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INVESTIGATION OF THE EFFECT OF

PARTIAL PULP RECIRCULATION IN A BLEACHING STAGE

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INVESTIGATION OF THE EFFECT OF PARTIAL PULP RECIRCULATION IN A BLEACHING STAGE

SUMMARY

A recirculation bleaching technique was investigated in which a certain fraction of the pulp product leaving a hypochlorite bleaching stage was continually recirculated within the stage and rebleached with an incoming charge of fresh pulp.

The experimental results of the work indicated that recirculation bleaching did not produce any better over-all bleaching characteristics or strength properties than the conventional single-stage processes. In fact, the recirculation bleaches usually appeared to produce somewhat lower pulp strengths, higher bleaching chemical costs, and longer bleaching time requirements. Improved brightness stability offset these detrimental effects to some extent, but an over-all consideration favored the conventional single-stage technique.

An analysis of the experimental data indicated a possibility that, under certain conditions, recirculation bleaching might prove more advantageous than conventional single-stage bleaching, whereas, under other conditions, the conventional single-stage process would tend to prove more advantageous than the recirculation techniques. It was further indicated that the relative advantages and disadvantages of recirculation bleaches might depend upon such factors as the extent of the brightness differential exhibited when the pulp is bleached by multi-stage processes rather than a single-stage process, the shape of the brightness *vs.* chemical demand curve, and the level of bleaching chemical applications employed.

It was definitely established that recirculation bleaching would not prove universally beneficial. However, there appeared to be a possibility that recirculation bleaches might prove beneficial under certain specific conditions. Consequently, a limited amount of future work was suggested.

INTRODUCTION

A series of experiments was performed to investigate the effects produced when a certain fraction of the pulp product leaving a hypochlorite bleaching stage was continually recirculated within the stage and re-bleached with an incoming charge of fresh pulp.

In these experiments, a charge of unbleached pulp was subjected to a single-stage hypochlorite bleaching and washing operation. A portion of the bleached pulp product was then mixed with unbleached pulp and the mixed pulp charge was again subjected to the hypochlorite bleaching and washing operation. A portion of this bleached pulp product was in turn mixed with unbleached pulp and the bleaching and washing operation was again repeated with this pulp mixture. This sequence was then repeated until essentially steady-state conditions were obtained in the experimental bleaching operation.

Under essentially steady-state conditions, the bleached pulp product leaving the experimental recirculation bleaching system consisted of a mixture of pulp fractions which had been subjected to a varying number of bleaching stages. (See Table I which represents a specific example of a recirculation bleaching operation involving a 25% recirculation of pulp.) Consequently, it was felt that the characteristics of a pulp bleached by a recirculation technique might differ considerably from the characteristics of a pulp bleached by means of a conventional single-stage bleaching process utilizing an equivalent application of available chlorine. Further, it appeared that a recirculation bleaching technique might conceivably tend to produce certain of the follow beneficial results:

TABLE I

EXAMPLE OF RECIRCULATION TYPE OF HYPOCHLORITE BLEACHING
Twenty-Five Per Cent Pulp Recirculation in Hypochlorite Bleaching Stage
[5.33% Equivalent Available Chlorine Applied to Bleached Pulp Product (Ovendry Pulp Basis)]

Pass	Fraction of Unbleached Pulp in Bleaching Charge, %	Fraction of Circulated Bl. Pulp Prod. in Bleaching Charge, %	Avail. Cl_2 Applied to Bl. Process/Pass (O.D. Pulp Basis), %	Equiv. Avail. Cl_2 Applied to Bl. Pulp Product (O.D. Pulp Basis), %	Characteristics of Bleached Pulp Leaving the Process[1] — Fraction of Stock Subjected to ( ) Stages, % (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	100	0	4.000	4.000	100	0	0	0	0	0	0	0
2	75	25	4.000	5.000	75	25	0	0	0	0	0	0
3	75	25	4.000	5.250	75	18.75	6.25	0	0	0	0	0
4	75	25	4.000	5.312	75	18.75	4.69	1.56	0	0	0	0
5	75	25	4.000	5.328	75	18.75	4.69	1.17	0.39	0	0	0
6	75	25	4.000	5.332	75	18.75	4.69	1.17	0.28	0.11	0	0
7	75	25	4.000	5.333	75	18.75	4.69	1.17	0.28	0.07	0.04	0
8	75	25	4.000	5.333	75	18.75	4.69	1.17	0.28	0.07	0.02	0.02

Note: It would seem that the bleached product would approach steady state conditions after the 8th pass.

[1] Assuming 100% yield.

(1) Recirculation bleaching might result in improved strength properties and an improved balance of pulp properties. (Recirculation bleaching might tend to produce a pulp with different fractions having varying degrees of treatment, chemical compositions, viscosities, etc. If this proved to be the case, it would be expected that the more highly treated fractions of the stock might refine at a relatively fast rate and produce high bonding characteristics, while the lesser treated fractions would be expected to refine at a slower rate and contribute good drainage characteristics and fiber-length properties. Thus, it would appear that a more desirable and beneficial balance of pulp properties might result--i.e., higher folding endurance properties may be obtained with lower refining requirements and better drainage characteristics, etc.).

(2) Recirculation bleaching might tend to produce some of the beneficial results usually associated with two-stage bleaching sequences, but at production costs lower than those generally involved in two-stage processes. (In general, lower chemical requirements, increasing brightness levels, and better pulp qualities result when a pulp is bleached by a two-stage hypochlorite process rather than with a single-stage bleach. Two-stage bleaching, however, requires more bleaching equipment, longer processing periods, and greater washing capacities. With recirculation bleaching, certain fractions of the pulp would be subjected to various multi-stage processes and these fractions may impart some of the desirable characteristics which generally accompany full-scale multi-stage bleaching operations. However, bleaching time requirements and equipment capacities would not be as great as those required for full-scale two-stage bleaching operations. Thus, a mill may be able to upgrade the quality of pulp obtained with a single-stage process, without the full increase in production costs and equipment costs

which would be involved in a two-stage bleaching process. Conversely, a mill presently using a two-stage hypochlorite process may be able to increase its bleaching capacity by utilizing single-stage recirculation and still maintain pulp quality superior to that obtained with a conventional single-stage process.)

The basic objective of this project, then, was to examine the characteristics of recirculation bleaching, particularly with regard to possible benefits of a commercial nature.

RAW MATERIALS

The pulp used in this experimental work was a bleachable grade of northern pine kraft pulp obtained from the wet lap machines at the Thilmany Pulp and Paper Company. This stock, containing 65.6% moisture, was thoroughly disintegrated in the laboratory pulp breaker, placed in pliofilm bags, and stored in the dark at 40°F. until required for further processing. In this condition, the pulp had a G.E. brightness of 28.1%.

The sodium hypochlorite utilized in the bleaching experiments consisted of a household bleach solution which was diluted to an available chlorine content of approximately 24 grams/liter. Control of pH in the bleaching slurries was maintained by a 50 g./l. solution of reagent-grade sodium hydroxide.

DESIGN OF EXPERIMENTAL WORK

The experimental work for this project followed the following outline:

(1) A bleachable grade of commercial kraft pulp was obtained.

(2) A number of single-stage hypochlorite bleaches were conducted for control purposes.

(3) A number of two-stage hypochlorite bleaches were also conducted for control purposes.

(4) A series of 8 hypochlorite bleaches or passes were performed in which 25% of the bleaching charge consisted of recirculated bleached pulp. (See bleaching pattern previously presented in Table I.) An available chlorine application of 4.0% (based on ovendry mixed pulp charge) was consumed per pass, and, under steady-state conditions, an equivalent available chlorine application of 5.33% (based on ovendry pulp) was utilized to completely process the unbleached pulp.

(5) A series of 8 hypochlorite bleaches or passes were performed in which 25% of the bleaching charge consisted of recirculated bleached pulp. (See bleaching pattern outlined in Table II.) An available chlorine application of 5.45% (based on ovendry mixed pulp charge) was consumed per pass, and, under steady state conditions, an equivalent available chlorine application of 7.27% (based on ovendry pulp) was utilized to completely process the unbleached pulp.

(6) A series of 12 hypochlorite bleaches or passes were performed in which 45% of the bleaching charge consisted of recirculated bleached pulp. (See bleaching pattern outlined in Table III.) An available chlorine

TABLE II

TWENTY-FIVE PER CENT PULP RECIRCULATION IN HYPOCHLORITE BLEACHING STAGE
[7.27% Equivalent Available Chlorine Applied to Bleached Pulp Product (Ovendry Pulp Basis)]

Pass	Fraction of Unbleached Pulp in Bleaching Charge, %	Fraction on Circulated Bl. Pulp Product in Bleaching Charge, %	Avail. Cl_2 Applied to Bl. Process/Pass (O.D. Pulp Basis), %	Equiv. Avail. Cl_2 Applied to Bl. Pulp Product (O.D. Pulp Basis), %	Characteristics of Bleached Pulp Leaving Process[1] Fraction of Stock Subjected to ( ) Stages, %: (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	100	0	5.45	5.450	100	0	0	0	0	0	0	0
2	75	25	5.45	6.562	75	25	0	0	0	0	0	0
3	75	25	5.45	7.090	75	18.75	6.25	0	0	0	0	0
4	75	25	5.45	7.122	75	18.75	4.69	1.56	0	0	0	0
5	75	25	5.45	7.231	75	18.75	4.69	1.17	0.39	0	0	0
6	75	25	5.45	7.258	75	18.75	4.69	1.17	0.28	0.11	0	0
7	75	25	5.45	7.264	75	18.75	4.69	1.17	0.28	0.07	0.04	0
8	75	25	5.45	7.266	75	18.75	4.69	1.17	0.28	0.07	0.02	0.02
9	75	25	5.45	7.266	--	--	--	--	--	--	--	--

Note: It would appear that the bleached product would approach steady state conditions after the 8th pass.

[1] Assuming 100% yield.

TABLE III

FORTY-FIVE PER CENT PULP RECIRCULATION IN HYPOCHLORITE BLEACHING STAGE
[7.27% Equivalent Available Chlorine Applied to Bleached Pulp Product (Ovendry Pulp Basis)]

Pass	(a)	(b)	(c)	(d)	Characteristics of Bleached Pulp Leaving the Process[1] Fraction of Pulp Subjected to ( ) Stages, %: (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1	100	0	4.000	4.000	100	0	0	0	0	0	0	0	0	0	0	0
2	55	45	4.000	5.800	55	45	0	0	0	0	0	0	0	0	0	0
3	55	45	4.000	6.610	55	24.75	20.25	0	0	0	0	0	0	0	0	0
4	55	45	4.000	6.974	55	24.75	11.14	9.11	0	0	0	0	0	0	0	0
5	55	45	4.000	7.138	55	24.75	11.14	5.01	4.10	0	0	0	0	0	0	0
6	55	45	4.000	7.212	55	24.75	11.14	5.01	2.25	1.85	0	0	0	0	0	0
7	55	45	4.000	7.246	55	24.75	11.14	5.01	2.25	1.01	0.84	0	0	0	0	0
8	55	45	4.000	7.260	55	24.75	11.14	5.01	2.25	1.01	0.45	0.39	0	0	0	0
9	55	45	4.000	7.267	55	24.75	11.14	5.01	2.25	1.01	0.45	0.20	0.19	0	0	0
10	55	45	4.000	7.270	55	24.75	11.14	5.01	2.25	1.01	0.45	0.20	0.10	0.09	0	0
11	55	45	4.000	7.271	55	24.75	11.14	5.01	2.25	1.01	0.45	0.20	0.10	0.05	0.04	0
12	55	45	4.000	7.272	55	24.75	11.14	5.01	2.25	1.01	0.45	0.20	0.10	0.05	0.02	0.02
13	55	45	4.000	7.272	--	--	--	--	--	--	--	--	--	--	--	--

Note: It would appear that the bleached product would approach steady state conditions after the 12th pass.

a = Fraction of unbleached pulp in bleaching charge, %
b = Fraction of circulated bleached pulp product in bleaching charge, %
c = Available chlorine applied to bleaching process/pass (ovendry pulp basis), %
d = Equivalent available chlorine applied to bleached pulp product (ovendry pulp basis), %[1]

[1] Assuming 100% yield

application of 4.0% (based on ovendry mixed pulp charge) was consumed per pass, and, under steady state conditions, an equivalent available chlorine application of 7.27% (based on ovendry pulp) was utilized to completely process the unbleached pulp.

(7) The brightness, oven fade, and yield characteristics of the various bleached pulps were determined.

(8) The strength characteristics of the pulps were determined by meahs of Jokro mill runs.

(9) The characteristics of the recirculation bleaches were compared with the characteristics of conventional single-stage and two-stage bleaching processes.

This exploratory work was designed with the immediate objective of determining the possible presence and direction of differences between the characteristics of pulps produced by conventional bleaching and recirculation bleaching operations. One of these probable differences would involve the attainment of different strength levels and/or balances of strength properties at a given level of brightness. Thus, it was desirable to initiate the experimental work with a pulp having a sensitive brightness vs. strength relationship so that possible differences might tend to be exaggerated and readily apparent.

In the present study, such relationship between brightness and strength was developed by processing a relatively high strength pulp (unbleached kraft pulp) with a relatively drastic bleaching agent (hypochlorite). It should be noted, however, that in commercial practice, kraft pulps are usually processed by multi-stage bleaching processes involving chlorinations, caustic extractions, and treatments with oxidative bleaching agents. Thus, the use of the single-stage hypochlorite treatment with the unbleached kraft pulp was merely an expedient procedure for attempting to quickly determine the probable utility of recirculation bleaching techniques.

An indication of the presence of desirable effects in the present studies would naturally prompt more detailed studies concerning a variety of commercial types of pulps and bleaching processes. Throughout this report, however, it should be remembered that the experimental investigations were based on only a single type of pulp and a single bleaching agent.

EXPERIMENTAL PROCEDURES

BLEACHING PROCEDURES

I. Constant Bleaching Conditions

1. Bleaching chemical: sodium hypochlorite

2. Pulp consistency (based on ovendry pulp charge): 12%

3. pH control point: 8.5

4. Method of pH control: 0.12% sodium hydroxide (based on ovendry pulp charge) was added as a 50 g./l. solution prior to the start of the bleach. Similar applications of sodium hydroxide were added whenever the pH of the bleaching slurry dropped to a level of 8.5.

5. Bleaching container: 2-gallon stoneware crock

II. Single-Stage Bleaches (see Table IV)

1. Pulp charge (ovendry basis): 250 g.

2. Available chlorine applications employed: 4.0, 5.45, 7.27, and 9.0% (based on ovendry pulp charge).

III. Two-Stage Bleaches (see Table V)

1. Pulp charge (1st stage) (ovendry basis): 250 g.

2. Pulp charge (2nd stage) (ovendry basis): 235 g.

3. Available chlorine application employed (1st stage) (based on ovendry pulp charge): 4.0%

4. Available chlorine applications employed (2nd Stage) (based on ovendry pulp charge): 1.0, 2.0, and 3.5%.

IV. Recirculation Bleaches

1. Series one (see Tables I and VI)

a. Mixed pulp charge per pass: 250 g. (ovendry basis)

b. Fraction of mixed pulp charge consisting of recirculated bleached pulp product: 25%

c. Available chlorine applied per pass (based on ovendry mixed pulp charge): 4.0%

d. Total number of passes performed: 8

2. Series two (see Tables II and VII)

a. Mixed pulp charge per pass: 250 g. (ovendry basis)

b. Fraction of mixed pulp charge consisting of recirculated bleached pulp product: 25%.

c. Available chlorine applied per pass [based on ovendry mixed pulp charge]: 5.45%

d. Total number of passes performed: 8

3. Series three (see Tables III and VIII)

a. Mixed pulp charge per pass: 250 g. (ovendry basis)

b. Fraction of mixed pulp charge consisting of recirculated bleached pulp product): 45%

c. Available chlorine applied per pass (based on ovendry mixed pulp charge): 4.0%.

d. Total number of passes performed: 12

V. Washing Procedures

1. After exhaustion of the available chlorine, the bleached pulp was dumped on a muslin-covered wash box and thoroughly washed with filtered tap water.

2. The washed stock was then dewatered on a filter paper placed on a Büchner funnel, passed through the laboratory pulp breaker, and stored at 40°F.

VI. Preparation of Bleaching Charges

1. The pulp charge (usually 250 g. ovendry basis) was diluted to a total of 10 liters with filtered tap water and dispersed for 10 minutes in a Williams disintegrator.

2. The dispersed charge was then dewatered on a filter paper placed on a Büchner funnel and subsequently diluted to the proper consistency for the bleaching operation.

