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The Effect of Chlorine, Hypochlorite, and Chlorine Dioxide Bleaching on the Hemicellulose Content of Pulp

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THE EFFECT OF CHLORINE, HYPOCHLORITE, AND CHLORINE DIOXIDE BLEACHING ON THE HEMICELLULOSE CONTENT OF PULP

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Introduction

Until the recent time hemicelluloses were regarded as an undesirable part of the cellulose fiber; the most desirable fiber for paper-making purposes was believed to be one containing 100% pure cellulose. This theory is fallacious, since it is now known that hemicellulose plays a major role in paper-making and in fact, a satisfactory paper cannot be formed from wood pulp without some hemicellulosic material being present. The best pulp is one which has been cooked to remove most of the lignin, but not so drastically cooked as to degrade the cellulose or remove too much of the hemicellulose fraction. Such a pulp will beat easily and have good strength characteristics, because a high proportion of the rapid beating hemicelluloses are left in the pulp. Because of the relationship between hemicellulose content and paper-making qualities of the pulp and also because of the economic factors involved, pulp chemists have turned their attention to the production of pulps containing the highest possible proportion of the carbohydrate constituents of the origianl wood.(1) Since the hemicelluloses are such an important part of the paper-making material it is desirable to determine their fate during bleaching. This is especially true since

the trend in modern paper-making is to obtain a brighter and stronger pulp and paper.

History

There have been no publications in the past concerned mainly with the effect of bleaching on the hemicellulose content of the pulp. All of the literature cited pertains to the problem, and the findings are probably valid. However, the results on the bleaching of hemicelluloses were reported as a by product of research which was concerned with other aspects of the bleaching process.

Effect of Chlorination on Hemicellulose

Richard H. Boehm(2) in a study on the effect of chlorination on the carbohydrate fraction of aspen, neutral sulfite semi-chemical pulp, says that the total loss of carbohydrate material during chlorination is exceedingly small. The loss in his case was within the experimental error of the methods used. Boehm(2) states that there is no change in the absolute amounts of either the alkali resistant cellulose or the hemicellulose.

The differences of opinion on the loss of hemicellulose is shown in the article written by A. G. Norman(3). He believes that the chlorination of wood

in an aqueous media releases hemicelluloses, a considerable portion of which is soluble in water. These hemicelluloses are therefore of no use in paper-making as they will be lost upon washing the pulp. This idea is substanciated by Trivedi(4) who states that the removal of lignin with chlorination bleaching releases water soluble hemicelluloses which consequently cannot be retained.

Effect of Hypochlorite Bleaching on Hemicellulose

There is little literature available which shows any direct conclusions as to the effect of hypochlorite bleaching on the hemicellulose content of pulp. It is thought however that hypochlorite does severely oxidize the carbohydrates in wood. This idea is presented by F. Loeschbrandt(5), Raschbach and Yorston(6) and Swartz and coworkers(7). The amount of this degradation which pertains to the hemicellulose alone is not made clear in any of these articles however.

According to Bjorkqvist and coworkers(8) however, polyuronic acids and pentosans are not removed by the hypochlorite bleaching process.

Wise(9) states that the degradation of carbohydrates by hypochlorite can be eliminated by dividing the bleaching operation into several stages. A direct counter diction of this idea is expressed by Loeschbrandt(5) who says

that degradation is accompanied with hypochlorite bleaching even when multi-stage processes are used. He says the decrease in strength properties of a pulp bleached in a multi-stage treatment including chlorination, caustic extraction, and a hypochlorite stage, seems to be principally associated with the final hypochlorite stage. A third idea given by Coster and Vincent(10) states that if the pulp is over bleached with hypochlorite you may possibly get a hemicellulose increase. Over bleaching in one case caused the alpha cellulose content to decrease from 88 to 85% while the beta cellulose was increased from 4 to 8%.

Effect of Chlorine Dioxide Bleaching on Hemicellulose

According to Samuelson and Ramsel(11) there is practically no change in the viscosity, copper number, or hot solubility of a pulp bleached with chlorine dioxide under normal conditions. This statement would tend to support the theory that chlorine dioxide does not degrade wood pulp to any extent when normal conditions are used.

Staudinger and Jurisch(12) while doing bleaching experiments on cotton fibers came to the conclusion that chlorine dioxide was the least degrading of all the chlorine bleaches. Their experiment included the use of chlorine, hypochlorite, and chlorine dioxide bleaches.

Although chlorine dioxide is considered by most bleaching experts to be milder than most processes, we again do not have any direct literature to cite. All of the work done in the past on degradation was done using viscosity or copper number measurements. None of the literature gives any figures pertaining to the effect of chlorine dioxide on the hemicelluloses of wood pulp.

EXPERIMENTAL PROCEDURE

Type of Pulp Used:

The pulp used throughout this thesis is a hardwood (Aspen) cold soda pulp. This pulp was chosen for several reasons. Since the work is concerned mainly with the fate of hemicellulose during bleaching, a pulp with a high hemicellulose content was needed to reduce the experimental error. Cold soda pulp, with a pulping yield of 90+, has almost all of the original hemicellulose present. The rising interest in cold soda and other similar chemi-mechanical pulps makes experimental work of this type practical for industrial use.

Lignin in Original Pulp.

The lignin content of the unbleached cold soda pulp was determined by difference. Using Tappi Standard T-9m54, the lignin was removed with repeated chlorinations and monoethanolamine extractions. The remaining holocellulose was then weighed and this weight was subtracted from the original weight to obtain the amount of lignin removed. From this value the percent of lignin was calculated.

Alpha, Beta, and Gamma Determination.

The alpha, beta, and gamma celluloses were determined by Tappi Standard T-203m58. This standard is based on the fact that alpha cellulose is insoluble in 17.5% NaOH at 20°C. The beta and gamma celluloses are soluble under these conditions, however, with the beta cellulose being able to reprecipitate when acidified. The holocellulose from the lignin determination is therefore treated with the 17.5% NaOH for forty-five minutes. After this time the pulp is filtered through a fritted crucible,,and the alpha cellulose retained in the crucible is washed and dried. The filtrate is used to determine the beta and gamma celluloses by titrations. The beta and gamma celluloses are determined in two separate titrations. One gives the beta and gamma celluloses combined. The other gives just the gamma cellulose after the betas have been acidified and removed. The beta cellulose is then calculated by difference.

