

8/11/48

April 5, 1949.

G. J. BRABENDER ET AL

2,466,633

METHOD OF BLEACHING CELLULOSIC PULP

Filed May 26, 1948

2 Sheets-Sheet 1

FIG. 1

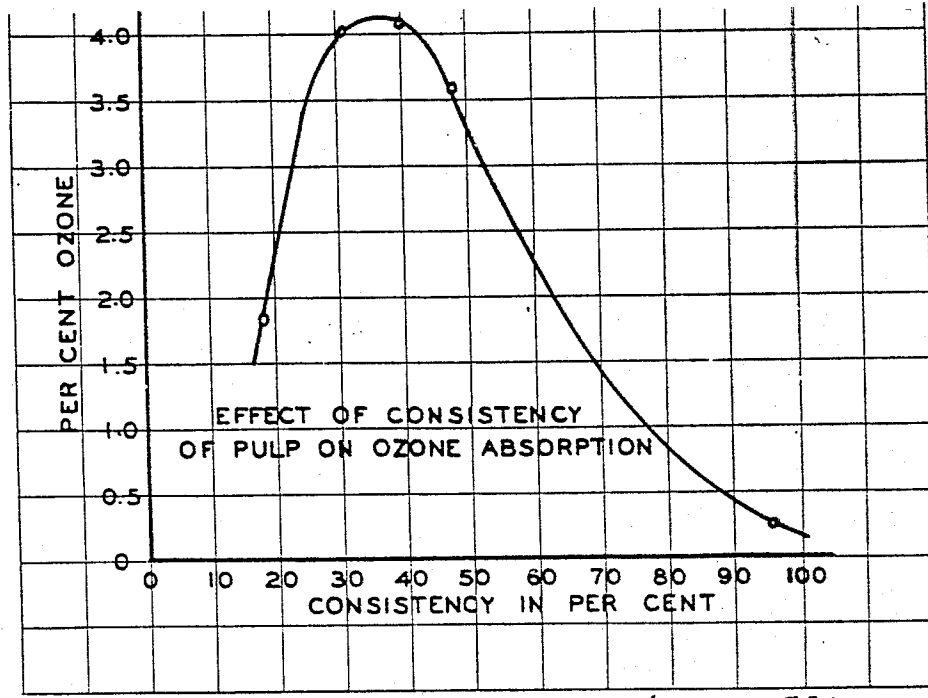
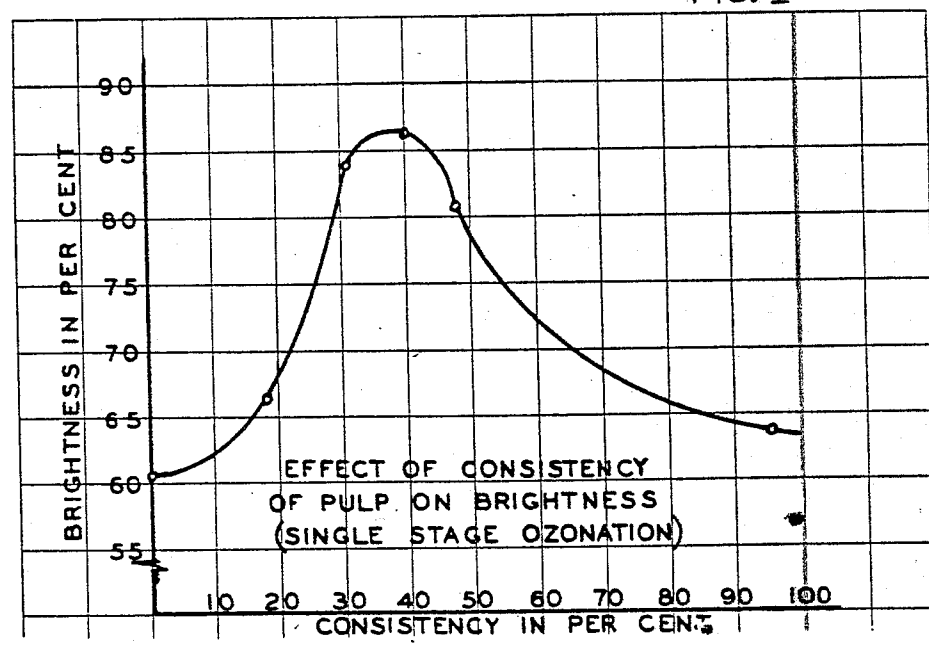


FIG. 2

INVENTORS:
George J. Brabender,
John W. Bard and
James M. Daily
By Joseph Rossman ATTORNEY

April 5, 1949.