3. In the recirculation experiments, the bleached and unbleached portions of the bleach charge were combined prior to the dispersion and blending operation in the Williams disintegrator.

EVALUATION PROCEDURES

I. Evaluation of Bleaching Characteristics

1. The following bleaching characteristics were determined for each of the bleached pulps:

a. Bleaching time requirements

b. Sodium hydroxide requirements for pH control

c. G.E. brightness

d. G.E. brightness after 1 hour fading in an air circulating oven maintained at 105°C.

e. Yield.

II. Evaluation of Strength Characteristics

1. Selected samples of the bleached pulps were refined in the Jokro mill.

a. Pulp charges: 16 g. (ovendry basis)

b. Refining consistency: 6.0% (based on ovendry weight of pulp charge).

2. Handsheets were prepared from the Jokro mill refined pulps and evaluated for basis weight, caliper, apparent density, bursting strength, tearing strength, tensile strength, stretch, and folding endurance.

EXPERIMENTAL DATA

The experimental data obtained for this project have been summarized in Tables IV through X.

Table IV relates to single-stage bleaching experiments.

Table V relates to two-stage bleaching experiments

Table VI relates to a recirculation bleaching experiment in which 25% of the bleached pulp product was recirculated and an available chlorine application equivalent to 5.33% (ovendry pulp basis) was utilized to completely process the unbleached pulp.

Table VII relates to a recirculation bleaching experiment in which 25% of the bleached pulp product was recirculated and an available chlorine application equivalent to 7.27% (ovendry pulp basis) was utilized to completely process the unbleached pulp.

Table VIII pertains to a recirculation bleaching experiment in which 45% of the bleached pulp product was recirculated and an available chlorine application equivalent to 7.27% (ovendry pulp basis) was utilized to completely process the unbleached pulp.

Table IX summarizes the strength characteristics of pulps prepared by conventional single-stage bleaching techniques.

Table X summarizes the strength characteristics of pulps prepared by recirculation bleaching techniques.

TABLE IV

SINGLE-STAGE SODIUM HYPOCHLORITE BLEACHING EXPERIMENTS

Bleach	1	2	3	4
Available chlorine applied (based on ovendry pulp charge), %	4.0	5.45	7.27	9.0
Bleaching time required for exhaustion of available chlorine, min.	56	106	209	288
Sodium hydroxide required for pH control (based on ovendry pulp charge), %	0.12	0.24	0.48	0.60
Yield of bleached pulp, %	96	94	95	94
G.E. brightness of bleached pulp, %	47.3	59.0	68.7	74.2
G.E. brightness of bleached pulp after 1 hr. fading at 105°C., %	43.1	52.7	60.9	65.9

Constant conditions:

Pulp charge (ovendry basis), g.	250
Pulp consistency (based on ovendry pulp charge), %	12
Temperature, °C.	35

TABLE V

TWO-STAGE SODIUM HYPOCHLORITE BLEACHING EXPERIMENTS

Bleaching Stage	First	Second		
Bleach	1,2,3[a]	1	2	3
Available chlorine applied (based on ovendry pulp charge), %	4.0	1.0	2.0	3.5
Total available chlorine applied in both stages (based on ovendry pulp charge), %	--	5.0	6.0	7.5
Bleaching time required for exhaustion of avail. chlorine, min.	54, 54, 41	130	232	343
Bleaching time required for both stages, min.	--	180	282	393
Sodium hydroxide required for pH control (based on ovendry pulp charge), %	0.12	0.24	0.36	0.60
Sodium hydroxide required for both stages (based on ovendry pulp charge), %	--	0.36	0.48	0.72
Yield of bleached pulp, %	98	97	98	96
Yield of bleached pulp after both stages (based on unbleached pulp), %	--	95	96	94
G.E. brightness of bleached pulp, %	46.2	57.3	64.7	73.2
G.E. brightness of bleached pulp after 1 hr. fading at 105°C., %	42.8	51.9	58.0	65.1

Constant conditions:

First-stage pulp charge (ovendry basis): 250 g.
Second-stage pulp charge (ovendry basis): 235 g.
Pulp consistency (based on ovendry pulp charge): 12%
Temperature: 35°C.

[a]The first-stage bleached pulp consisted of a blend of three separate single-stage bleaches.

TABLE VI

RECIRCULATION BLEACHING EXPERIMENTS (SERIES ONE)

[25% Pulp Recirculation: 4.0% Available Chlorine Applied Per Pass; 5.33% Available Chlorine Utilized to Completely Process the Unbleached Pulp]
(See Table I)

Pass	1	2	3	4	5	6[a]	7[a]	8[a]
Fraction of unbleached pulp in bleaching charge, %	100	75	75	75	75	75	75	75
Fraction of recirculated bleached pulp product in bleaching charge, %	0	25	25	25	25	25	25	25
Available chlorine applied to bleaching process per pass (based on ovendry mixed pulp), %	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Equivalent available chlorine utilized to completely process the unbleached pulp (based on ovendry pulp), %	4.00	5.00	5.25	5.31	5.33	5.33	5.33	5.33
Bleaching time required for exhaustion of available chlorine, min.	45	87	91	94	79	78	83	75
Bleaching time required to completely process a full charge of unbleached pulp[b], min.	--	--	--	--	--	104	111	100
Sodium hydroxide required for pH control (based on ovendry mixed pulp charge), %	0.12	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Equivalent sodium hydroxide utilized to completely process the unbleached pulp (based on ovendry pulp), %	0.12	0.27	0.31	0.32	0.32	0.32	0.32	0.32
Yield of bleached pulp product (based on ovendry mixed pulp charge), %	97	97	98	98	97	98	96	97
Yield of bleached pulp product (based on unbleached pulp), %	96	96	97	97	96	97	95	96
G.E. brightness of bleached pulp, %	45.9	54.9	57.6	57.1	56.3	56.0	56.7	55.0
G.E. brightness of bleached pulp after 1 hour fading at 105°C., %	42.4	49.7	51.8	51.6	51.2	51.4	52.3	50.6

[a] It was assumed that the 6th, 7th, and 8th passes represented steady state conditions.

[b] Only 75% of the bleach charge was completely processed in each pass. Consequently, under steady state conditions, the bleaching time required to completely process a full charge of unbleached pulp = bleaching time required per pass/0.75. A comparison between these calculated values of bleaching time requirements and the bleaching time requirements for the single-stage and the two-stage processes would indicate the relative treatment periods which would be required to process a given quantity of pulp in a given bleach installation. Thus, such comparison would tend to indicate the relative production rates obtainable with the various types of bleaching techniques.

Constant conditions:

Mixed pulp charge per pass, g.	250
Pulp consistency (based on O.D. mixed pulp charge), %	12
Temperature, °C.	35

TABLE VII

RECIRCULATION BLEACHING EXPERIMENTS (SERIES TWO)

[25% Pulp Recirculation; 5.45% Available Chlorine Applied Per Pass; 7.27% Available Chlorine Utilized to Completely Process the Unbleached Pulp--See Table II]

Pass	1	2	3	4	5	6[a]	7[a]	8[a]
Fraction of unbleached pulp in bleaching charge, %	100	75	75	75	75	75	75	75
Fraction of recirculated bleached pulp product in bleaching charge, %	0	25	25	25	25	25	25	25
Available chlorine applied to bleaching process per pass (based on ovendry mixed pulp), %	5.45	5.45	5.45	5.45	5.45	5.45	5.45	5.45
Equivalent available chlorine utilized to completely process the unbleached pulp (based on ovendry pulp), %	5.45	6.56	7.09	7.12	7.23	7.26	7.27	7.27
Bleaching time required for exhaustion of available chlorine, min.	101	175	177	188	152	157	166	144
Bleaching time required to completely process a full charge of unbleached pulp[b]	--	--	--	--	--	210	221	192
Sodium hydroxide required for pH control (based on ovendry mixed pulp charge), %	0.24	0.48	0.36	0.36	0.48	0.48	0.48	0.48
Equivalent sodium hydroxide utilized to completely process the unbleached pulp (based on ovendry pulp), %	0.24	0.54	0.50	0.48	0.60	0.63	0.64	0.64
Yield of bleached pulp product (based on ovendry mixed pulp charge), %	97	97	95	96	97	96	97	96
Yield of bleached pulp product (based on unbleached pulp), %	96	96	93	95	96	95	96	95
G.E. brightness of bleached pulp, %	58.4	66.0	68.3	68.3	67.5	66.6	65.8	65.8
G.E. brightness of bleached pulp after 1 hr. fading at 105°C., %	52.1	59.8	61.1	60.8	62.5	60.8	60.4	60.0

[a]It was assumed that the 6th, 7th, and 8th passes represented steady state conditions.

[b]Only 75% of the bleach charge was completely processed in each pass. Consequently, under steady state conditions, the bleaching time required to completely process a full charge of unbleached pulp = bleaching time required per pass/0.75. A comparison between these calculated values of bleaching time requirements and the bleaching time requirements for the single-stage and the two-stage processes would indicate the relative treatment periods which would be required to process a given quantity of pulp in a given bleach installation. Thus, such comparison would tend to indicate the relative production rates obtainable with the various types of bleaching techniques.

Constant conditions:

Mixed pulp charge per pass, g.	250
Pulp consistency (based on mixed pulp charge), %	12
Temperature, °C.	35

TABLE VIII

RECIRCULATION BLEACHING EXPERIMENTS (SERIES THREE)
[45% Pulp Recirculation; 4.0% Available Chlorine Applied Per Pass; 7.27% Available Chlorine Utilized to Completely Process the Unbleached Pulp]
(See Table III)

Pass	1	2	3	4	5	6	7	8	9	10[a]	11[a]	12[a]
Fraction of unbleached pulp in bleaching charge, %	100	55	55	55	55	55	55	55	55	55	55	55
Fraction of recirculated bleached pulp product in bleaching charge, %	0	45	45	45	45	45	45	45	45	45	45	45
Available chlorine applied to bleaching process per pass (based on ovendry mixed pulp), %	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Equivalent available chlorine utilized to completely process unbleached pulp (based on O.D. pulp), %	4.00	5.80	6.61	6.97	7.14	7.21	7.25	7.26	7.27	7.27	7.27	7.27
Bleaching time required for exhaustion of available chlorine, min.	43	135	184	188	156	182	169	170	168	147	195	163
Bleaching time required to completely process a full charge of unbleached pulp[b], min.	--	--	--	--	--	--	--	--	--	268	268	354
Sodium hydroxide required for pH control (based on O.D. mixed pulp charge), %	0.12	0.36	0.36	0.36	0.36	0.48	0.36	0.48	0.48	0.48	0.48	0.48
Equivalent sodium hydroxide utilized to completely process unbleached pulp (based on O.D. pulp), %	0.12	0.39	0.45	0.47	0.48	0.60	0.51	0.60	0.63	0.64	0.64	0.64
Yield of bleached pulp product (based on ovendry mixed pulp charge), %	97	99	96	98	98	98	99	98	97	97	98	98
Yield of bleached pulp product (based on unbleached pulp), %	95	98	93	96	96	96	98	96	95	95	96	96
G.E. brightness of bleached pulp, %	46.4	61.8	65.8	67.9	65.7	67.9	68.2	67.3	58.5	69.1	57.9	56.3
G.E. brightness of bleached pulp after 1 hr. fading at 105°C., %	42.8	55.7	59.6	61.0	60.1	61.5	61.7	61.9	61.3	61.6	60.9	60.6

[a]It was assumed that the 10th, 11th, and 12th passes represented steady state conditions.

[b]Only 55% of the bleach charge was completely processed in each pass. Consequently, under steady state conditions, the bleaching time required to completely process a full charge of unbleached pulp = bleaching time required per pass/0.55. A comparison between the calculated values of bleaching time requirements and the bleaching time requirements for the single-stage and two-stage processes would indicate the relative treatment periods which would be required to process a given quantity of pulp in a given bleach installation. Thus, such comparison would tend to indicate the relative production rates obtainable with the various types of bleaching techniques.

Constant conditions:

Mixed pulp charge per pass, g.	250
Pulp consistency (based on ovendry mixed pulp charge), %	12
Temperature, °C.	35

TABLE IX

STRENGTH CHARACTERISTICS OF PULPS BLEACHED BY CONVENTIONAL SINGLE-STAGE BLEACHING TECHNIQUE (SEE TABLE IV)

Refining Time, min.	Schopper-Riegler Freeness, ml.	Basis Weight (25x40--500), lb.	Caliper, mils	Apparent Density	Bursting Strength, pt./100 lb.	Tear Factor	M.I.T. Folding Endurance, double folds	Tensile Strength, lb./in./45-lb. sheet	Stretch, %
			Available Chlorine Utilized in Single-Stage = 4.0%; G.E. Brightness = 47.3%						
0	875	47.3	4.3	11.0	63	2.18	76	18.0	2.5
10	860	47.0	3.4	13.8	127	1.11	773	32.8	2.5
20	800	47.2	3.3	14.3	137	0.97	751	34.5	2.4
35	720	47.0	3.2	14.7	141	0.96	1005	36.7	2.5
50	600	47.3	3.1	15.3	144	0.99	1219	32.2	2.0
70	360	47.0	3.0	15.7	141	0.91	1102	35.3	2.3
			Available Chlorine Utilized in Single-Stage = 5.45%; G.E. Brightness = 59.0%						
0	870	46.1	3.9	11.8	67	1.89	106	18.9	2.6
10	855	47.0	3.4	13.8	124	1.09	638	33.5	2.4
20	825	46.1	3.2	14.4	134	1.02	789	33.1	2.4
35	685	46.8	3.1	15.1	138	0.92	890	35.3	2.6
50	565	46.9	3.0	15.6	140	0.90	1071	34.9	2.3
70	350	47.1	2.9	16.2	141	0.85	1413	35.4	2.3
			Available Chlorine Utilized in Single-Stage = 7.27%; G.E. Brightness = 68.7%						
0	870	47.4	4.1	11.6	69	1.69	109	19.1	2.4
10	850	46.9	3.3	14.2	117	0.94	537	31.8	2.3
20	800	47.5	3.2	14.8	118	0.86	665	34.5	2.4
35	600	46.6	3.0	15.5	126	0.82	689	33.9	2.4
50	310	47.5	2.9	16.4	118	0.74	684	32.6	2.0
70	210	47.6	2.8	17.0	125	0.71	906	33.0	2.3
			Available Chlorine Utilized in Single-Stage = 9.0%; G.E. Brightness = 74.2%						
0	875	46.8	3.9	12.0	68	1.37	63	18.8	2.2
10	840	46.4	3.2	14.5	104	0.75	325	29.5	2.1
20	770	47.1	3.1	15.2	101	0.72	349	29.9	2.0
35	475	46.9	2.9	16.2	107	0.64	476	30.9	2.2
50	240	47.5	2.7	17.6	102	0.57	875	29.3	1.8

TABLE X

STRENGTH CHARACTERISTICS OF PULPS BLEACHED BY RECIRCULATION BLEACHING TECHNIQUE

Refining Time, min.	Schopper-Riegler Freeness, ml.	Basis Weight (25x40--500), lb.	Caliper, mils	Apparent Density	Bursting Strength, pt./100 lb.	Tear Factor	M.I.T. Folding Endurance, double folds	Tensile Strength, lb./in./45-lb. sheet	Stretch, %
	Bleached Pulp Investigated After 8th Pass (Essentially Steady State Conditions) in Series One Recirculation Experiments (See Tables I and VI) [Pulp Recirculation = 25%; Equivalent Available Chlorine Utilized to Completely Process the Unbleached Pulp = 5.33%; G.E. brightness = 55.0%]								
0	870	45.4	4.0	11.4	69	1.94	85	18.5	2.4
10	860	47.5	3.4	14.0	121	1.09	636	33.8	2.5
20	835	47.1	3.3	14.3	131	0.98	749	33.7	2.1
35	755	47.3	3.2	14.8	138	0.95	1140	37.1	2.6
50	585	47.1	3.1	15.2	134	0.89	935	38.8	2.6
70	345	47.2	3.0	15.7	135	0.87	1363	38.3	2.6
	Bleached Pulp Investigated After 8th Pass (Essentially Steady State Conditions) in Series Two Recirculation Experiments (See Tables II and VII) [Pulp Recirculation = 25%; Equivalent Available Chlorine Utilized to Completely Process the Unbleached Pulp = 7.27%; G.E. Brightness = 65.8%]								
0	865	46.7	3.9	12.0	69	1.58	89	20.8	2.4
10	840	47.7	3.3	14.5	116	0.90	468	32.5	2.2
20	780	46.8	3.1	15.1	118	0.81	605	32.0	2.1
35	565	47.0	3.0	15.7	121	0.74	611	34.9	2.4
50	365	47.1	2.9	16.2	120	0.72	648	35.4	2.2
70	195	47.2	2.7	17.5	119	0.64	1246	34.0	2.0
	Bleached Pulp Investigated After 12th Pass (Essentially Steady State Conditions) in Series Three Recirculation Experiments (See Tables III and VIII) [Pulp Recirculation = 45%; Equivalent Available Chlorine Utilized to Completely Process the Unbleached Pulp = 7.27%; G.E. Brightness = 66.3%]								
0	870	46.9	3.9	12.0	70	1.56	86	18.9	2.9
10	845	46.7	3.4	13.7	112	0.86	433	31.8	2.3
20	790	46.7	3.1	15.1	116	0.79	570	32.8	2.4
35	620	46.7	3.0	15.6	119	0.77	874	32.1	2.2
50	310	46.8	2.9	16.5	118	0.67	946	33.4	2.3
70	150	47.4	2.6	18.2	119	0.59	1432	30.8	1.8