Bleaching with Chlorine.

In order to obtain results that may be correlated, the three bleaching processes should be performed under their optimum conditions. The conditions used for the chlorination are as follows:

Temperature----------20°C

p.H.----------2.0

Consistency----------3%

Time----------65 minutes

Although consistencies higher than 3% are preferred with all of the bleaches used, 3% was used because of the ease of handling in the laboratory equipment which was available.

The pulp was bleached using 50% and 100% of the equivalent bleach requirement as obtained from the Tappi conversion table of permanganate number verses bleach requirement.

The bleaching yield was determined after the bleaching. A brightness hand sheet was then made. The percent of alpha, beta, and gamma celluloses was determined by Tappi T-203m58 as previously described. The percentages obtained were multiplied by the bleaching yields to convert the alpha, beta, and gamma celluloses to a basis of the original pulp.

Bleaching with Hypochlorite.

The pulp was again bleached using 50% and 100% of the equivalent bleach requirement. This time it was in terms of hypochlorite bleach.

The conditions used for each bleach with the hypochlorite are as follows:

Temperature----------40°C

p.H.----------9.0

Consistency----------3%

Time----------65 minutes

The bleaching yield and brightness of the bleached pulp was again determined. The alpha, beta, and gamma celluloses were then determined and converted to the original pulp basis.

Bleaching with Chlorine Dioxide.

The pulp was bleached using 50% and 100% of the equivalent bleach requirement in terms of chlorine dioxide.

Chlorine dioxide is a reddish gas which has an irritating odor. It is highly explosive and when concentrated will explode in air. It also explodes when it comes into contact with certain organic materials or oxidizable substances. For these reasons it is desirable to generate the chlorine dioxide directly into the reaction vessel in order to reduce the hazards involved. This was accomplished in this case by acidifying sodium chlorite with hydrochoric acid.

$$5NaClO_2 + 4HCL \longrightarrow 4ClO_2\uparrow + 5NaCL + 2H_2O$$

The bleaching conditions used for the chlorine dioxide bleach are as follows:

Temperature----------70°C

p.H.----------4.0

Consistency----------3.0%

Time----------65 minutes

The bleaching yield and bleached brightness were determined along with the alpha, beta, and gamma celluloses as previously explained.

EXPERIMENTAL DATA

Unbleached Pulp:

The brightness was 34.7% G. E.

The permanaganate number was 33.3.

The chlorine equivalent from the permanaganate number verses the equivalent chlorine was 21.0%.

By analysis the pulp contained the following percentages of alpha, beta, and gamma celluloses and lignin.

Alpha Cellulose ------- 51.5%

Beta Cellulose ------- 6.5%

Gamma Cellulose ------- 15.9%

Lignin ------- 23.7%

Bleached Pulps:

Table 1 shows the yields and brightnesses of the various bleached pulps.

Table 1

Type of Bleach	Bleaching Yield	Brightness (G.E.)
50% Chlorination	96.0%	50.2%
100% Chlorination	93.0%	57.3%
50% Hypochlorite	95.0%	58.7%
100% Hypochlorite	92.0%	62.8%
50% Chlorine Dioxide	95.0%	45.4%
100% Chlorine Dioxide	92.8%	62.3%

Table 2 shows the percents of alpha, beta, and gamma celluloses after correcting for the bleaching yield. These percents are based on 100% of the unbleached pulp.

Table 2

Type of Pulp	Percent Alpha	Percent Beta	Percent Gamma
Unbleached	51.5%	6.5%	15.9%
50% Chlorination	50.5%	7.0%	11.8%
100% Chlorination	49.6%	5.4%	12.9%
50% Hypochlorite	49.8%	2.75%	21.1%
100% Hypochlorite	48.7%	2.3%	15.45%
50% Chlorine Dioxide	51.4%	5.8%	15.4%
100% Chlorine Dioxide	51.25%	5.6%	14.0%

Table 3 shows the amounts of each constituent, of the pulp, lost or gained during bleaching.

Table 3

Type of Bleach	Cellulose	Percent Change
	Alpha	-1.0%
50% Chlorination	Beta	+0.5%
	Gamma	-4.1%
	Alpha	-1.9%
100% Chlorination	Beta	-1.1%
	Gamma	-3.0%

(Table 3 continued)

Type of Bleach	Cellulose	Percent Change
	Alpha	-1.7%
50% Hypochlorite	Beta	-3.75%
	Gamma	+5.2%
	Alpha	-2.8%
100% Hypochlorite	Beta	-4.2%
	Gamma	-0.45%
	Alpha	-0.1%
50% Chlorine Dioxide	Beta	-0.7%
	Gamma	-0.5%
	Alpha	-0.25%
100% Chlorine Dioxide	Beta	-0.9%
	Gamma	-1.9%

Table 4 shows a comparison of the total cellulose lost on each bleaching compared to the hemicellulose lost.

Table 4

50% Chlorination	Total Cellulose Loss	-4.6%
	Hemicellulose Loss	-3.6%
100% Chlorination	Total Cellulose Loss	-6.0%
	Hemicellulose Loss	-4.1%

(Table 4 continued)

50% Hypochlorite	Total Cellulose Loss	-0.25%
	Hemicellulose Loss	+1.45%
100% Hypochlorite	Total Cellulose Loss	-7.45%
	Hemicellulose Loss	-4.65%
50% Chlorine Dioxide	Total Cellulose Loss	-1.3%
	Hemicellulose Loss	-1.2%
100% Chlorine Dioxide	Total Cellulose Loss	-3.05%
	Hemicellulose Loss	-2.8%

All of the values that are shown in the four previous tables were obtained by averaging the results obtained from three or more complete pulp fractionations. These values are also shown on Charts 1 through 9.

DISCUSSION OF DATA

The total loss in cellulose content of the pulps, as shown in Table 4, is in agreement with the accepted theories. The hypochlorite bleach caused the greatest total loss in cellulose. The next greatest total loss was the chlorine bleach followed by the chlorine dioxide.

