Jan. 2, 1951 H. C. N. HECKEL ET AL 2,536,285

PROCESS OF MAKING HIGH WET STRENGTH PAPER

Filed July 25, 1946

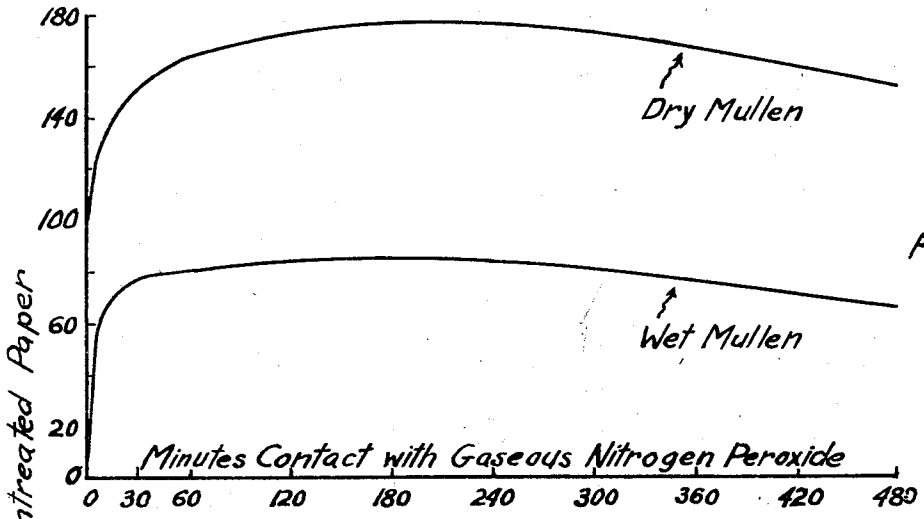


Fig. 1

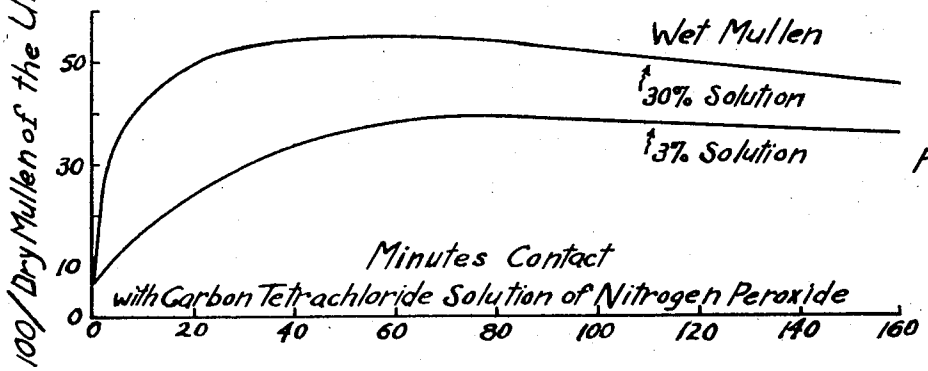


Fig. 2

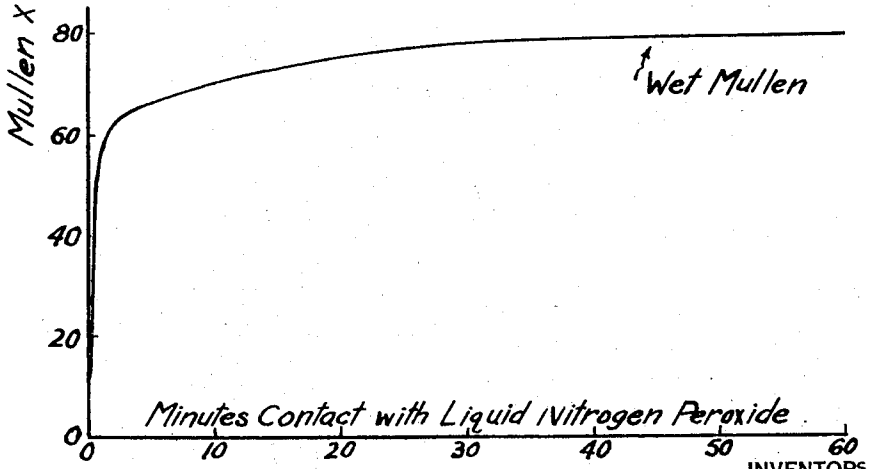


Fig. 3

Mullen X 100/Dry Mullen of the Untreated Paper

INVENTORS
Herman C. N. Heckel
Arthur C. Salisbury
BY
J. Edward Kunafey
ATTORNEY

Patented Jan. 2, 1951 2,536,285

UNITED STATES PATENT OFFICE

2,536,285

PROCESS OF MAKING HIGH WET STRENGTH PAPER

Herman C. N. Heckel, Oxford, and Arthur C. Salisbury, Hamilton, Ohio, assignors to The Champion Paper and Fibre Company, Hamilton, Ohio, a corporation of Ohio

Application July 25, 1946, Serial No. 686,125

9 Claims. (Cl. 8—116)

1

This invention relates to high wet strength paper and to a method of manufacturing it.