EXPERIMENTAL RESULTS

EFFECT OF VARIOUS BLEACHING TECHNIQUES ON BLEACHED PULP YIELD

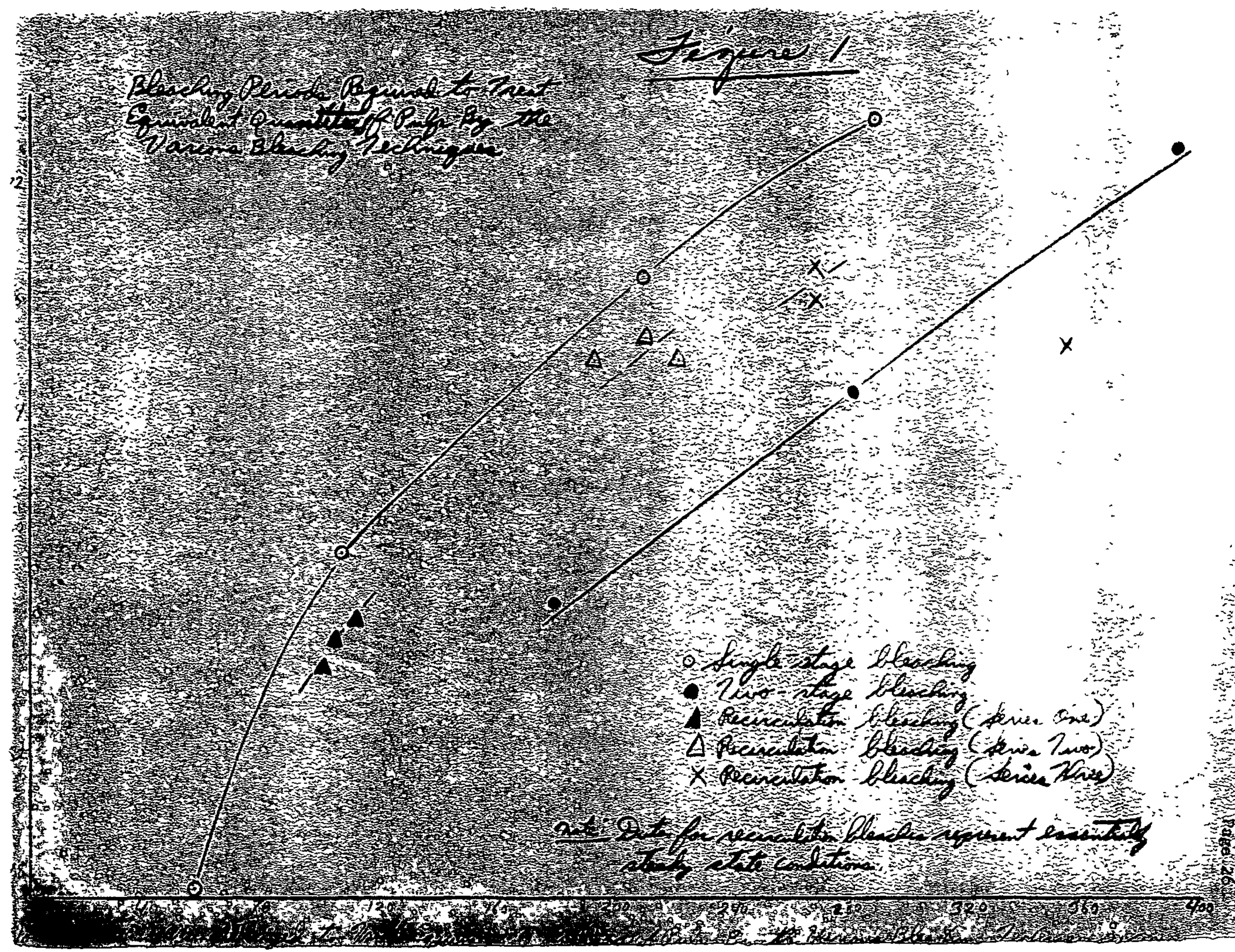
The pulp yield data presented in Tables IV through VIII indicate that there was essentially no difference between the over-all yield characteristics produced by single-stage, two-stage, or recirculation bleaching techniques. Some relatively minor differences might have conceivably existed, but it would require much more extensive experimentation and larger-scale trials to establish such possibility.

EFFECT OF VARIOUS BLEACHING TECHNIQUES ON BLEACHING TIME REQUIREMENTS

Figure 1 represents the comparative bleaching time periods required to completely process a given quantity of unbleached pulp in a processing installation of a given capacity[1]. On the basis of this figure, it may be ascertained that the two-stage processing technique required considerably longer treatment periods to attain a given brightness level than the single-stage technique. Also, the treatment periods for recirculation processes were generally between the treatment period requirements for single-stage and two-stage bleaching processes. Thus, from a production rate viewpoint, the single-stage process would prove more advantageous than the recirculation technique, and the recirculation technique would tend to show an advantage over two-stage processes (the relative extent of this advantage would, of course, depend upon a number of factors such as recirculation rates, etc.).

[1]See Tables IV through VIII, particularly the footnotes to Tables VI through VIII, for a description of the data presented in Figure 1.

Figure 1


Bleaching Periods Required to Treat Equivalent Quantities of Pulp By the Various Bleaching Techniques
○ Single stage bleaching
● Two-stage bleaching
▲ Recirculation bleaching (Series One)
△ Recirculation bleaching (Series Two)
× Recirculation bleaching (Series Three)
Note: Data for recirculation bleaches represent essentially steady state conditions.
40
80
120
160
200
240
280
320
360
400

EFFECT OF VARIOUS BLEACHING TECHNIQUES
ON BLEACHING CHEMICAL REQUIREMENTS

Figure 2 indicates the brightness levels attained when various quantities of bleaching chemical were utilized in the different bleaching techniques. From this figure it may be seen that the two-stage bleaching technique utilized the least amount of bleaching chemical to attain a given brightness level, and the recirculation bleaching technique required the greatest amount of bleaching chemical. Thus, from the viewpoint of bleaching chemical costs, the single-stage process proved to be inferior to the two-stage process, and the recirculation technique proved to be inferior to either the single-stage or the two-stage processes.

EFFECT OF VARIOUS BLEACHING TECHNIQUES
ON BRIGHTNESS STABILITY CHARACTERISTICS

The oven fade characteristics of the various bleached pulps have been represented in Figure 3. From this figure it may be ascertained that the brightness stability characteristics of the two-stage bleached pulps were somewhat better than for the single-stage pulps, and the brightness stability characteristics of the pulps prepared by the recirculation technique were notably better than for either the single-stage or the two-stage processed pulps.

Although the specific reasons for differences in stability cannot be definitely established from this work, it would appear that they might be associated with varying degrees of washing and the different quantities of sodium hydroxide utilized during the bleaching processes--i.e., both the recirculation and the two-stage processed pulps received more washing than the single-stage pulps. Also, as indicated in Figure 4, more caustic was utilized during two-stage processing than during single-stage processing, and somewhat more caustic appeared to be

Bleaching Chemical Required to Bleach by the Various Bleaching Techniques

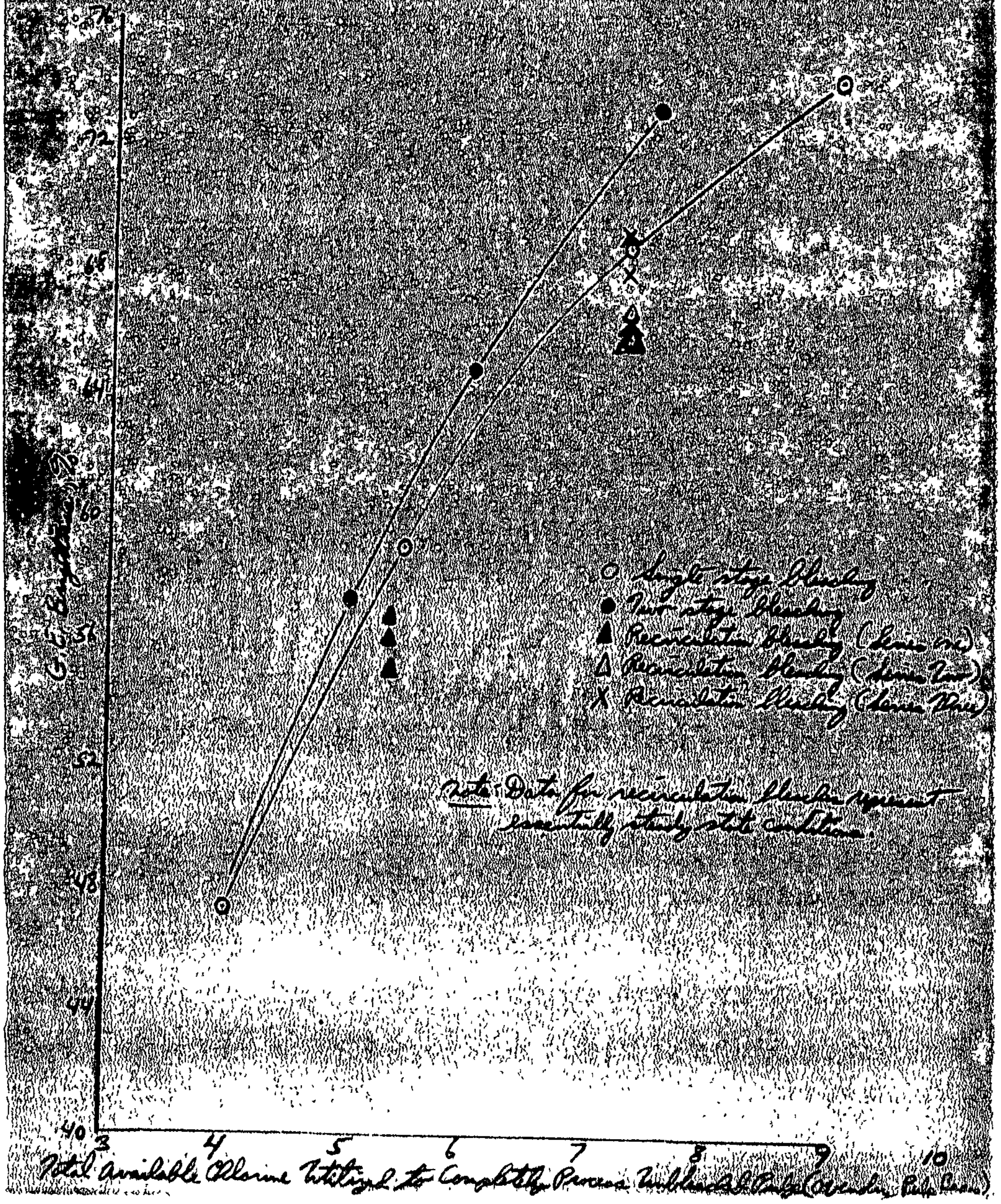


Figure 3

Brightness Stability Characteristics of Pulps Bleached By the Various Bleaching Techniques

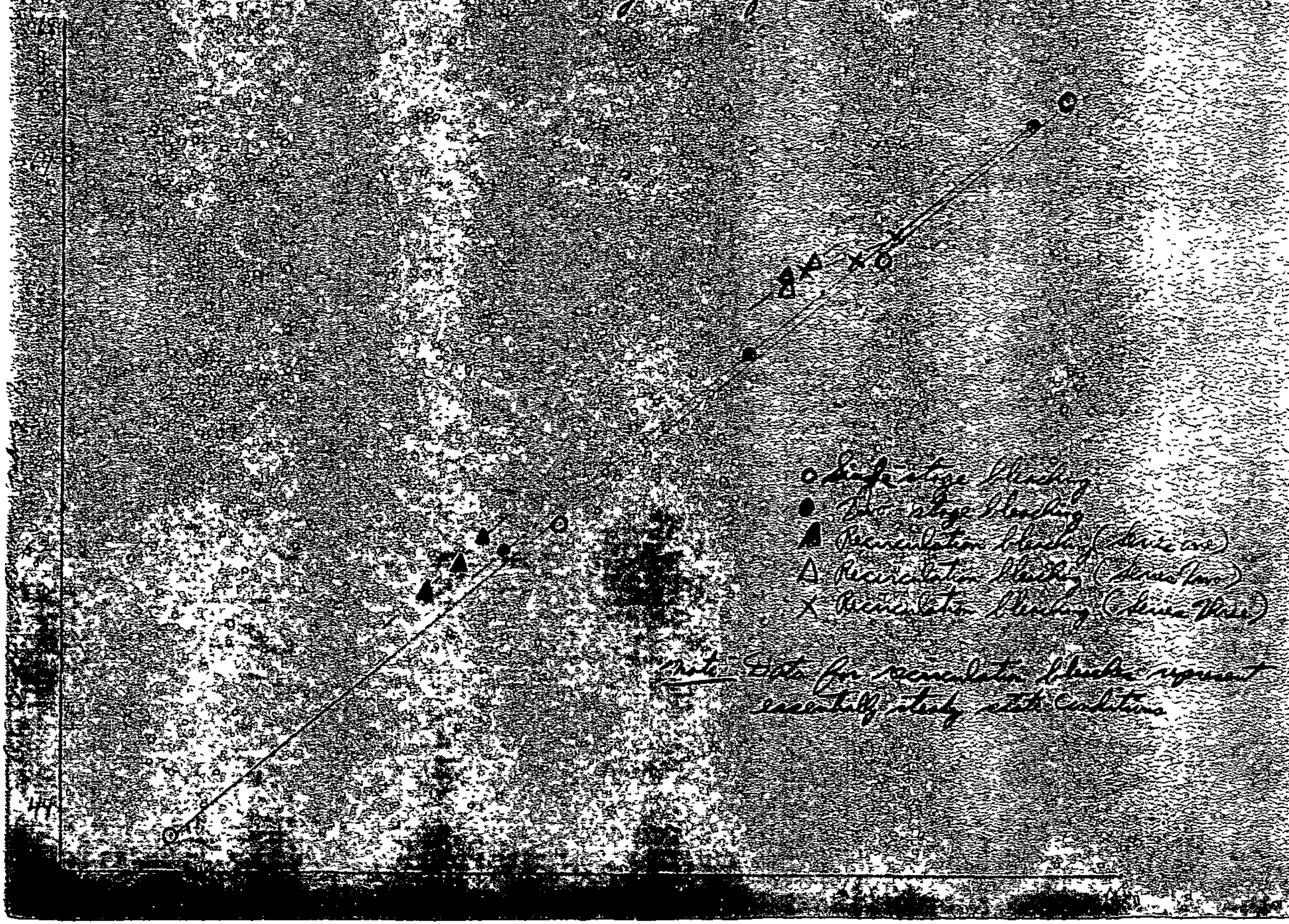
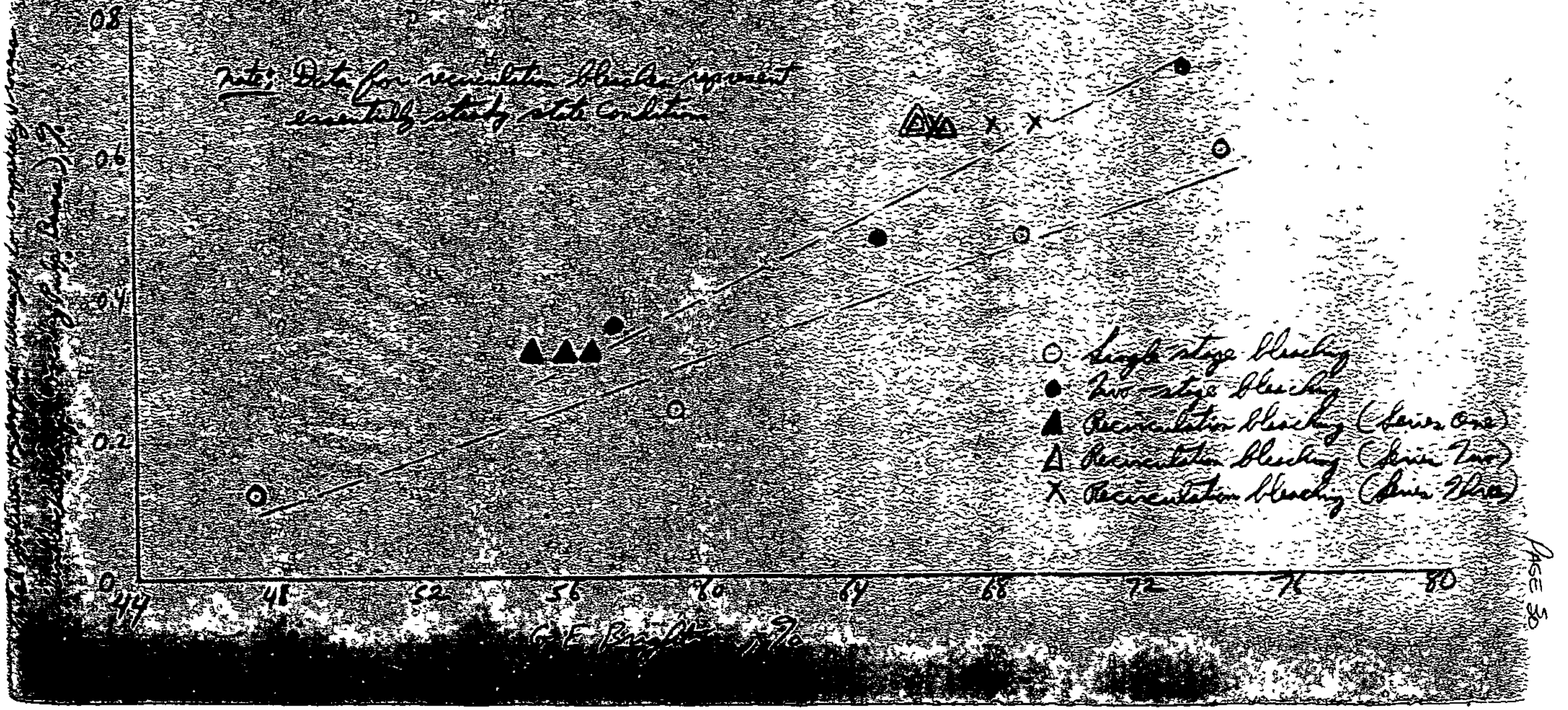