The only questionable point in the total cellulose loss is shown by the 50% hypochlorite bleach. It showed a loss of 0.25% which is very low. However, the loss of alpha and beta celluloses is 5.45% which is quite large. The interesting point is that the gamma cellulose showed a gain of 5.2%. This gain can be explained by the fact that most of the alpha and beta celluloses that were lost must have been degraded to a D.P. that was within the gamma cellulose range. This shows that even though the total loss is quite small, the alpha and beta celluloses lost are rather large. This is important to notice because the gamma cellulose is the least important of the three celluloses determined.

Since this thesis is interested mainly in the fate of the hemicelluloses during bleaching, the beta and gamma celluloses will be discussed separately.

The effect of bleaching on the beta cellulose is shown very clearly on Chart 2. This shows that the loss

in beta cellulose parallels the total loss in cellulose. The hypochlorite is the most degrading, followed by the chlorine. The least degrading bleach is again the chlorine dioxide.

The 50% chlorination shows a 0.5% increase in beta cellulose which again shows that a higher D.P. cellulose has been degraded to form the beta. Although the 50% chlorination is the least degrading of all the bleaches on the beta cellulose, it is necessary to evaluate the bleaches on the whole. In other words, in speaking about chlorination, one must look at its effect at both 50% and 100% of the equivalent requirement. This then places chlorination in the middle, as previously stated, for its effect on beta cellulose.

The amount of degradation of the gamma cellulose is quite different than either the total cellulose or beta cellolose losses as previously discussed.

From Chart 3 it is apparent that the hypochlorite bleach is the least degrading of the bleaches to the gamma cellulose. In the 50% hypochlorite bleach there is a gain in gammas, and in the 100% hypochlorite bleach the gamma loss is only 0.45%.

The most degrading bleach to the gamma cellulose is the chlorination with the chlorine dioxide being the next in line.

Although the hypochlorite bleach shows the smallest gamma cellulose loss, it is not as significant as it might appear. Alpha cellulose is usually considered to be any cellulose chain with a degree of polymerization (D.P.) of 200 or more. Beta cellulose is considered to have a D.P. of 10 to 150 while gamma cellulose has a D.P. of less than 10. These very short chains of gamma cellulose are not as important for paper making as the longer chained alpha and beta celluloses.

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SUMMARY

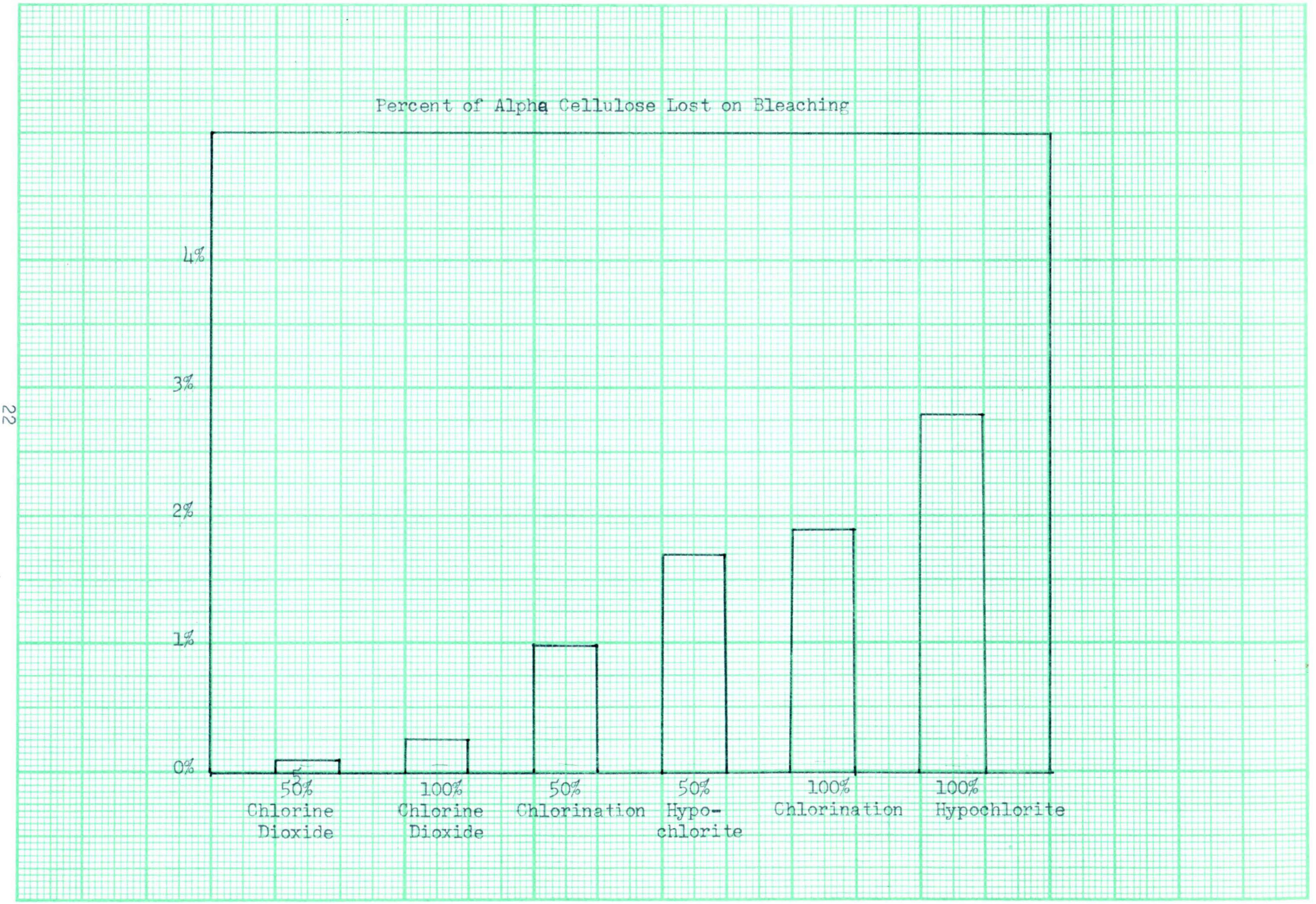
The pulp bleached with hypochlorite bleach showed the greatest loss of alpha and beta celluloses. This pulp showed the least loss of gamma cellulose.