G. J. BRABENDER ET AL

2,466,633

METHOD OF BLEACHING CELLULOSIC PULP

Filed May 26, 1948

2 Sheets-Sheet 2

FIG. 3

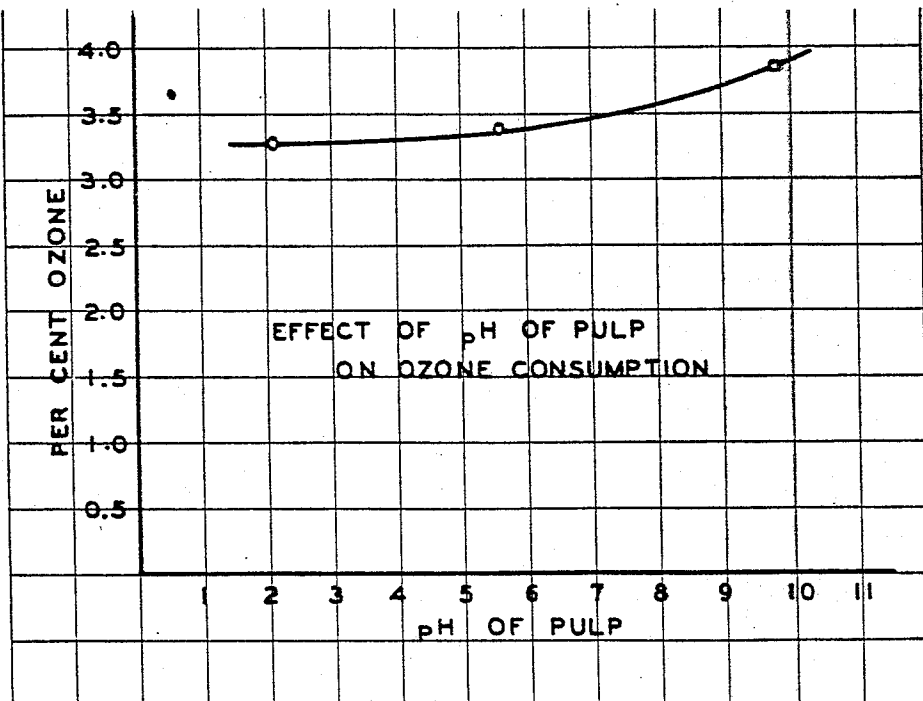
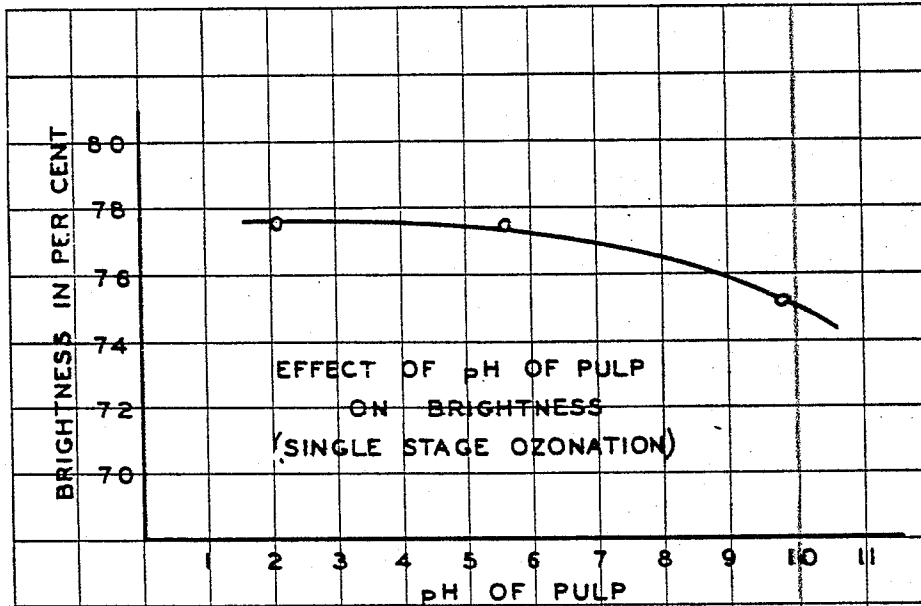


FIG. 4

INVENTORS:
George J. Brabender,
John W. Bard, and
James M. Daily
By Joseph Rossmann
ATTY.

UNITED STATES PATENT OFFICE

2,466,633

METHOD OF BLEACHING CELLULOSIC PULP

George J. Brabender and John W. Bard, Wausau, Wis., and James M. Dally, Portland, Oreg., assignors to James M. Dally, Portland, Oreg., Francis L. Dally, Chicago, Ill., and Joseph F. Ryan, McAllen, Tex.

