05% based on dry fiber

Starch Penford Gum 280 (6% solids) @ size press

Laboratory Sidehill Washer

50-42 screen mesh
pans have 8 liter capacity
screen angle 49^{o}

APPENDIX B

Printing plate is in original

[illegible]queous-pigmented coatings are used to prepare paper primaril[illegible] [illegible]sthetic purposes; to be whiter, glossier, more opaque and, e[illegible]pecially, to print with more fidelity and usual impact.

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APPENDIX C

The following are examples of the samples that were run for this experiment. Note comparison of ink coverage between sheets in each set.

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100% TiO2
10% Add

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100% TiO_2

13% Add

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100% TiO_2

20% Add

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100% TiO_2

25%

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100% TiO_2
38%. Add

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75% TiO_2

25% Clay

10% Add

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75% TiO_2

25% Clay

15% Add

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75% TiO_2
25% Clay
26% Add

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75% TiO_2
25% Clay
25% Add

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75% TiO_2
25% Clay
30% Add

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50/50
10% Add

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50/50
15% Add

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50/50
20% Add

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50/50
25% Add

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50/50

30% Add

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25% TiO_2

75% Clay

10% Add

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25% TiO_2
75% Clay
15% Add

[redacted]queous-pigmented coatings are used to prepare paper primaril[redacted] [redacted]sthetic purposes; to be whiter, glossier, more opaque and, e[redacted] pecially, to print with more fidelity and usual impact.

Coated papers which are prepared without mechanical (groundwood pulps are refereded to as "merchant" grades. They are clossed into grades depending on their brightness and gloss levels. The glossiest grades are the "enamals", semiglossy grades are called "velvets", while the dull and matle grades are of very low gloss levels. Merchant grades of increasing basis weight are termed text, label, and cover papers. Label papers are generally termed C-1S (coated one-side), whereas most other paper grades are C-2S. Sheet-Fed offset printing paper are in the higher quality ranges of [redacted] grades while web-offset printing papers would tend toward the [redacted]ality range of brightness and lower gloss.

So-called publication pa[redacted]es include a wide range of lighter--weight papers containing vary[redacted]nts of mechanical (groundwood) pulps. These papers are used in magazine, mail-order catalogs, newpaper supplements, and for brochures of all but the highest qualities. Many of the high-formage-web-offset printing paper contain mechanical pulp fibers and, in this way compete market-wise with the lower quality enamel grades.

Paperboards are classed into fourdrinier board and multi-cylinder board. The former typically is comparied of solid bleached kraft fiber, while the latter is generally prepared from secondary fibers with only the top one or two layers (levels) being comprised bleached fibers. (although, in some grades the back side may be made of one or two layers of bleached or semi-bleached fiber, also). Typically, paperboards are [redacted]d on one side only for use in making folding cartons and other [redacted]

25% TiO_2
75% Clay
20% Add

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25% T.02
75% U44
25% Add

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25% TiO_2

75% Clay

30% Add

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No filler

APPENDIX D

October 11, 1972

CITY OF KALAMAZOO

CITY WATER UTILITIES

WATER ANALYSIS

	PARTS PER MILLION
Total Solids	290 to 590
SiO_2 (Silica)	5.5 to 20
Fe_2O_3 (Iron)	.25 to 2
Ca (Calcium)	40 to 120
Mg	13 to 34.1
Na + K	2.3 to 15.4
Cl (Chloride)	2 to 18
SO_4	15 to 139
HCO_3 (Bicarbonate)	150 to 350
CO_3 (Carbonate)	none
Fluorine	1
Hardness as $CaCO_3$	250 to 425
pH value	7.3 to 7.9

The water comes from different sources at different times, and accordingly the analysis may vary between the limits given above

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