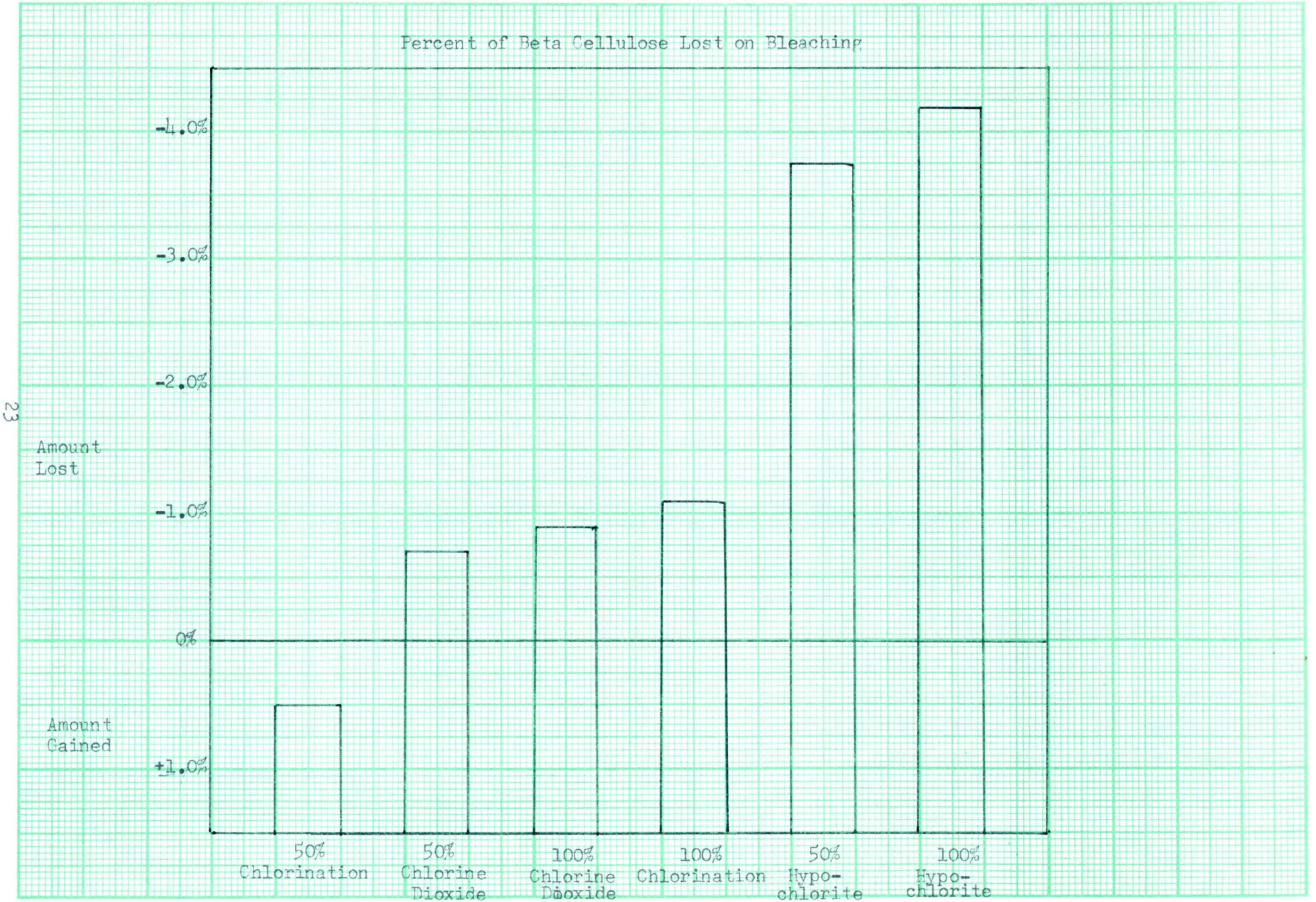
The pulp bleached with the chlorination showed the greatest loss of gamma cellulose. This pulp showed only moderate effects on the alpha and beta celluloses.

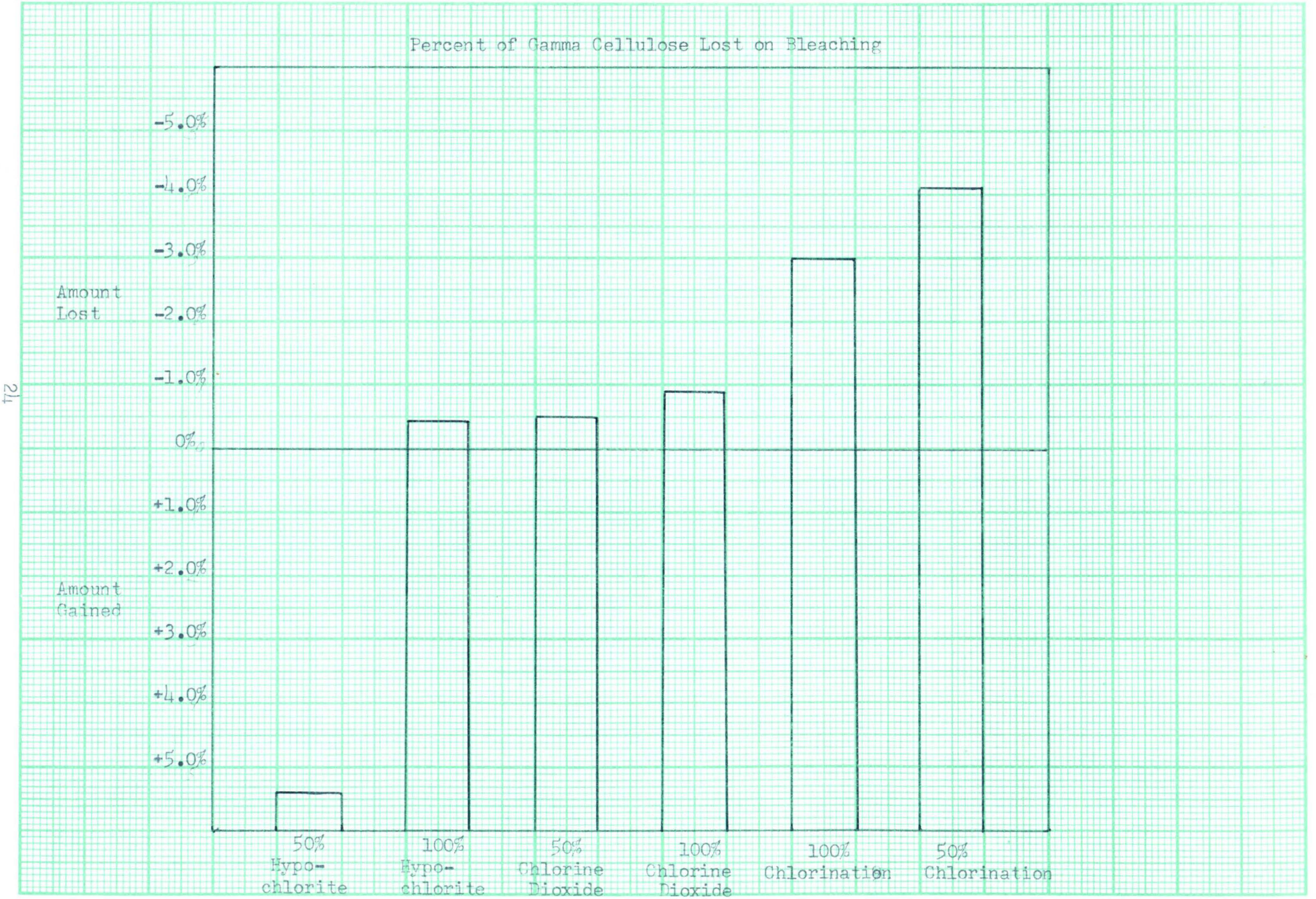
Chlorine dioxide was the least degrading of the bleaches on the alpha and beta celluloses, and it showed only moderate losses of gamma cellulose