Figure 4

Utilization of Sodium Hydroxide for pH Control When Bleaching By Various Bleaching Techniques



utilized during recirculation bleaching than during either two-stage or single-stage processing. Increased utilizations of caustic might, of course, tend to improve the removal of alkaline soluble and alkaline reacted materials from the pulp, and hence improve brightness stability in much the same manner as regular caustic extraction operations.

CONSIDERATION OF THE DESIRABILITY OF VARIOUS BLEACHING TECHNIQUES

When bleaching to a specified brightness level, the conventional single-stage process required shorter bleaching time periods and smaller bleaching chemical costs than the recirculation process. Thus, the single-stage process proved to be more desirable than the recirculation technique. However, bleached pulps generally fade during the usual drying and processing treatments involved in papermaking operations, and the extent of this fading or decrease in brightness depends upon the brightness stability characteristics of the bleached stocks. Recirculation bleached pulps exhibited better brightness stability characteristics than single-stage bleached pulps. Hence, when both single-stage and recirculation processed pulps are bleached to the same brightness level, the pulp prepared by the recirculation technique would tend to exhibit higher brightness properties in a finished paper product.

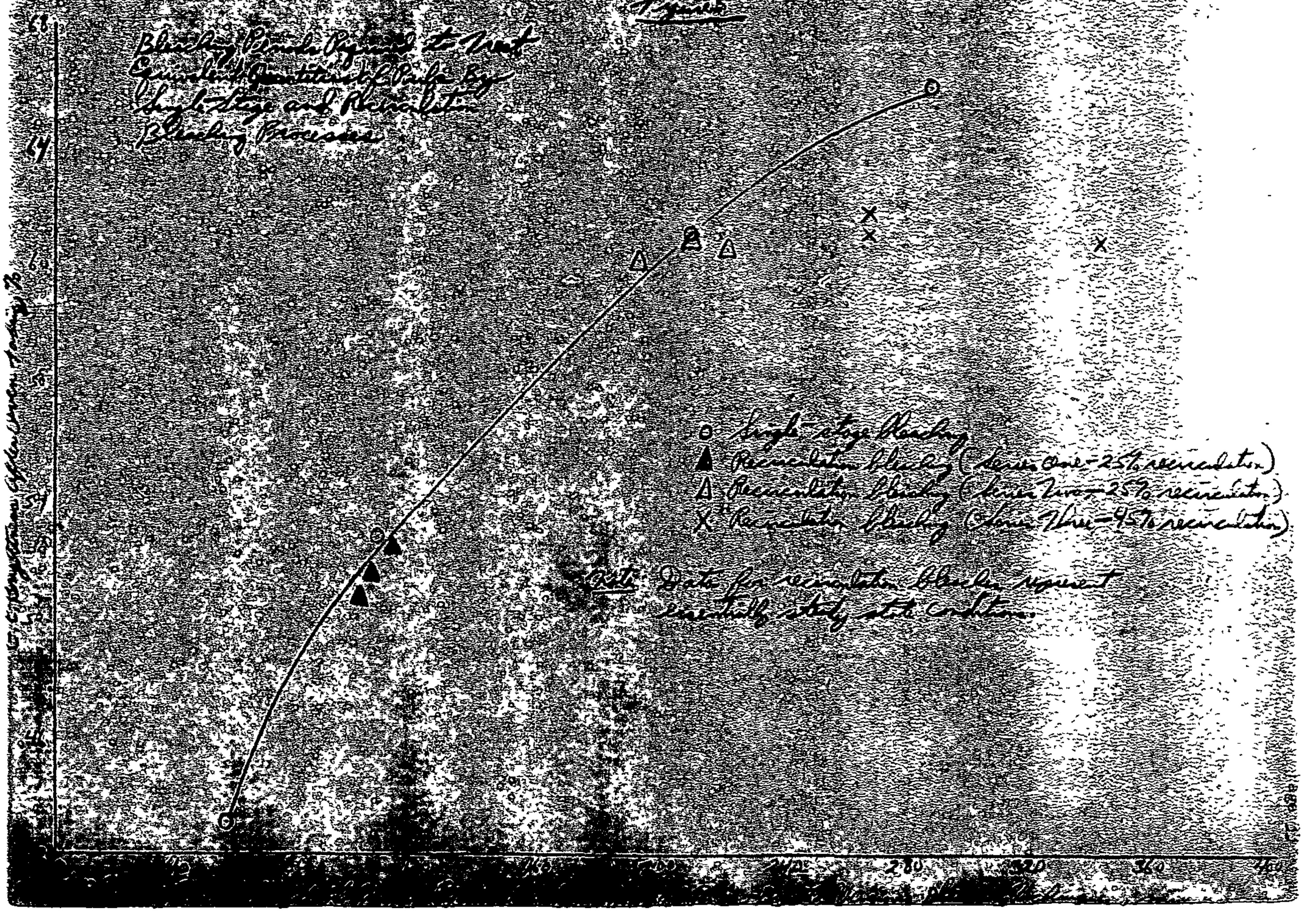
Thus, the better brightness stability characteristics would be a distinct advantage for the recirculation technique. However, this advantage could be eliminated if the single-stage pulps were bleached to higher brightness levels than the recirculation bleached pulps--i.e., the advantage would be eliminated if each of the two types of pulps were bleached to levels where they both showed the same brightness properties after heat treatment and fading. Such action would, of course, tend to increase the bleaching time requirements and bleaching chemical costs of the single-stage process, and consequently reduce the desirable features it exhibited over the recirculation technique.

Figures 5 and 6 represent the relative bleaching time periods and bleaching chemical applications necessary to produce equivalent oven faded pulp brightnesses, by the single-stage and the recirculation bleaching techniques. Thus these figures would be an indication of the bleaching periods and bleaching chemical costs required to produce pulps with essentially equivalent brightness characteristics after the usual papermaking operations. From these figures, it may be seen that:

(1) The bleaching chemical requirements for both the single-stage and the recirculation prepared pulps were essentially equivalent. (Thus, on the basis of finished product brightness, both types of bleaching processes proved eqqally desirable with regard to bleaching chemical costs. The single-stage process, however, would be simpler and easier to operate.)

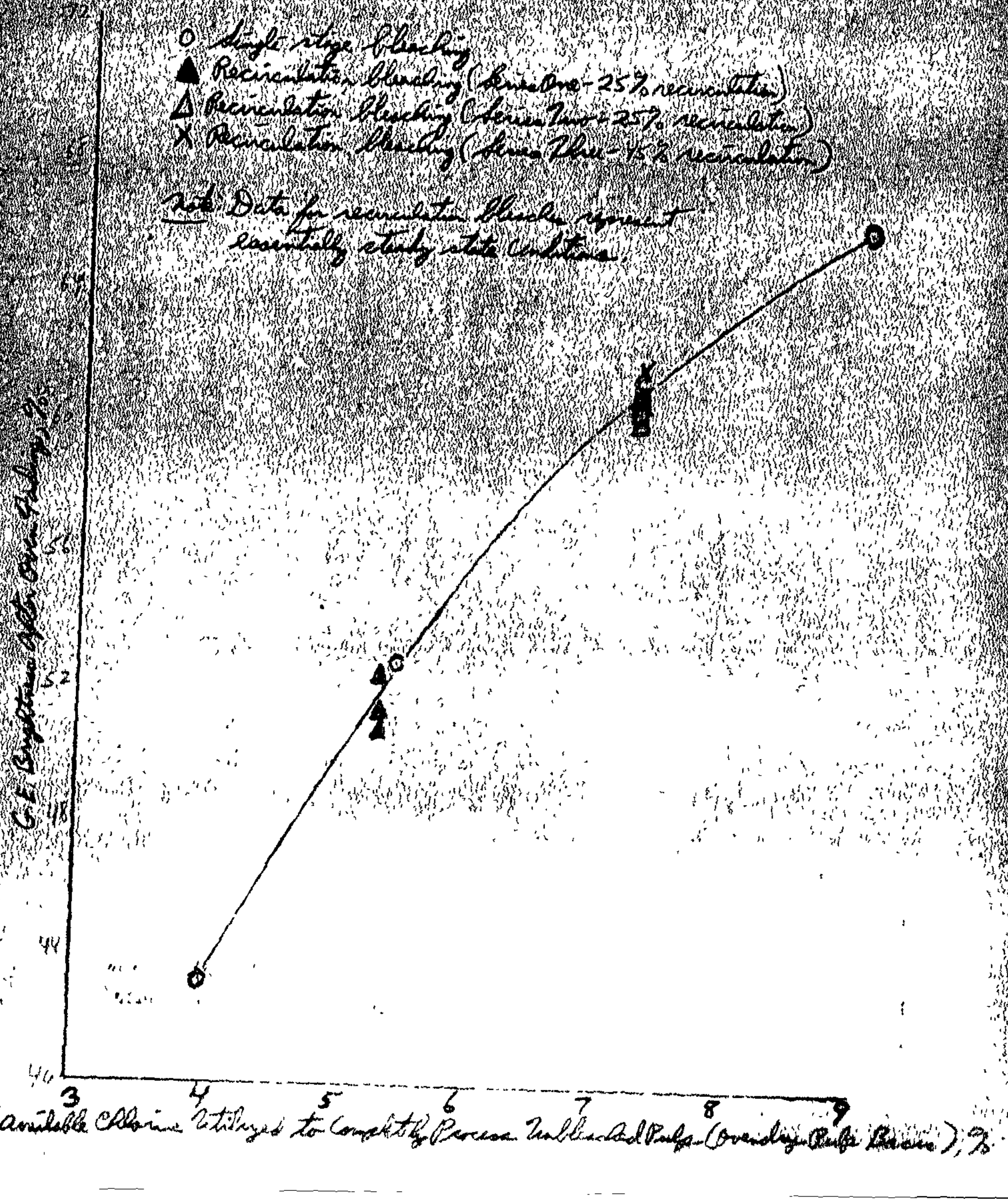
(2) The bleaching time requirements for the 25% recirculation bleaching processes were essentially equivalent to the bleaching time requirements for the single-stage bleaching process. However, higher recirculation ratios (45%) resulted in longer bleaching periods than those required for single-stage bleaching. (Thus, on the basis of finished product brightness, the single-stage technique appeared to be equally or more desirable with regard to bleaching time or production rate characteristics.)

When preparing pulp at a given brightness level, then, the lower bleaching chemical costs and bleaching time requirements of the single-stage process made it more desirable than the recirculation techniques. The recirculation techniques, however, possessed the advantage of better brightness stability. The single-stage process could compensate for this advantage if the pulp was bleached to a higher brightness level, but such method of compensation would tend to increase the relative bleaching time requirements and chemical costs of the single-stage process. However, there were indications that these increases would not be



Bleaching Periods Required to Treat Equivalent Quantities of Pulp By Single Stage and Recirculation Bleaching Processes
Single-stage bleaching
Recirculation bleaching (Series One—25% recirculation)
Recirculation bleaching (Series Two—25% recirculation)
Recirculation bleaching (Series Three—45% recirculation)
Note: Data for recirculation bleaches represent essentially steady state conditions.
280
320
360
400

Bleaching Chemical Required to Bleach by the Single-stage and Recirculation Bleaching Processes



large enough to make a recirculation process more desirable than a single-stage technique.

Thus, under the conditions of the present experimental work, the bleaching characteristics of the single-stage processes generally proved to be more desirable than the bleaching characteristics of the recirculation processes. Consequently, it would not prove practical to substitute a recirculation process for a single-stage bleaching process. Likewise, it would be impractical to substitute a recirculation process for a two-stage process--i.e., substitution by a single-stage process would be more advantageous than substitution by a recirculation process. Therefore, when considering the bleaching processes studied in this project, the only logical choice would be between conventional single-stage and two-stage processes. In this respect it might be noted that the use of a two-stage, rather than a one-stage process, would tend to improve brightness stability while reducing both production capacity and bleaching chemical costs.