Paper as normally manufactured, unlike fabrics, loses practically all its strength when it becomes thoroughly wet; accordingly, for many purposes it is desirable to impart "wet strength" to paper. Wet strength paper is ordinarily regarded as paper which retains 40 to 50% or more of its strength when it becomes thoroughly wet. This high wet strength paper has assumed a place of considerable importance in the manufacture of bags and other wrappings for wet foods, construction papers, map and blueprint paper, toweling, paper fabrics, twine, etc.

Wet strength may be imparted to paper by parchmentizing with sulfuric acid, zinc chloride or the like; but such processes also impart a stiffness and harshness, reduce the porosity and otherwise profoundly change the physical properties of the paper. Certain resin-forming materials may be incorporated with the papermaking fibers in the beater or may be used to impregnate the paper web, the resinous properties being subsequently developed in the paper by the aid of heat and of a suitable catalyst. Such materials are relatively expensive, and if the necessary conditions of temperature, time, concentration, etc. are not strictly controlled, curing of the resin is likely to be more or less incomplete, resulting in variations in the degree of wet strength in the finished paper. In methods where the resin-producing materials are added to the beater, adequate retention of the resin in the sheet is an additional problem.

One object of the present invention is to produce a paper which when wet has high tensile strength, high bursting strength, and good abrasion resistance. Another object is to produce a paper of high wet strength properties without serious impairment of its flexibility, porosity, softness, absorptive capacity or other physical properties. A further object is to impart high wet strength properties to paper economically. Another object is to produce high wet strength papers which are uniform in quality and substantially free from variations due to processes which depend upon curing operations. Another object is to produce high wet strength paper in which the bonding agents is formed from the cellulose fibers of the sheet. Other objects of the invention will be apparent from the hereinafter described process.

We have discovered that when a formed web or sheet of paper is treated first with nitrogen peroxide, that is NO_2 or its dimer, N_2O_4, and then

2

with water, the fibers become more or less bonded together with a water-resistant cement to produce a paper having high wet strength properties. This amounts to a cementing of the fibers in situ in the sheet; consequently the desired results are obtained only with a formed web of interlaced cellulose fibres such as is found in a sheet of paper. On the contrary, if cellulose pulp as such is treated with nitrogen peroxide it can subsequently be formed into a sheet of paper only with great difficulty and the sheets made therefrom do not possess wet strength characteristics.

We have further discovered that by controlling the time and intensity of the treatment, it is possible to impart the above mentioned wet strength properties without materially altering flexibility, porosity, softness, and other desirable properties of the paper.

The action of nitrogen peroxide on the cellulose fibers in the paper sheet according to the present invention appears in some respects to be similar to a controlled or selective parchmentizing, but is limited to the surface of the fibers. Although the exact mechanism of the reaction is not clearly understood it may be that the nitrogen peroxide reacts with absorbed moisture of the fibers to form nitric acid, with subsequent formation of a solution of nitrogen peroxide in nitric acid and this may act upon the fibers, probably forming a plastic gel-like material on the surface which is precipitated when the sheet of paper is treated with water to form a water resistant adhesive. Whatever the explanation may be the web of paper is improved in wet strength and wet abrasion resistance with no further processing such as heating or drying or curing.

Neither the kind of paper nor its moisture content appears to be critical in carrying out the invention; the paper may contain chemical wood pulp, groundwood, cotton, or other cellulosic fibers. In the case of papers of abnormally high moisture content, there may be sufficient acid developed in the paper to produce a deleterious parchmentizing effect.

The time of treatment necessary for the development of wet strength depends upon the concentration of nitrogen peroxide employed. In treating paper with gaseous nitrogen peroxide, the greater part of the wet strength results from the first 15 to 20 minutes of exposure; thereafter the wet strength increases slowly and after from about 1 to 4 hours starts to decrease. Advantageously the exposure of the paper to gaseous nitrogen peroxide is from 5 to 60 minutes. This is illustrated in the accompanying drawing, Fig-

ure 1 of which is a graph showing the increase in dry and wet bursting strength, as measured by the Mullen tester, of a paper made from lightly beaten bleached kraft pulp when treated with gaseous nitrogen peroxide for various intervals and then with water. The increase in bursting strength is expressed in terms of percentage dry bursting strength of the untreated sheet. The temperature has little effect on the rate of production of wet strength but high temperatures are conducive to the secondary reaction wherein oxidation to carboxyl groups takes place. Room temperature is satisfactory for most purposes. The nitrogen peroxide may contain other gases inert to itself and cellulose but in such cases the rate of action is reduced.