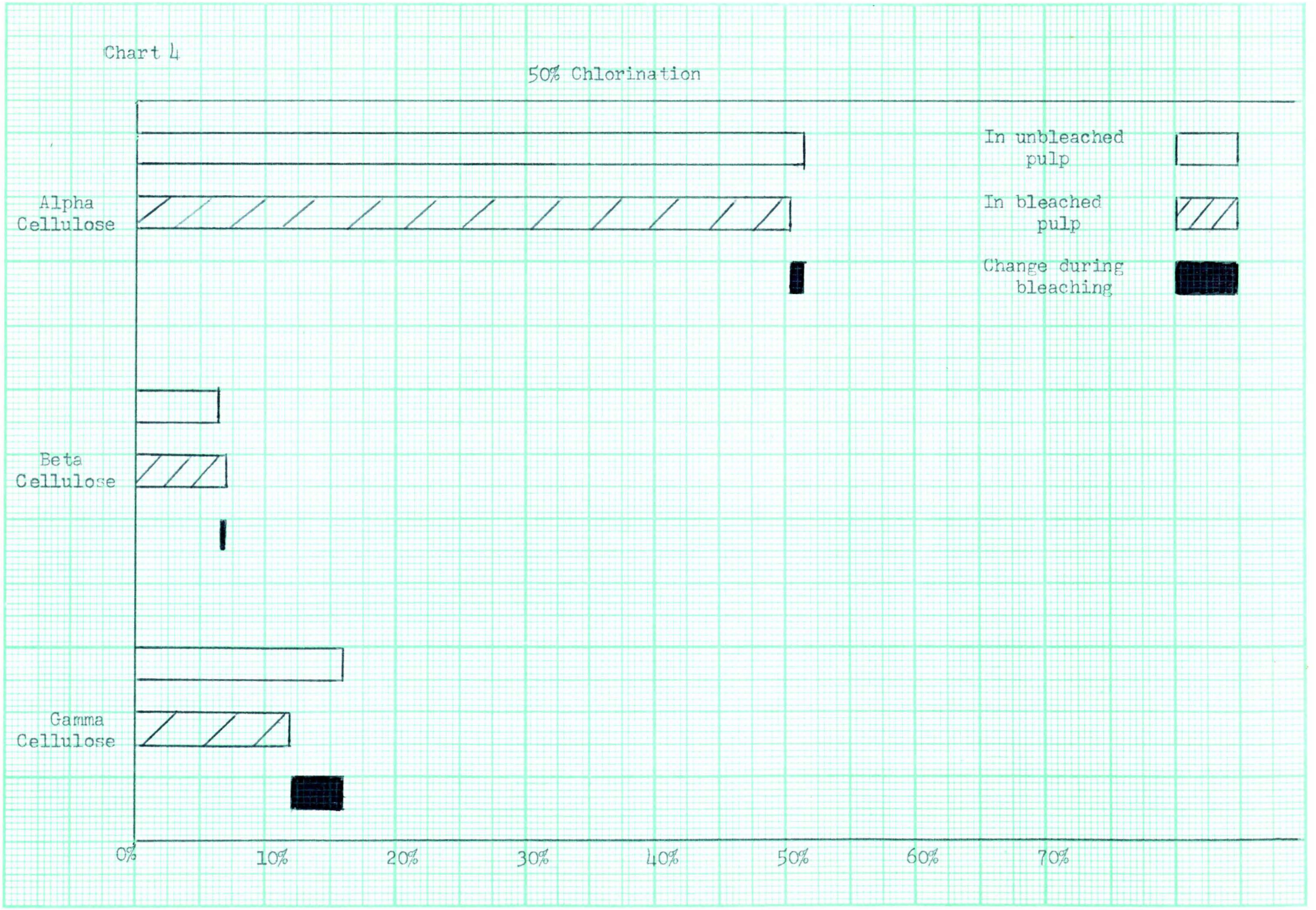
In conclusion, the bleaches may be listed as follows:

1. Chlorine dioxide---very little degradation of pulp
2. Chlorination--------moderate degradation of pulp
3. Hypochlorite--------most degradation of pulp