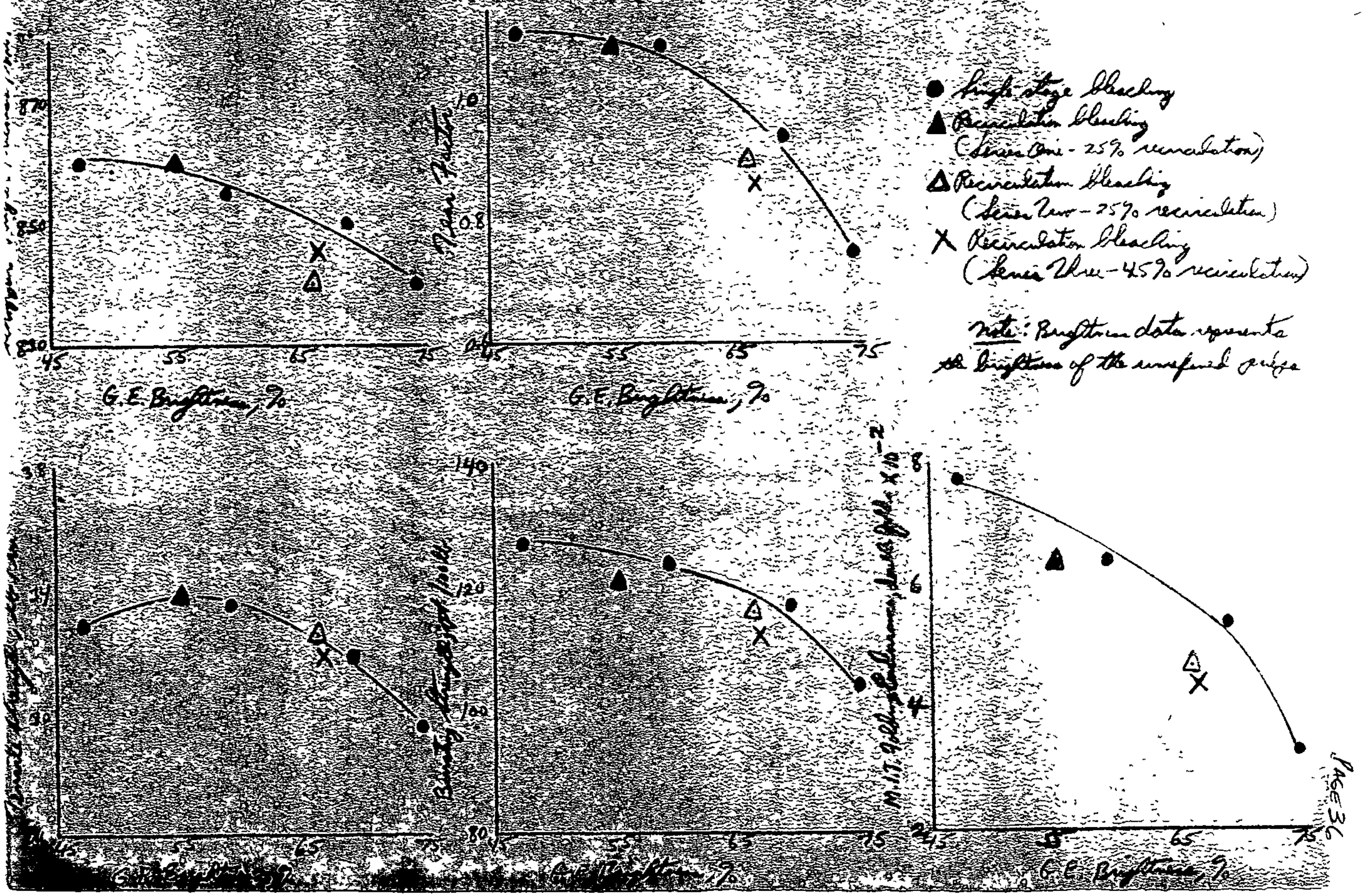
PULP STRENGTH CHARACTERISTICS PRODUCED BY THE VARIOUS BLEACHING TECHNIQUES

Figures 7 through 9 represent the refining time, freeness, and strength characteristics of pulps which had been bleached to various brightness levels by means of single-stage and recirculation bleaching processes. On the basis of these figures it may be ascertained that:

(1) Progressively lower tearing strength, tensile strength, bursting strength, and folding endurance properties, as well as lower freeness characteristics, generally resulted when pulps of increasing brightness levels were refined for given periods in the Jokro mill. Thus increased utilizations of hypochlorite during the bleaching operation proved detrimental to both the drainage characteristics and the strength properties of the refined pulps. Also, the fact that all of the strength properties of the pulp simultaneously decreased with increased brightness,

Figure 7

Freeness and Strength Characteristics of Bleached Pulps after 10 minutes Refining in the Jokro Mill



● Single-stage bleaching

▲ Recirculation bleaching (Series One - 25% recirculation)

△ Recirculation bleaching (Series Two - 25% recirculation)

X Recirculation bleaching (Series Three - 45% recirculation)

Note: Brightness data represents the brightness of the unrefined pulps

Figure 8

Fineness and Strength Characteristics of Bleached Pulps after 20 minutes Refining in the Jokro mill

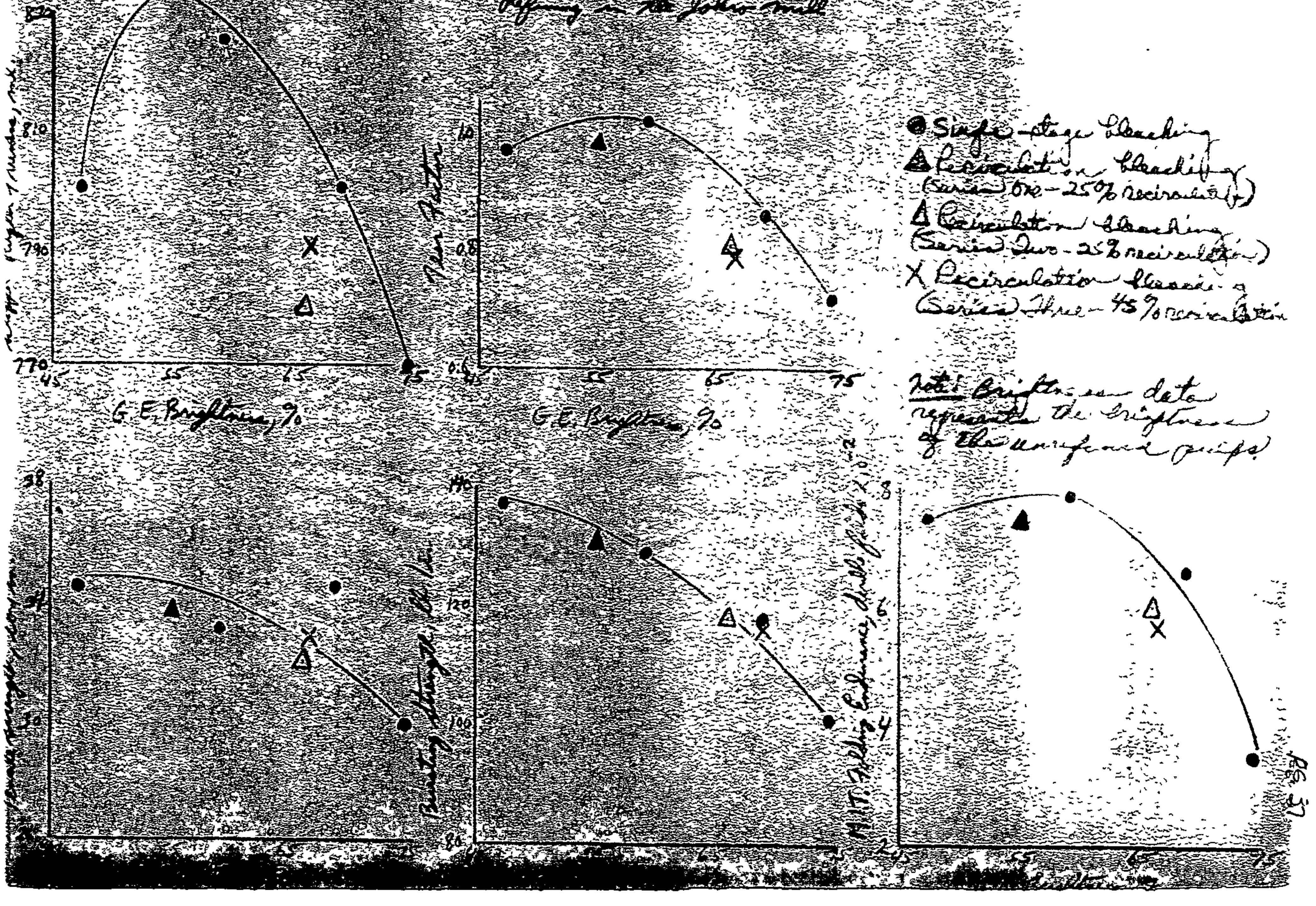
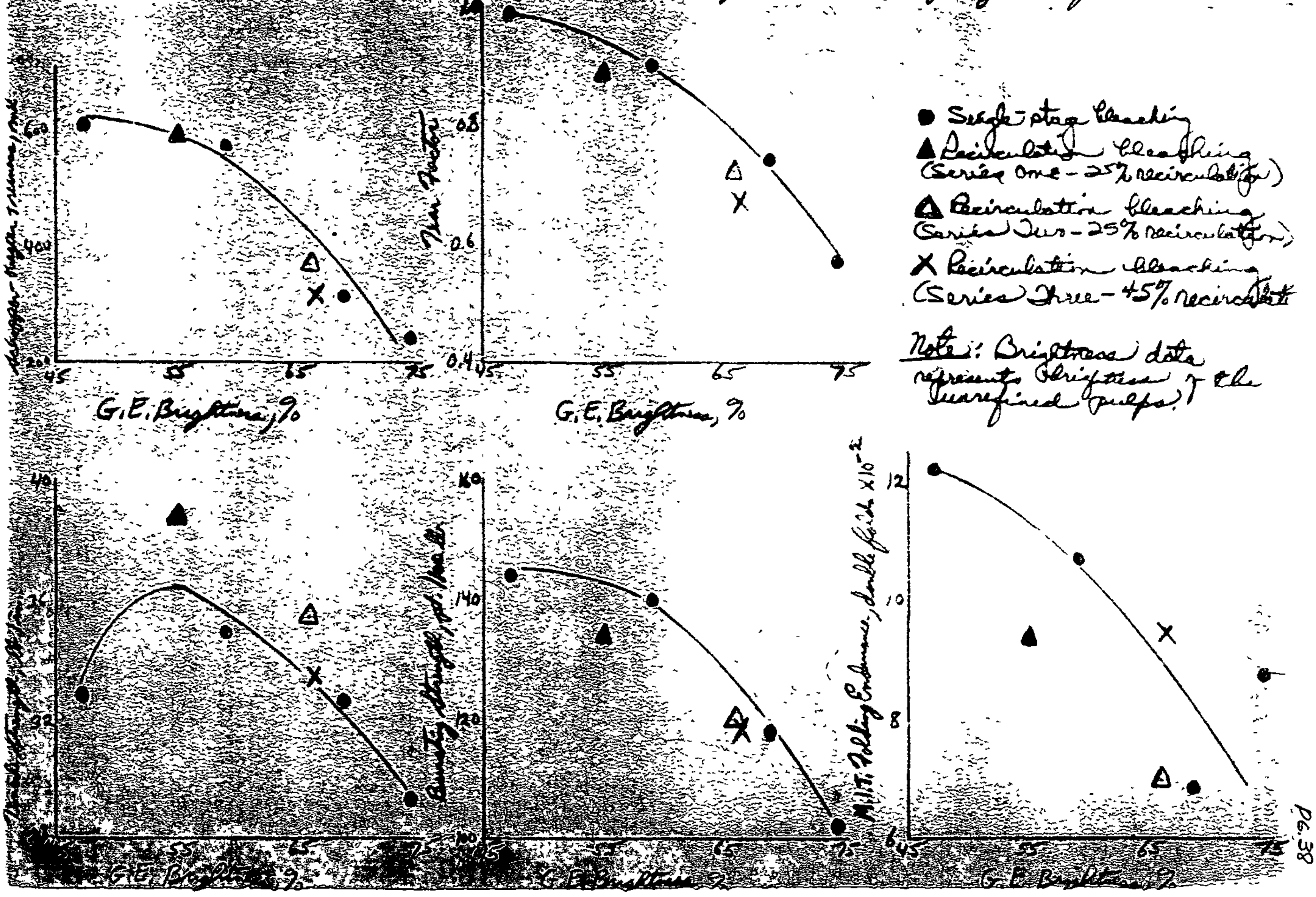


Figure 9

Freeness and Strength Characteristics of Bleached Pulps after 50 minutes Refining in the Jokro Mill



would suggest that the hypochlorite treatments actually degraded and weakened the pulp fibers.

(2) When single-stage and recirculation pulps were refined for equal periods, the pulps bleached by the recirculation technique usually exhibited essentially similar, or lower, freeness and strength properties than single-stage pulps of equivalent brightness levels. Thus the recirculation technique of bleaching did not produce any strength or drainage advantages over the single-stage pulps. In fact, there appeared to be a possibility that the recirculation technique was more detrimental to the strength properties of the pulp than the single-stage process, perhaps because of the somewhat higher hypochlorite applications required to produce equivalent brightness levels in the recirculated pulps.

Since the recirculated pulps did not exhibit any strength advantage over single-stage pulps, it was considered unnecessary to investigate the strength properties of the two-stage bleached pulps--i.e., the experimental strength results presently available would indicate that recirculation bleaching would not be considered as a substitute for a single-stage process. Thus it follows that the substitution of a single-stage process for a two-stage process would prove as desirable, or more desirable, than the substitution of a recirculation process for a two-stage process.

ANALYSIS AND DISCUSSION OF THE EXPERIMENTAL RESULTS

The experimental results of this exploratory work indicated that recirculation bleaching did not produce any better over-all bleaching characteristics or strength properties than the conventional single-stage processes. In fact the recirculation bleaches usually appeared to produce somewhat lower pulp strengths, higher bleaching chemical costs, and longer bleaching time requirements. Improved brightness stability characteristics offset these detrimental effects to some extent, but an over-all consideration of the processes favored the conventional single-stage technique.

The present work was performed with a single type of pulp and within a relatively narrow range of experimental conditions. Consequently, without additional work, it would be impossible to develop generalized or inclusive conclusions regarding the relative value of recirculation bleaching techniques. However, from a practical viewpoint, such additional work would not be warranted unless there was some indication or assurance that specific conditions would exist under which recirculation techniques might prove beneficial or desirable. Thus, before considering further investigations or generalized conclusions, it would be highly desirable to examine the present work and consider the following possibilities:

(1) Could the present work supply any indication of the factors which might govern or influence the bleaching chemical consumption vs. brightness relationship in recirculation bleaches?

(2) Could the present work supply any indication of the factors which caused similar applications of bleaching chemical to produce lower brightness results in the recirculation processes than in the single-stage

processes? Would such factors be present under all experimental conditions or with all types of pulps?

(3) Could the present work supply any information regarding under what conditions recirculation bleaches might produce advantageous and desirable brightness properties?

(4) Could the present work supply any indication of the factors which might be involved in the relative strength characteristics of recirculated and single-stage bleached pulps? Would recirculation bleaches always tend to produce equivalent or weaker pulps than the single-stage process? Under what conditions might a recirculation process exhibit a pulp strength advantage?

Possibilities such as these have been considered in the following analysis and discussion of the experimental data.

CONSIDERATION OF THE GENERAL NATURE OF RECIRCULATION BLEACHING

Under essentially steady state conditions, the charge of pulp for a recirculation bleaching process consists of a complex mixture of different pulp fractions which had been subjected to a varying number of bleaching stages. For the sake of simplicity, however, the mixed charge may be considered to consist of a mixture of the following two components:

Component 1: Unbleached pulp (fresh charge of pulp entering the bleaching process).

Component 2: Bleached pulp (charge of pulp recirculated in the bleaching process).

Thus, under essentially steady state conditions in Series One recirculation bleaches (see Tables I and VI), the charge of pulp could be considered as consisting of 75% of Component 1 (unbleached pulp) and 25% of

Component 2 (recirculated bleached pulp). In this case the recirculated pulp component had already been processed with the equivalent of 5.33% available chlorine (based on the pulp) and an application of 4.0% available chlorine (based on the two component pulp charge) was utilized during the bleaching process. However, this 4.0% application of available chlorine could have been utilized in several different ways. Three examples of different possibilities would be as follows:

Example 1: Both Component 1 and Component 2 may have responded equally to the bleach liquor--i.e., Component 1 may have utilized 4.0% available chlorine (based on Component 1) and Component 2 may have utilized 4.0% available chlorine (based on Component 2). Thus the bleached product could be considered as consisting of a component bleached with 4.0% available chlorine (Component 1), and a component bleached with a total of 5.33 + 4.0% or 9.33% available chlorine (Component 2). [The equivalent available chlorine utilized by the bleached product would, of course, have been 5.33% (based on the two component pulp).[1]]

Example 2: All of the applied available chlorine might have been utilized to bleach only the unbleached portion (Component 1) of the mixed pulp charge. Thus, Component 1 may have utilized 5.33% available chlorine (based on Component 1)[2], and Component 2 may have utilized 0% available chlorine (based on Component 2). Consequently, Component 1 would have been bleached with 5.33% available chlorine and Component 2 would have also been bleached with a total of 5.33 + 0% or 5.33% available chlorine.

[1] 25% of the bleached pulp product would have been processed with 9.33% available chlorine. This would amount to (0.25)(9.33%) or 2.33% avail. chlorine based on the bleached product. 75% of the bleached pulp product would have been processed with 4.0% avail. chlorine. This would amount to (0.75)(4.0%) or 3.0% avail. chlorine based on the bleached product. Total avail. chlorine utilized (based on the bleached pulp product) = 2.33% + 3.0% or 5.33%.

[2] If 4.0% avail. chlorine (based on the two component pulp charge) was applied and utilized by only 75% of the charge, the 75% fraction of the charge would have utilized 4.0%/0.75 or 5.33% available chlorine.