Application May 26, 1948, Serial No. 29,358

7 Claims. (Cl. 8—104)

1

This invention relates to the use of ozone or ozone-bearing gases for bleaching cellulosic materials. The invention relates to improved methods whereby such bleaching operations may be carried out efficiently and in reasonably short periods of time.

Prior methods for bleaching cellulosic materials, for example, paper-making pulps and "dissolving" types of pulp for making cellulose derivatives employ corrosive and toxic bleaching agents, such as elemental chlorine and calcium hypochlorite bleaching liquor. These materials shorten the life of equipment and thus cause frequent replacement. They also constitute a hazard to operators necessitating special training and precautions. These disadvantages are overcome by the present invention by the use of ozonized air for bleaching cellulosic materials which permits replacement of previously used materials by the relatively less toxic and corrosive ozonized air. In addition, no storage facilities are required for the raw materials which were previously necessary for use with chlorine, since the ozone can be manufactured in situ by use of air or oxygen and electricity.

Another disadvantage of prior bleaching practices is the considerable effluent from the bleaching process which contributes to the pollution of lakes and rivers. The effluent from an ozone bleaching plant constitutes a relatively minor disposal problem.

A further disadvantage of the use of present bleaching methods is the tendency of the bleached pulp to revert to a dark color or to become less white, on aging. We have discovered that our ozone bleaching processes produce a more permanent white than bleaching methods currently practiced.

Further advantages and details of our invention will be apparent from the following specification and drawings, wherein

Figure 1 is a chart showing the effect of consistency of pulp on brightness in a single stage of ozonation,

Figure 2 is a chart showing the effect of consistency of pulp on ozone absorption,

Figure 3 is a chart showing the effect of pH of the pulp on brightness produced by ozone treatment, and

Figure 4 is a chart showing the effect of pH of the pulp on ozone consumption during bleaching.

It has been proposed previously to use ozone broadly for bleaching purposes. However, heretofore no one has discovered the critical factors to control during the bleaching operations. We

2

have found that the moisture content of the pulp to be bleached is a very critical factor. The critical nature of the moisture content is illustrated in Figure 1, based on our experimental work showing that rapid absorption of ozone takes place only in the range 25 and 55 per cent consistency of oven dry pulp, i. e. 75 to 45 per cent by weight of water. Failure to control this range of moisture content makes the operation of this process impractical, since little bleaching effect on the pulp is then observed.

We have also discovered that the maximum absorption and utilization of the ozone occurs when we control the consistency within the limits previously stated as graphically shown in Figure 2 based on our experimental data. Our process is thus highly efficient in producing under our controlled operating conditions a pulp of maximum brightness with the most efficient use of the ozone present in the minimum time.

We have also found that the acidity of the pulp to be treated with ozone must be carefully controlled within critical limits which we have discovered. While other investigators have suggested using acid at some point in a bleaching process, the critical nature of the acidity range has not heretofore been disclosed. Figure 3 based on our experimental data illustrates the desirable range of acidity. It will be noted that above pH 4 the brightness of the bleached pulp becomes progressively less, despite increased ozone consumption. Below a pH of 4 the brightness for a given ozone consumption is substantially constant. However, excessive acidity is undesirable since it contributes to weakening the strength of the cellulose. We have also found that the increase of pH above 4 increases the consumption of ozone as shown in the chart of Figure 4. Therefore, it is apparent that the desirable pH of the stock to be bleached with ozone should be from about 4 to about 7, dependent upon the quality of the specific stock to withstand acid degradation and upon the efficiency required in the use of ozone.

As an example of our process, we take washed unbleached sulphite pulp sheets of 35 per cent oven dry consistency and subject them to a shredding action so that the ozonized air is mixed intimately with the fiber. We then admit in a closed chamber, air containing $\frac{1}{2}$ per cent by weight ozone and allow it to pass through the pulp, reaching virtual exhaustion of its ozone content before escaping to the air. The treatment takes place at room temperature and is continued until the desired pulp brightness is

3

reached. The stock is then diluted with water and washed to remove degraded products.