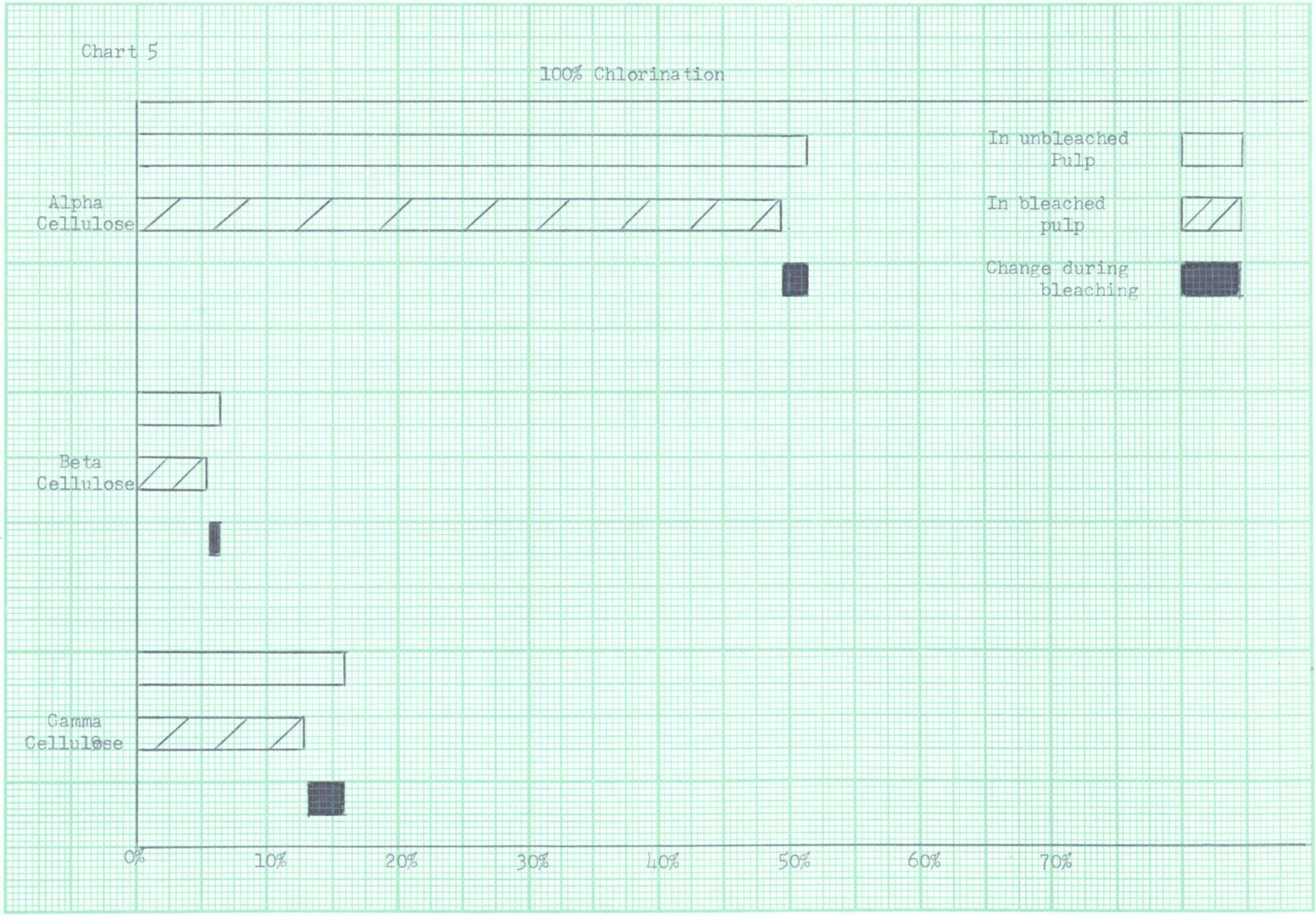
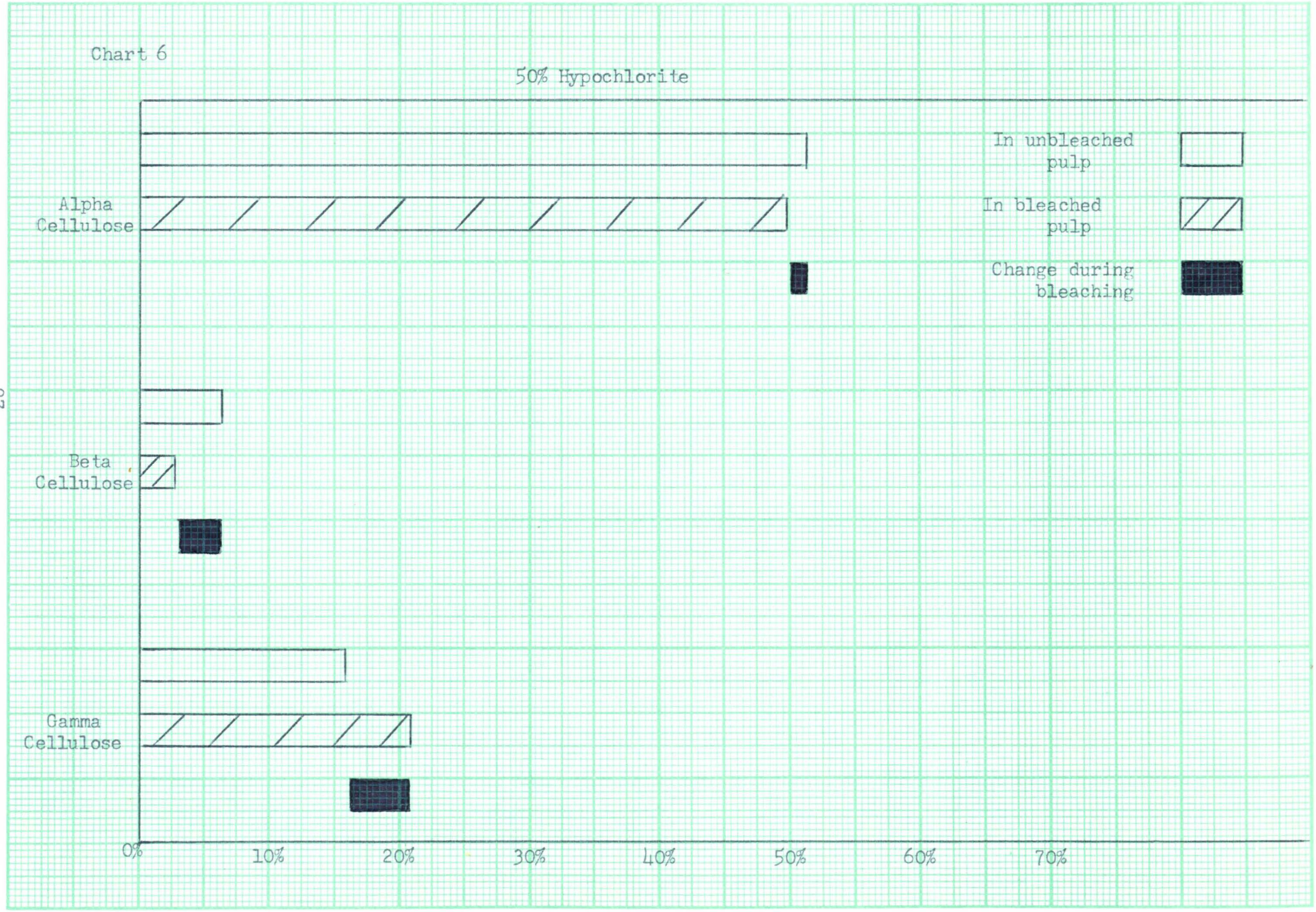