Example 3: Both components may have responded to the bleaching liquor, but the unbleached pulp portion (Component 1) may have responded somewhat better than the bleached portion (Component 2). Such situation would, of course, represent some point of balance between the conditions represented in Examples 1 and 2 above, i.e., the bleached product could be considered as consisting of a Component (Component 1) bleached with more than 4.0% available chlorine, but less than 5.33% available chlorine; and another component (Component 2) bleached with more than 5.33% available chlorine, but less than 9.33% available chlorine. [The exact split in the utilization of available chlorine would naturally have to be of such nature that the equivalent available chlorine utilized by the bleached product would be 5.33% (based on the two component pulp).]

Figures 10 through 12 and Table XI were prepared in an effort to determine which, if any, of these three possible examples might represent the conditions experienced in the experimental work.

Figure 10 represents the bleaching periods required when similar quantities of available chlorine were applied to mixed pulp recirculation charges and single-stage unbleached pulp charges. As indicated by the figure, the recirculation charges, consisting of a mixture of unbleached and bleached pulps, required longer bleaching periods than the single-stage charges, consisting entirely of unbleached pulp. Obviously, these longer bleaching time requirements were due to the presence of the bleached pulp, and they indicated that the bleached pulp component of the recirculation bleaching charges reacted more slowly than the unbleached component. Hence, the response of the unbleached component to bleach liquor was better than the response of the bleached component. Apparently, then, the experimental data did not fit the description of Example 1 above, wherein both the unbleached

Figure 10

Bleaching Periode Required for Utilization of Various Applications of Available Chlorine

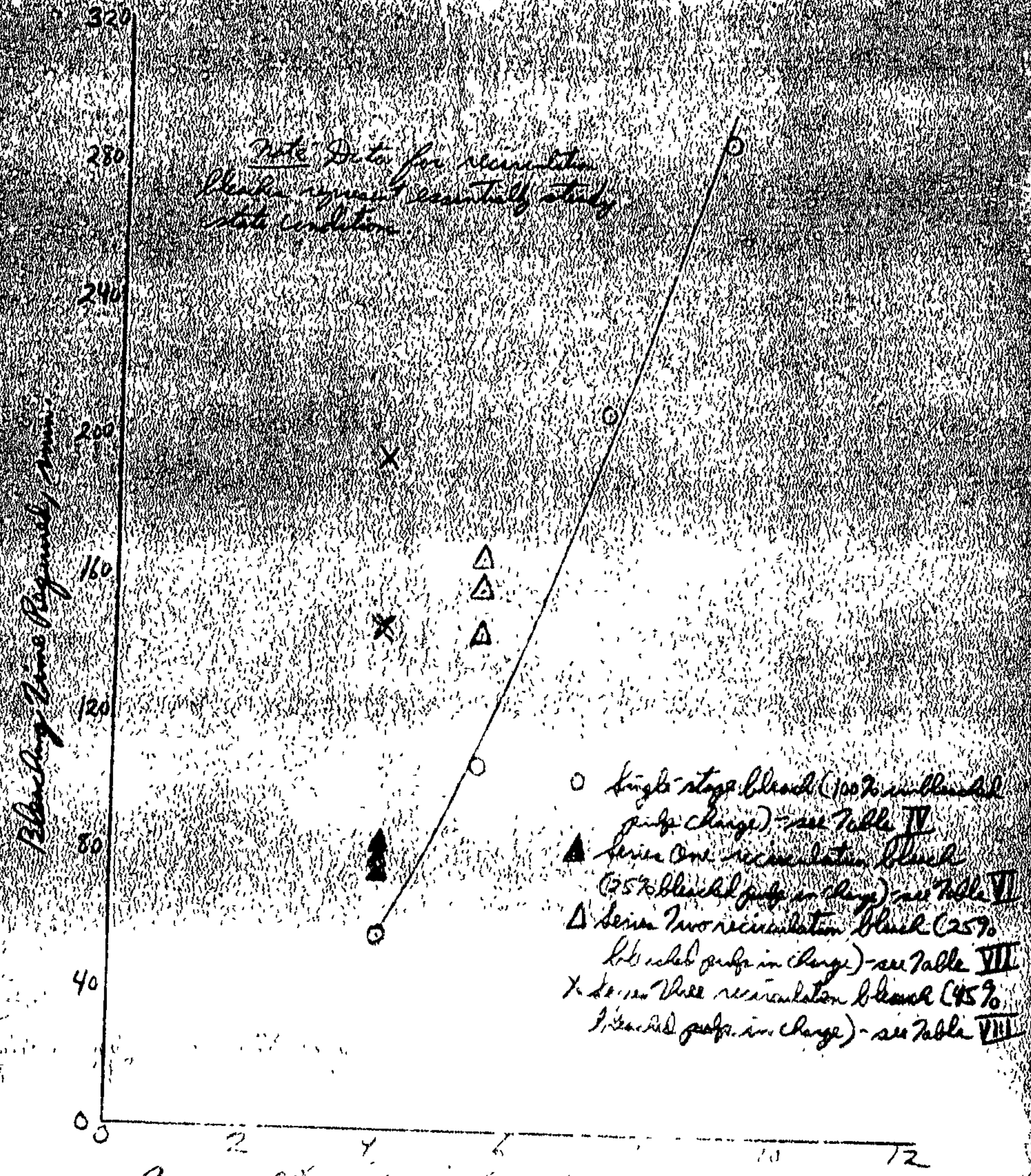


Figure 11

Available Chlorine Concentration Characteristics of Experimental and Equivalent Single-Stage Bleaches

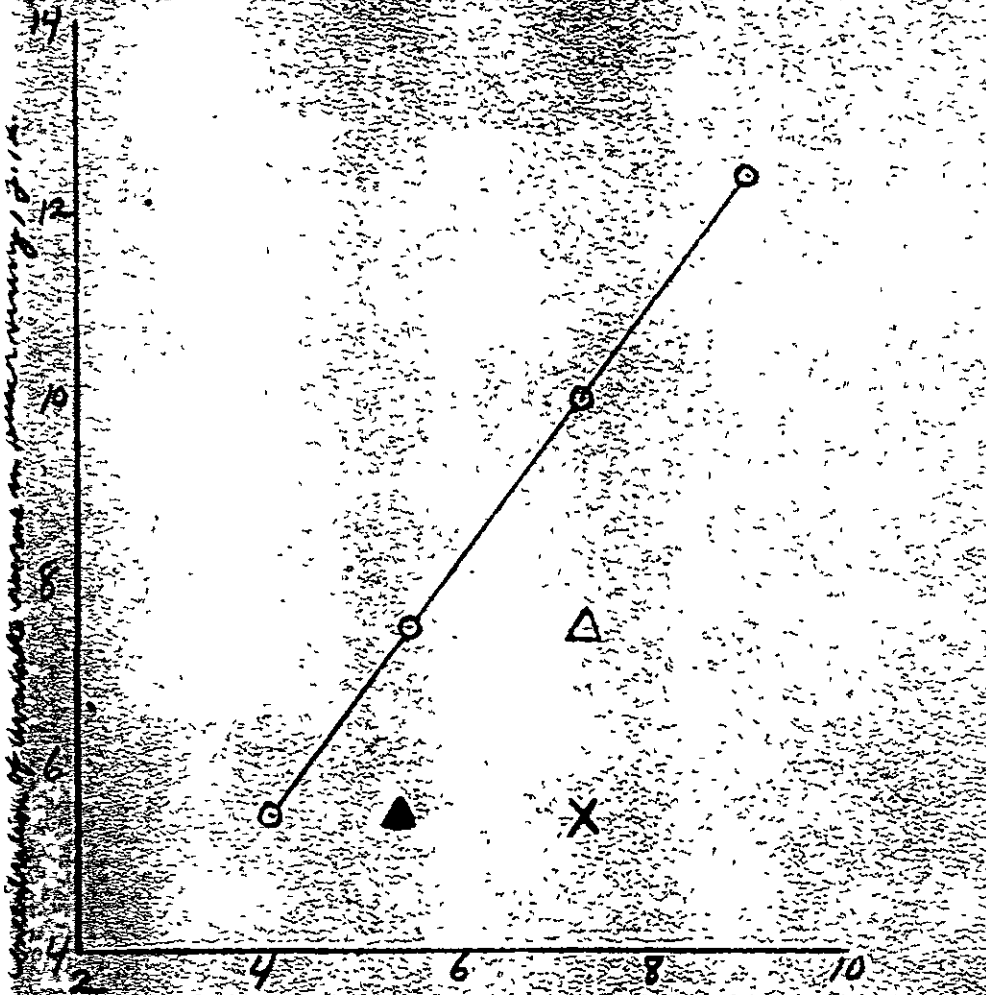
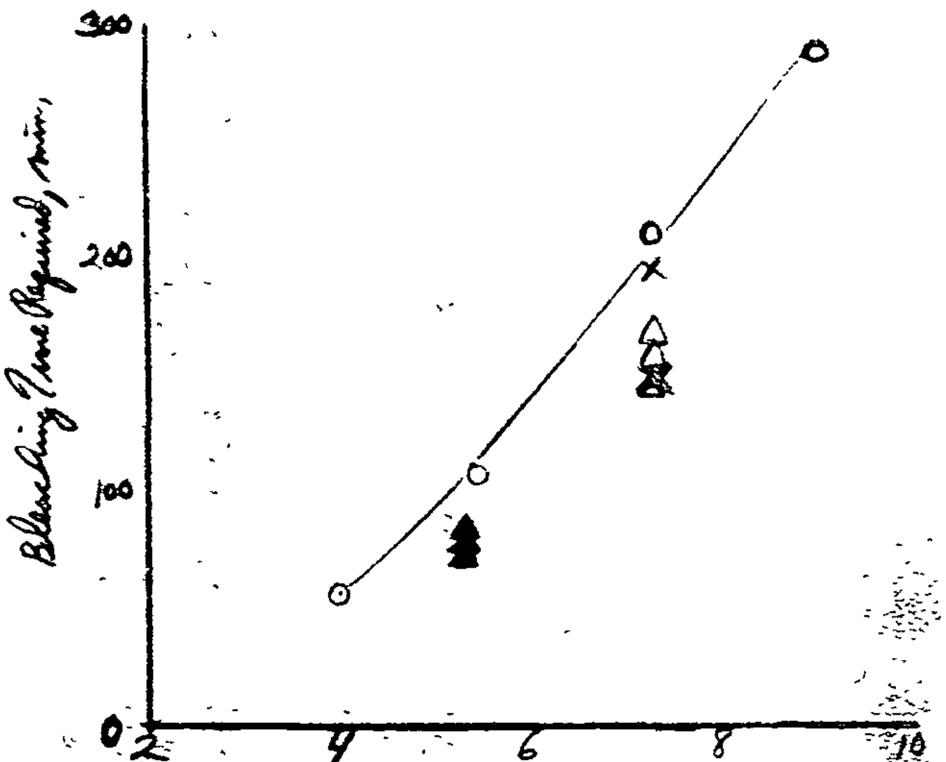


Figure 12

Bleaching Period Requirements for Experimental and Equivalent Single-Stage Bleaches



○ Experimental single-stage bleach (see Table VI)
▲ Equivalent single-stage bleach representing Series One recirculation bleach (see Table XI)
△ Equivalent " " " " Series Two " " (see Table XI)
× Equivalent " " " " Series Three " " (see Table XI)

TABLE XI

Representation of Recirculation Bleaches by Means of Equivalent Single-Stage Bleaches
(These representations were based on the assumption that only the unbleached component of the mixed pulp charge reacted with the bleaching chemical)

	Recirculation Bleach	Equivalent Single-Stage Bleach
Series 1	Unbleached component in mixed pulp charge = 75% Pulp consistency (based on mixed pulp charge)= 12% Concentration of avail. chlorine in bleach slurry = 5.45 g./l. Avail. chlorine applied (based on mixed pulp charge) = 4.0% Bleaching time under essentially steady state conditions = 78, 83, 75 min.	Effective pulp consistency (based on unbleached component of mixed pulp charge) = 9.28%[1]. Concentration of avail. chlorine in bleach slurry = 5.45 g./l. Available chlorine applied (based on unbleached component of mixed pulp charge) = 5.33%[2]. Bleaching time = 78, 83, 75 min.
Series 2	Unbleached component in mixed pulp charge = 75% Pulp consistency (based on mixed pulp charge)= 12% Concentration of available chlorine in bleach slurry = 7.44 g./l. Avail. chlorine applied (based on mixed pulp charge) = 5.45% Bleaching time under essentially steady state conditions: 157, 166, 144 min.	Effective pulp consistency (based on unbleached component of mixed pulp charge) = 9.28% Concentration of avail. chlorine in bleach slurry= 7.44 g./l. Avail. chlorine applied (based on the unbleached component of mixed pulp charge) = 7.27% Bleaching time = 157, 166, 144 min.
Series 3	Unbleached component in mixed pulp charge = 55% Pulp consistency (based on mixed pulp charge)= 12% Concentration of avail. chlorine in bleach slurry = 5.45 g./l. Avail. chlorine applied (based on mixed pulp charge) = 4.0% Bleaching time under essentially steady state conditions = 147, 147, 195 min.	Effective pulp consistency (based on unbleached component of mixed pulp charge) = 6.60% Concentration of avail. chlorine in bleach slurry = 5.45 g./l. Avail. chlorine applied (based on unbleached component of mixed pulp charge) = 7.27% Bleaching time = 147, 147, 195 min.

[1] It was assumed that only the unbleached pulp component of the mixed pulp charge was involved in the bleaching action. Therefore the effective pulp consistency would be based upon the weight of the unbleached pulp and the liquid phase of the slurry--i.e., effective consistency = (100 x wt. of unbleached pulp)/(wt. of unbleached pulp + wt. of the liquid phase of the bleach slurry).

[2] If 4.0% available chlorine (based on mixed pulp charge) was applied and utilized by only 75% of the charge, the unbleached 75% of the charge would have utilized 4.0%/0.75 or 5.33% avail. chlorine (based on the unbleached component of the mixed pulp charge).

and the bleached components of the charge responded equally well toward the bleach liquor.

Conceivably, the description presented under Example 2 above might fit the experimental data--i.e., the applied available chlorine might have been completely utilized by the more responsive unbleached pulp component in the mixed pulp recirculation bleach charges.

This contention was checked in the following manner:

(1) It was reasoned that, if only unbleached portions of the mixed pulp charges responded to the hypochlorite bleach liquor, the recirculation bleaches would actually constitute conventional single-stage bleaches. Thus, in such situation, the recirculation bleaches could be truly defined and represented by the equivalent single-stage bleaches presented in Table XI.

(2) In Figures 11 and 12, the equivalent single-stage bleaches presented in Table XI were compared with actual experimental single-stage bleaches. The purpose of this comparison was to determine whether the pseudo single-stage bleaches actually possessed characteristics which were typical of real single-stage processes involving only unbleached pulp--i.e., to determine if the recirculation bleaches could be represented by single-stage unbleached pulp bleaches, and hence, to determine whether the bleaching liquor did react with only the unbleached component of the mixed pulp charge.

(3) Table XI and Figure 11 indicate that the pseudo single-stage bleaches possessed lower effective pulp consistencies, and hence lower concentrations of bleaching chemical at a given level of available chlorine application. Consequently, it would be expected that the pseudo single-stage bleaches would require longer bleaching periods than the actual single-stage bleaches.[1]

[1] If all other factors remain constant, the bleaching rate generally decreases with a decrease in the concentration of bleaching chemical in the pulp slurry.

Figure 12, however, indicates that equal applications of available chlorine resulted in shorter bleaching periods for the pseudo bleaches. This inconsistent effect would, of course, indicate that the recirculation bleaches could not be truly represented or defined by a single-stage bleaching action on unbleached pulp, i.e., the shorter bleaching periods would indicate that the recirculation bleaches did not behave as bleaches involving only unbleached pulp, but that the bleaching chemical was utilized by both the unbleached and the bleached component of the mixed pulp charge.

Apparently, then, the experimental data did not fit the description of Example 2 above, but they did fit the description of Example 3--i.e., both the unbleached and bleached components of the mixed pulp recirculation bleaching charges responded to the bleaching chemical, although the unbleached component responded better.

SIMPLIFIED REPRESENTATION OF A RECIRCULATION BLEACHING PROCESS

Consider a recirculation bleaching process in which 25% of the bleached pulp component is recirculated and 4.0% bleach is applied in each pass. Then, the bleached pulp product would consist of a pulp which had been processed with the equivalent of 4.0%/0.75 or 5.33% bleach.

Previous discussions would indicate that the charge for such recirculation bleaching process would consist of a complex mixture of different pulp fractions which had been subjected to a varying number of bleaching stages. However, in the interest of simplicity, this charge may be considered as a mixture containing an unbleached pulp component, and a bleached pulp component previously processed with the equivalent of 5.33% bleach.