Another example of our process relates to bleaching pulp produced by the sulphate or kraft process. We subject the pulp to an acidifying agent such as sulphur dioxide to bring it to a pH of 5 to 6. The pulp is then pressed or otherwise converted to a consistency of about 35 per cent oven dry stock. It is then thoroughly shredded and put into a suitable gas-tight container where it is subjected at room temperature to a stream of ozonized air containing, for example, ½ per cent by weight ozone. By moving the pulp counter current to the entering stream of ozonized air, complete utilization of the ozone is obtained. Sufficient time of treatment is allowed to obtain the desired degree of bleaching. The pulp is then removed from the container, washed, and may be subjected, if desired, to further commonly known bleaching steps as, for example, treatment with caustic soda and calcium hypochlorite.

Our process is particularly effective for producing bleached cellulosic pulps having a low ash content. By using ozone as the bleaching agent a minimum of inorganic substances is introduced in the pulp as compared with prior bleaching methods using ordinary bleach liquor. We have found for example, that the same pulp bleached with ordinary bleach liquor contains 2 or 3 times more ash as compared with the pulp bleached by our method. Furthermore, the color reversion of pulp bleached by our method is very small over prolonged storage periods as compared with the rapid color reversion of pulp bleached with ordinary bleach liquor.

The specific examples given are not intended to limit the scope of our invention. For example, we can use our method of bleaching either in single stage operation or in any one of a sequence of several bleaching stages together with commonly practiced bleaching procedures. Furthermore we do not maintain counter current flow of the ozone and pulp as a necessary condition, nor the temperatures and concentration of bleaching agents as noted in the examples given. These conditions may be suitably modified in conjunction with other procedures as previously indicated and it is intended to include such modifications and changes of our invention within the scope of the appended claims.

We claim:

1. The method of bleaching cellulosic pulp which comprises the steps of adjusting the moisture content of the pulp to an oven dry consistency between 25 and 55 per cent, adjusting the pH of the pulp within a range of 4 to 7, passing ozone through said pulp and substantially absorbing all said ozone present to yield a bleached pulp having a good permanence of color and low ash content.

2. The method of bleaching cellulosic pulp which comprises the steps of adjusting the moisture content of the pulp to an oven dry consistency between 25 and 55 per cent, adjusting the pH of the pulp within a range of 4 to 7, passing air containing about ½% by weight of ozone through said pulp, said pulp absorbing substantially all of the ozone present.

3. The method of bleaching unbleached sulfite paper-making pulp which comprises the steps

4

of adjusting the moisture content of the pulp to an oven dry consistency between 25 and 55 per cent, adjusting the pH of the pulp within a range of 4 to 7, passing ozone through said pulp and substantially absorbing all said ozone present to yield a bleached pulp having a good permanence of color.

4. The method of bleaching cellulosic pulp which comprises the steps of adjusting the moisture content of the pulp to an oven dry consistency between 25 and 55 per cent, acidifying said pulp to a pH of 4 to 7, passing ozone through said pulp and substantially absorbing all said ozone present to yield a bleached pulp having a good permanence of color.

5. The method of bleaching cellulosic pulp which comprises the steps of adjusting the moisture content of the pulp to an oven dry consistency between 25 and 55 per cent, acidifying said pulp with sulfur dioxide to a pH of the range of 4 to 7, passing ozone through said pulp and substantially absorbing all said ozone to yield a bleached pulp having a good permanence of color.

6. The method of bleaching cellulosic pulp which comprises the steps of adjusting the moisture content of the pulp to an oven dry consistency between 25 and 55 per cent, adjusting the pH of the pulp within a range of 4 to 7, passing ozone through said pulp and substantially absorbing all said ozone present and washing the bleached pulp to remove degraded products to yield a bleached pulp having a good permanence of color and low ash content.

7. The method of bleaching cellulosic pulp which comprises the steps of adjusting the moisture content of the pulp to an oven-dry consistency between 25 and 55 per cent, acidifying the pulp to a pH of 5 to 6, passing air containing about ½ per cent by weight of ozone through said pulp and substantially absorbing all said ozone, and washing the bleached pulp to remove degraded products and yield a bleached pulp having a good permanence of color.

GEORGE J. BRABENDER.

JOHN W. BARD.

JAMES M. DAILY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
396,325	Brin	Jan. 15, 1889
1,820,502	Schuber	Aug. 25, 1931
1,907,548	John	May 9, 1933
1,942,622	Traquair	Jan. 9, 1934
1,957,937	Campbell	May 8, 1934
2,031,485	John	Feb. 18, 1936

FOREIGN PATENTS

Number	Country	Date
6,677	Great Britain	1914
185,421	Great Britain	Aug. 31, 1922
432,552	France	Dec. 9, 1911

OTHER REFERENCES

Vosmaer, "Ozone," D. Van Nostrand, New York, 1916, pages 176-177. Book in Division 43.