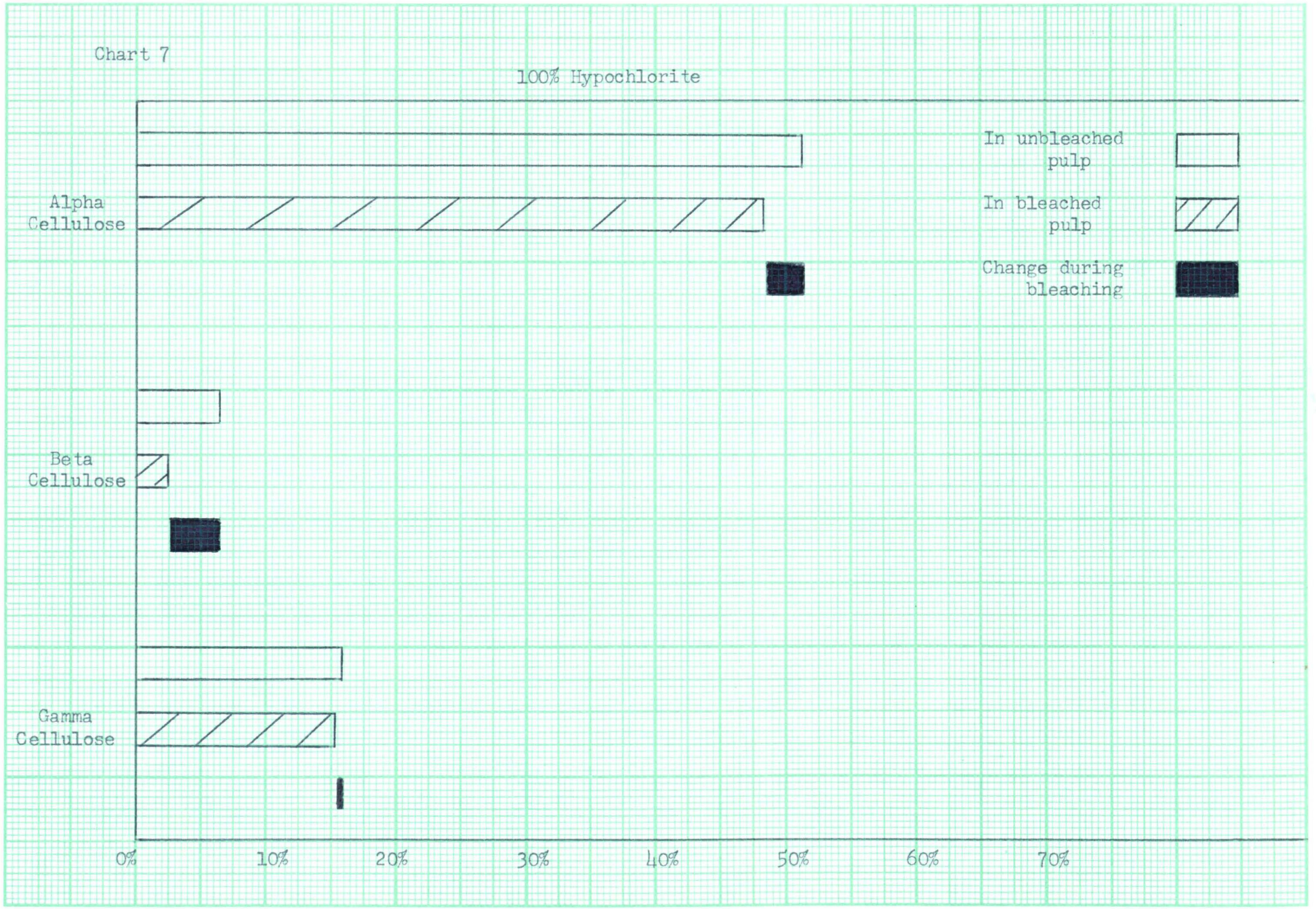