During the bleaching process, the unbleached component of the charge would be bleached with a quantity of bleach somewhere between 4.0 and 5.33% (based on the unbleached pulp component). Previous discussions would also indicate that the bleached component would be bleached with a quantity of bleach less than 4.0% (based on the bleached pulp component). Thus, the bleached pulp component, which had already been processed with 5.33% bleach prior to the treatment, would be ultimately bleached with a total quantity of bleach greater than 5.33% (based on the bleached pulp component), whereas the unbleached component would be bleached with less than 5.33% bleach (based on the unbleached pulp component). Also, the over-all mixed pulp product would have been processed with the equivalent of 5.33% bleach.

Thus, the pulp product leaving a recirculation bleaching process may be considered as a mixture having the following composition:

(1) A single-stage treated pulp bleached with "A"% bleach.

(2) A combination of various multi-stage treated pulps bleached with the equivalent of more than "A"% bleach.

Since the pulp components utilized different amounts of bleach, it would appear that they would also attain different brightness levels. Thus, the product from a recirculation bleaching process would consist of a mixture of pulps bleached to different brightness levels. Consequently, a more complete understanding of the experimental results may perhaps be obtained from a consideration of some of the effects produced when pulps of different chemical consumption and brightness characteristics are mixed.

CONSIDERATION OF THE CHARACTERISTICS OF BLEACHED PULP MIXTURES

Figure 13 denotes a typical pulp brightness and bleaching chemical demand curve. Bleached pulp "P" in this figure represents a single-stage treated pulp bleached to a G.E. brightness level of 40% with 3.5% bleach, while pulp "Q" represents a pulp bleached to a brightness level of 50% with 5.0% bleach.

If the brightness characteristics of these two bleached pulps were directly additive, any mixture of the pulps would exhibit brightness properties and equivalent bleach demand characteristics which would fall on line "P-Q" in Figure 13. Thus, a mixture containing 70% of Pulp "P" and 30% of Pulp "Q" would be represented by mixture "O" in Figure 13.

In this case:

Brightness of mixture "O" = (brightness of Pulp "P") (0.70) + (brightness of Pulp "Q") (0.30) = (40%) (0.70) + (50%) (0.30) = 43%

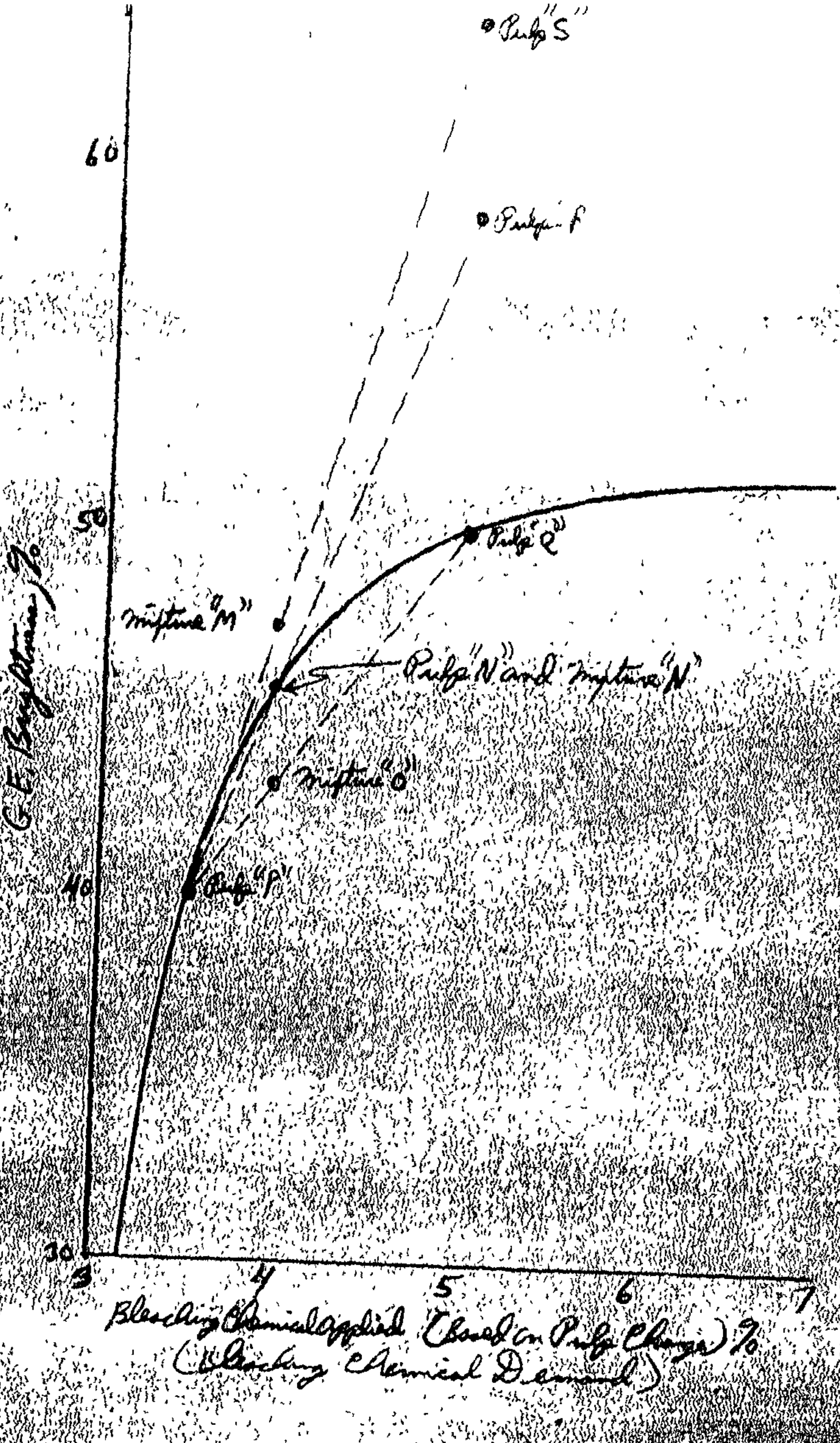
and:

Equivalent bleach demand for mixture "O" = (Bleach demand for Pulp "P") (0.70) + (Bleach demand for Pulp "Q") (0.30) = (3.5%) (0.70) + (5.0%) (0.30) = 3.95%.

Thus, a mixture of 70% Pulp "P" and 30% Pulp "Q" would require a bleaching chemical utilization of 3.95% and exhibit a brightness of 43.0%. As indicated by the figure, however, a single pulp could have been bleached to a brightness of 45.7% with the same bleaching chemical application of 3.95% (see Pulp "N" in Figure 13). Consequently, the preparation of the pulp mixture would prove to be less efficient and satisfactory than the preparation of the single stage bleached pulp.

In this illustration, the pulp mixture consisted of two single-stage treated pulps; however, it may be seen that the same principles would apply if one of the bleached pulps in the mixture had been a multi-stage bleached pulp. As an example, assume that the 5.0% of bleaching chemical were used in a multi-stage process to produce the higher brightness Pulp "R" rather than Pulp "Q." Then a mixture of 70% Pulp "P" (brightness = 40%) and 30% of Pulp "R" (brightness = 58.6%) would produce mixture "N" having a brightness of 45.7% and an equivalent bleach demand of 3.95%. Such mixture would be equally as effective as a

Typical Pulp Brightness vs. Chemical Demand Curve



a single pulp bleached with 3.95% bleaching chemical (see Pulp "N" in the figure). However, had the multi-stage process produced a pulp with a lower brightness than Pulp "R" (lower than 58.6%), the preparation of the same mixture would have proved less effective than the preparation of a single pulp bleached by a single-stage process. If, on the other hand, the multi-stage process produced a pulp with a higher brightness than Pulp "R" (see Pulp "S"), the preparation of the mixture would have been more efficient and satisfactory than the preparation of a single pulp bleached by a single-stage process (see mixture "M" and Pulp "N").

Pulp mixtures of this type would tend to somewhat parallel the situation produced in recirculation bleaches, where the bleached product consists of a mixture of a single-stage treated pulp (bleached with a relatively low chemical application) and a combination of multi-stage treated pulps (bleached with a higher chemical application). Thus, at a given level of bleaching chemical utilization, the recirculation bleaching process could conceivably produce bleached pulps of lower, equivalent, or higher brightnesses than produced by conventional single-stage processes (see Figure 13). Also, one of the factors influencing the relative brightness characteristics of single-stage and recirculation bleaches would be the extent of brightness increase produced when a pulp is subjected to a multi-stage rather than a single-stage process (see Figure 13, particularly Pulps "F" and "S" and mixtures "M" and "N").

The previous analysis of pulp mixtures presented in Figure 13 was made in a region where the slope of the brightness vs. bleaching chemical demand curve progressively decreased. Actually, as indicated by Figure 14, there are usually three general regions in a brightness vs. bleaching chemical demand curve; a region of constant slope, a region of decreasing slope, and a region of zero slope.

Figure 14

Different Regions in a

Typical Pulp Brightness vs. Chemical Demand Curve

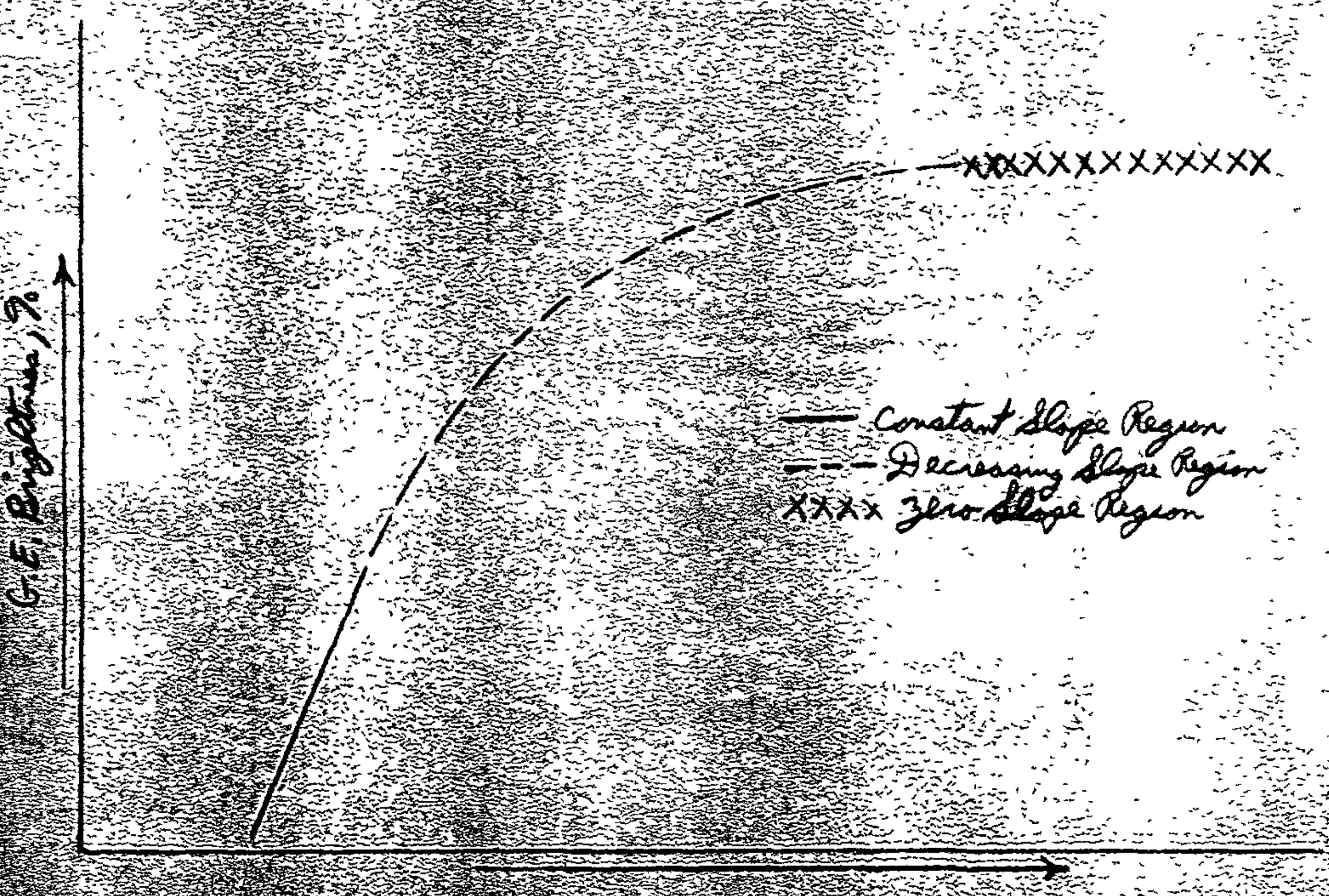


Figure 15 represents the same type of analysis as Figure 13. In this case, however, the analysis was made in the constant slope region of the brightness *vs.* bleaching chemical demand curve, whereas the analysis involving Figure 13 was made in the region of decreasing slope. Likewise, Figure 16 represents the same type of analysis as Figures 13 and 15. In this case, however, the analysis was made in the zero slope region of the brightness *vs.* chemical demand curve.

On the basis of previous discussions and Figures 13 through 16, it would appear that:

(1) The analysis of pulp mixtures presented in Figures 13, 15, and 16 parallel the situation produced in recirculation bleaching.

(2) At a given level of bleaching chemical utilization, the recirculation bleaching process could produce bleached pulps of higher, equivalent, or lower brightnesses than produced by conventional single-stage processes.

(3) If a given application of chemical produces the same brightness characteristics in both a single-stage and a multi-stage process, the pulp would not exhibit better brightness characteristics when bleached by a recirculation process rather than a conventional single-stage technique.

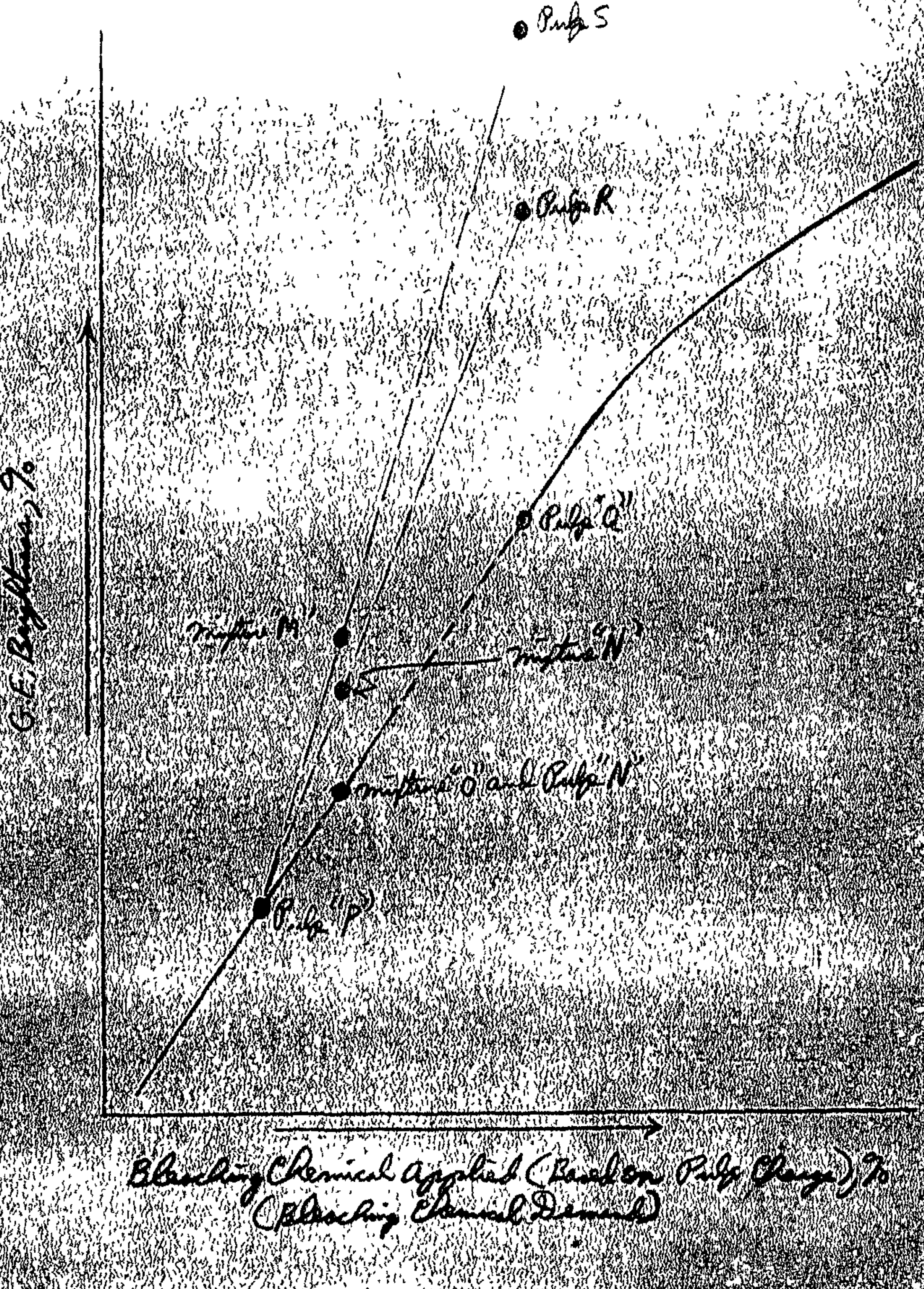
(4) Pulps which exhibit brightness increases when bleached by a multi-stage process, rather than a single-stage process, would not necessarily tend to exhibit better brightness characteristics when bleached by a recirculation process, rather than the conventional single-stage technique.