Chart 6





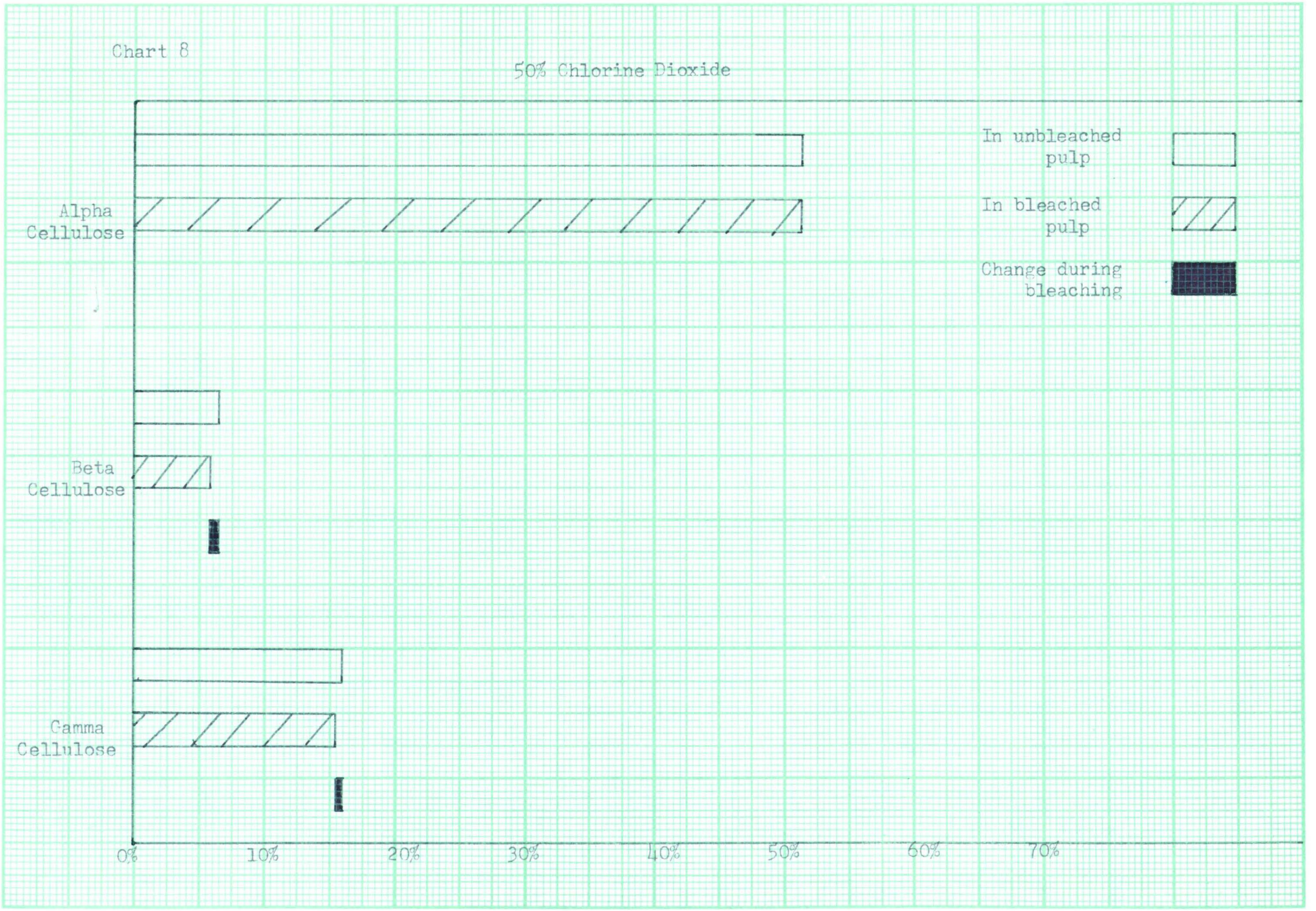
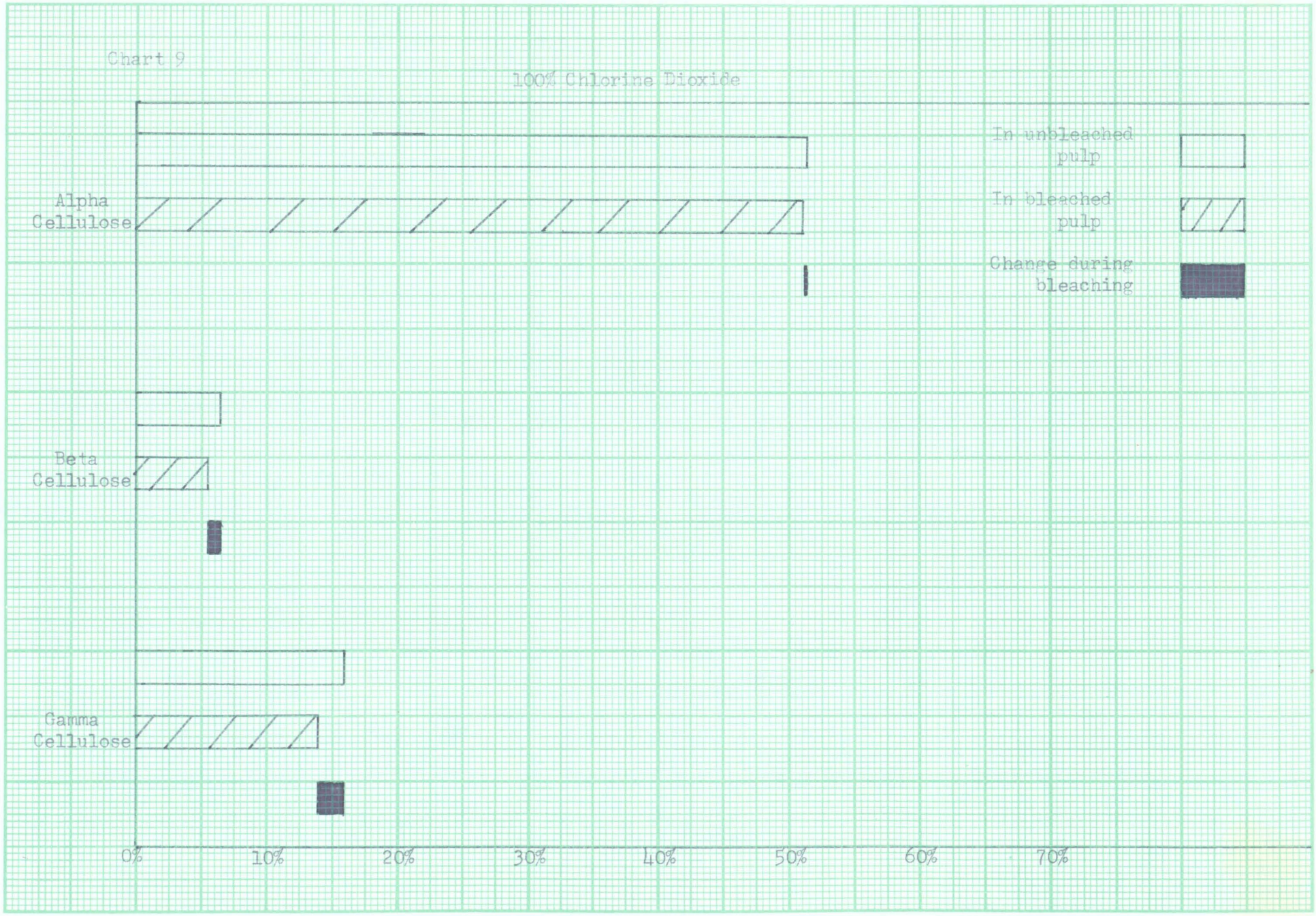


Chart 8
50% Chlorine Dioxide
In unbleached pulp
In bleached pulp
Change during bleaching
Alpha Cellulose
Beta Cellulose
Gamma Cellulose
0%
10%
20%
30%
40%
50%
60%
70%

Chart 9



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