(5) The ability to produce better brightness results with a recirculation bleach rather than a single-stage bleach would partially depend upon the brightness differential the pulp exhibits when bleached by single-stage and multi-stage processes. An increase in this differential would tend to improve the chances that a recirculation bleach would produce better brightness characteristic than a single-stage bleach.

FIGURE 15

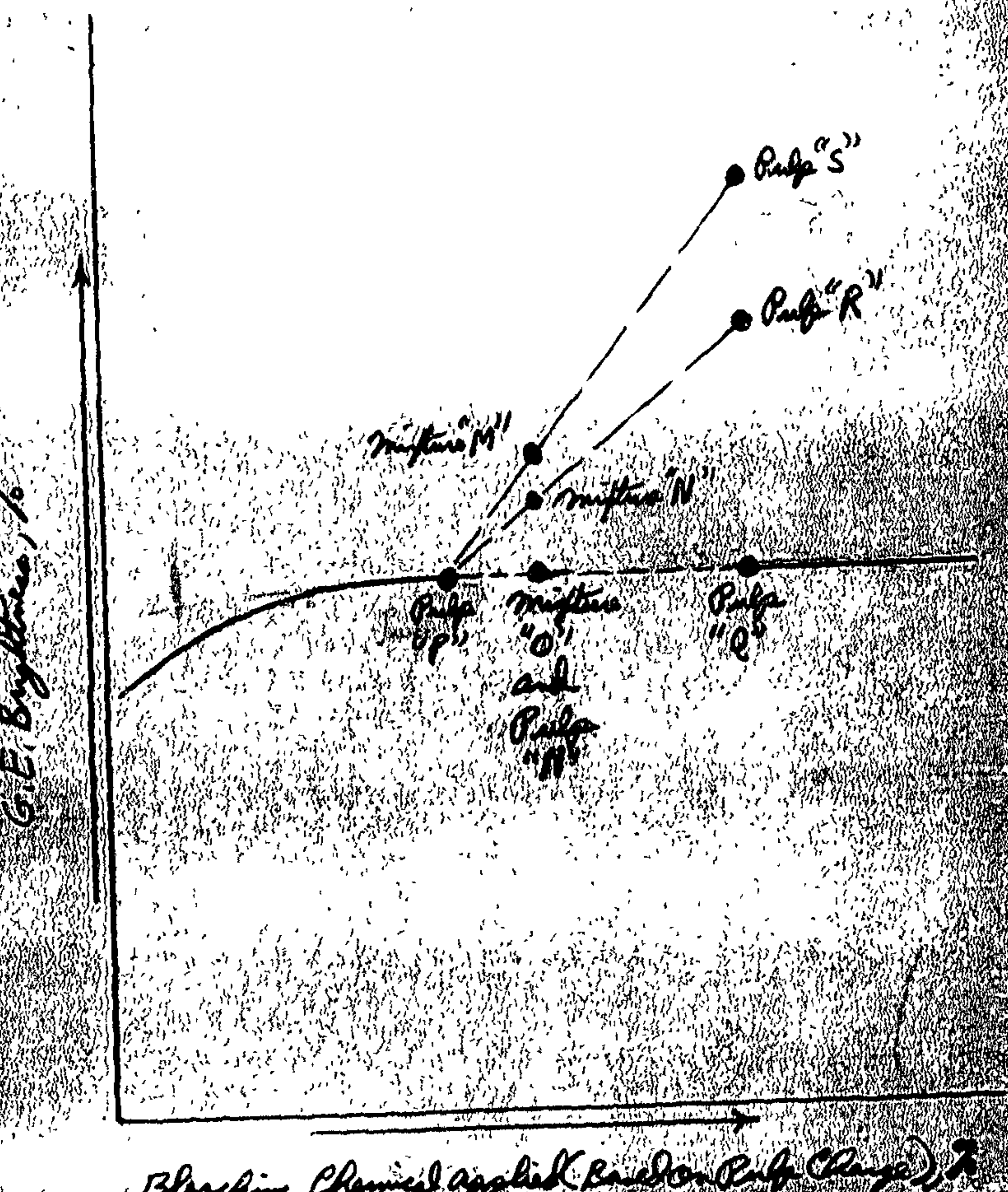
Typical Pulp Brightness vs. Chemical Demand Curve

(Pulp Mixture Analyses in Constant Slope Region of Curve)



Typical Pulp vs. Chemical Demand Curve

(Pulp Mixture Analysis in Zero Slope Region of Curve)



(6) The ability to produce better brightness results with a recirculation bleach would partially depend upon the region of the brightness <u>vs</u>. chemical demand curve in which the bleaches were conducted. In general, recirculation bleaches would seem to have an improved chance of producing better brightness results than single-stage bleaches if the bleaches were conducted in the constant slope or zero slope regions of the curve rather than in the region of decreasing slope.

(7) The ratio of pulp recirculated in a recirculation operation would be expected to influence the relative brightness characteristics obtained with recirculation and conventional single-stage bleaching processes. Very little experimental information was obtained on this factor, but it would appear that increased recirculation ratios would tend to produce more favorable results with the recirculation process.

(8) The actual split in bleaching chemical utilization between the single-stage treated component and the multi-stage treated component of the bleached pulp product would be expected to influence the brightness results obtained with recirculation bleaches. Likewise, such split would influence the relative brightness characteristics produced with recirculation and conventiona single-stage processes. In the present work, no numerical values could be obtained for this split in bleaching chemical, and consequently possible detailed effects could not be thoroughly analyzed. (It was possible, however, to determine the relative quantities utilized by each of the pulp components in the recirculation charge.)

It should be pointed out that the preceding analysis of pulp mixtures (see Figures 13, 15 and 16) was based on the assumption that the brightness characteristics of two bleached pulps in a mixture were directly additive.

This assumption, however, does not strictly apply in actual practice--i.e., work by Foote (1), as well as MacLaurin and Aflenzer (2), indicates that actual mixtures of dissimilar brightness pulps would exhibit brightness characteristics which would be somewhat lower than those calculated by the additive technique used in these discussions. This fact would, of course, not alter the general nature of the brightness characteristics of pulp mixtures developed in this report. It would, however, affect exact numerical relationships. Thus, although the direct addition technique was a simplified approach for characterizing the brightness characteristics of mixtures, it was sufficiently accurate and adequate for the present discussions. It should be noted, however, that a more accurate treatment of mixtures would perhaps be possible through the use of the empirical relationships employed by Foote, MacLaurin, and Aflenzer .

CONSIDERATION OF CONDITIONS UNDER WHICH RECIRCULATION BLEACHING MIGHT PROVE ADVANTAGEOUS OR DISADVANTAGEOUS

On the basis of previous considerations, it would appear that:

(1) Recirculation bleaching might tend to produce advantageous brightness and chemical consumption characteristics under the following conditions:

(a) When the pulp exhibits a large brightness differential between multi-stage and single-stage bleaching operations.

(b) When the bleaching takes place in the constant slope region of the brightness vs. chemical demand curve.

(c) When the bleaching takes place in the zero slope region of the brightness vs. chemical demand curve.

(2) When employing a strength degrading bleaching agent (such as hypochlorite), recirculation bleaches would tend to produce advantageous brightness and strength results under the same conditions listed in (1) above--i.e., in this

case, the attainment of a given brightness with less chemical would automatically tend to result in better strength characteristics at the given level of brightness.

(3) Perhaps no strength advantage s would tend to result when using non-degrading bleaching agents (such as chlorine dioxide and peroxides) in recirculation bleaches, but brightness and chemical consumption advantages might result under the conditions listed in (1) above.

(4) In a recirculation bleach, the bleaching agent tends to react faster with the unbleached components and slower with the more highly bleached components. This action has a tendency to level out the action of the treatment on the various portions of pulp. A complete leveling action is, of course, not obtained, but the effects appear to be sufficient to prevent the attainment of drastically different <u>balances</u> between the different properties in recirculation processed pulps and in single-stage processed pulps. As stated before, however, different levels of strength properties could apparently be attained at a given brightness level.

(5) Recirculation bleaches might tend to exhibit detrimental brightness and chemical consumption characteristics under the following conditions:

(a) When the pulp exhibits a low brightness differential between multi-stage and single-stage bleaching operations.

(b) When the bleaching takes place in the decreasing slope region of the brightness <u>vs.</u> chemical demand curve.

(6) When using a degrading bleaching agent in a recirculation bleach, the conditions listed in (5) above might also tend to produce detrimental strength results at a given level of brightness.

CONCLUSIONS

(1) The recirculation bleaches investigated in the exploratory work tended to produce somewhat lower pulp strengths, higher bleaching chemical costs and longer bleaching time requirements than conventional single-stage bleaches. Improved brightness stability characteristics offset these detrimental effects to some extent, but an over-all consideration of the processes did not favor the recirculation technique.

(2) An analysis of the experimental data indicated a possibility that, under certain conditons, recirculation bleaching might prove more advantageous than conventional single-stage bleaching, whereas, under other conditions, the conventional single-stage bleaching processes would tend to prove more advantageous than the recirculation bleaching techniques.

(3) The relative advantagessand disadvantages of recirculation bleaches might depend upon such factors as the extent of the brightness differential exhibited when the pulp is bleached by multi-stage processes rather than a single-stage process, the shape of the brightness vs. chemical demand curve for the pulp, and the level of bleaching chemical applications employed.

(4) It is apparent that recirculation bleaching would not tend to prove universally beneficial. Also, further work would be required to substantiate whether recirculation bleaching techniques might tend to prove advantageous in certain situations, and under certain specific experimental conditions. Experimental conditions which might prove suitable for such further work have already been determined from the completed work, and consequently it would appear that at least a limited amount of additional work might be warranted.

FUTURE WORK

According to the results of the present work, there appeared to be a possibility that a recirculation bleaching action would prove advantageous when the bleaching action is performed in the constant slope or the zero slope portions of the brightness *vs.* chemical demand curve. Consequently, it is suggested that further work be done in at least one of these areas. Work in both of these areas might prove to be of commercial significance and interest. It would appear, however, that work in the zero slope area might tend to hold the most immediate interest, particularly in view of the current demands and trends toward ever increasing brightness levels.

If recirculation bleaches actually proved advantageous in the zero slope region, it might indicate a method for increasing the brightness ceiling in a present process without the full cost of one or two additional stages. Consequently, it is suggested that further work be performed along the lines of the following outline:

(1) Subject a bleachable grade of kraft pulp to chlorination and caustic extraction treatment stages.

(2) Perform a number of small-scale bleaches with chlorine dioxide and obtain the brightness *vs.* chemical demand curve for this third stage chlorine dioxide treatment (see Figure 17 for an illustration of the type of curve expected in this work.)

(3) Select the point on the curve where brightness starts to level off (see Point "A").

(4) Prepare a number of third stage chlorine dioxide bleaches at this point (Point "A"). Combine the pulps, caustic extract them, and perform two or three fifth-stage chlorine dioxide bleaches (see Points "B,", "C" and "D" in

Figure 17

Illustrative Bleaching Curves for Chlorine Dioxide Treatments

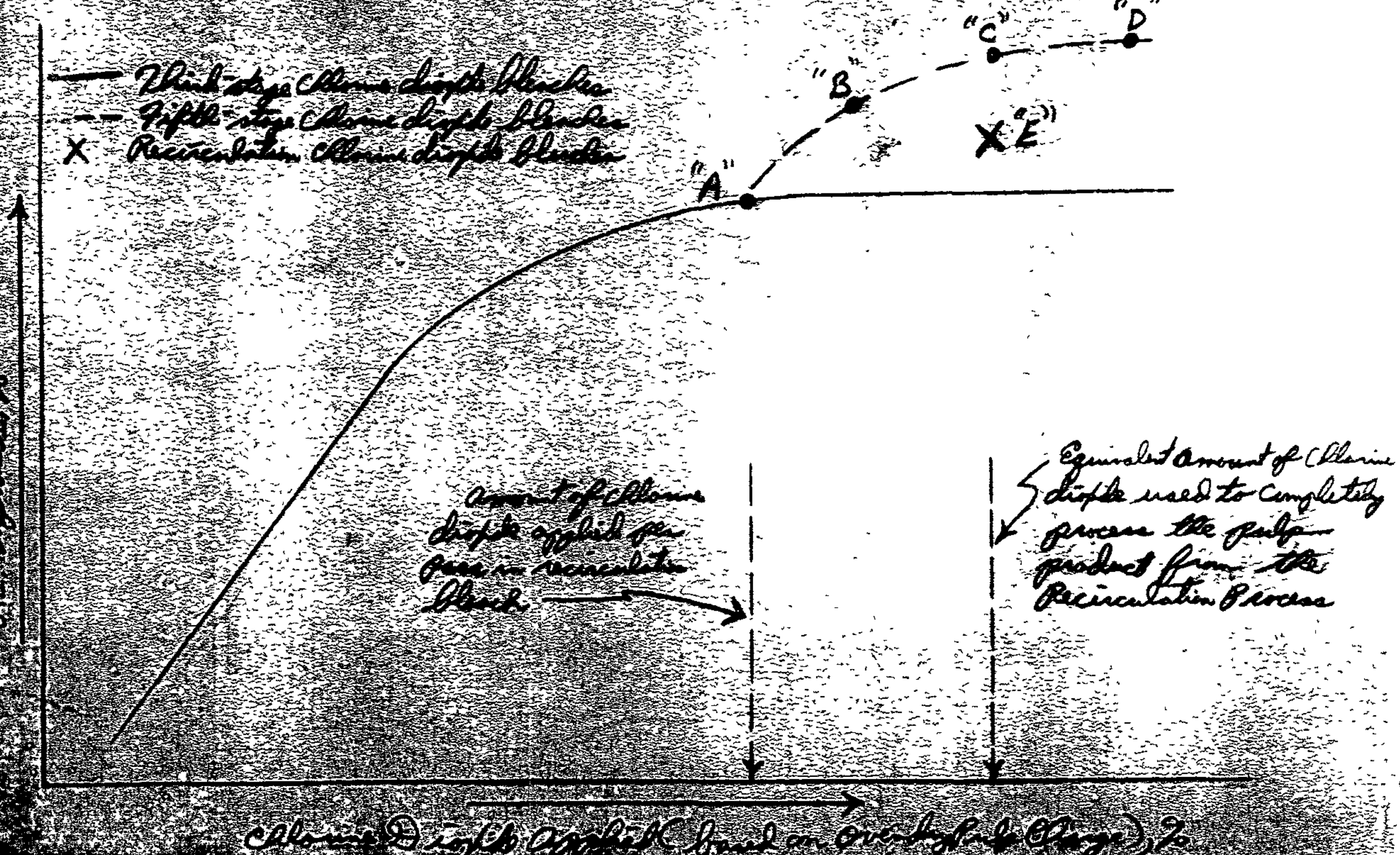


Figure 17).

(5) Perform 8 passes of a recirculation bleach in which 25% of the bleached pulp product is recirculated. In each pass apply the amount of chlorine dioxide indicated by point "A" and caustic extract the recirculated portion of the charge before it enters the bleaching process.

(6) An advantage would be indicated for the recirculation technique if it produced a brightness level above that obtained in the third stage chlorine dioxide stage (see point "E" in Figure 17). The quality characteristics and economics of the three-stage, five-stage, and recirculation bleaching techniques could then be compared and the possible desirability of a recirculation technique evaluated.

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(2) MacLaurin, D. J., and Aflenzer, F. A. Predicting the brightness of groundwood-sulfite pulp mixtures. Tappi 37, no. 9:388-392(Sept., 1954).