In the case where liquid nitrogen peroxide is employed, the major portion of the wet strength is imparted during the first minute. For instance, a sheet of paper contacted by liquid nitrogen peroxide at about 70° F. for 1 minute, followed by immediate removal of free nitrogen peroxide and then immersion in water, developed a wet bursting strength as determined by the Mullen tester of 24 points; a similar sheet contacted for 2 minutes developed a wet bursting strength of 25 points, a third sheet contacted for 20 minutes developed a wet bursting strength of 30 points while a fourth sheet contacted for 60 minutes developed a wet bursting strength of 32 points. In comparison the untreated paper had a wet bursting strength of about 5 points and a dry bursting strength of 40 points. The rate of increase of wet bursting strength when treated with liquid nitrogen peroxide is shown in Figure 3 in terms of percentage dry bursting strength of the untreated sheet. A lower treating temperature decreases the rate of development of wet strength; accordingly liquid nitrogen peroxide is used advantageously at a temperature just below its boiling point.

A solution of nitrogen peroxide in a suitable solvent, e. g. carbon tetrachloride, develops the wet strength properties of paper at a rate proportional to its nitrogen peroxide content, see Figure 2. Thus a 30% solution is almost equivalent in effect to 100% gaseous nitrogen peroxide while a 3% solution is much slower acting than the undiluted gas.

Where a solution of nitrogen peroxide is employed in treating the paper, the solvent must be capable of forming solutions of sufficient strength to bring about the required effect on the paper within a reasonable time but should be substantially inert, i. e., unaffected by nitrogen peroxide, and should itself have no detrimental effect on the paper.

In general a 20 minute interval of contact with the paper when undiluted gaseous nitrogen peroxide or a 30% solution of nitrogen peroxide in carbon tetrachloride is used, and a 1 minute interval when liquid nitrogen peroxide is used, is sufficient to obtain a high degree of wet strength, of the order of at least 50 to 60% of the dry strength of the untreated paper. As indicated by the previous data and the accompanying drawing the wet strength continues to increase as the interval of contact is increased and then levels off or decreases. Thus the time of contact can conveniently be varied to obtain varying degrees of wet strength; where only a partial development of the wet strength properties of a paper may be required it can be produced by a shorter interval of peroxide contact. For example, paper which has been dipped in and removed from a bath of liquid nitrogen peroxide as quickly as possible, then immediately passed over a suction box and treated with water has increased wet strength.

Ordinarily exposures of beyond 1 hour are unnecessary regardless of whether the nitrogen peroxide be liquid, gaseous or in solution. The softness, flexibility, porosity, and tear strength do decrease with length of treatment with the nitrogen peroxide but become significant only over a protracted time of exposure, of the order of several hours where gaseous nitrogen peroxide is employed; therefore long periods of contact with the nitrogen peroxide are preferably avoided. Papers having a high alpha cellulose content show the least decrease in softness.

Neither oxidation nor nitration appears to be a primary reaction in imparting wet strength to paper with nitrogen peroxide. Papers produced according to the herein described process in the preferred form where the interval of contact is of the order of about 20 minutes for gaseous nitrogen peroxide and about 1 minute for liquid nitrogen peroxide are found to have a carboxyl content on the cellulose of less than 1% and only a negligible amount of nitrogen (less than 0.2% N). On long exposure of the paper to nitrogen peroxide, as for example, 2 or 3 hours contact with the gas, a noticeable increase in carboxyl content is obtained but with little or no effect on the wet strength although as noted above, there may be a decrease in softness and flexibility. Advantageously a relatively short peroxide treatment is employed whereby the optimum increase in wet strength for the least amount of deleterious oxidation is obtained.

At the conclusion of the nitrogen peroxide treatment, the paper should be well freed of mechanically held or adsorbed nitrogen peroxide by any suitable means before treatment with water. Where gaseous nitrogen peroxide has been employed this is not so important, but where the paper has been saturated with liquid nitrogen peroxide or with a nitrogen peroxide solution, the liquid should be removed by drainage, suction, evaporation or the like before the water treatment as otherwise an overall parchmentizing effect is obtained which renders the paper stiff and hard. For some purposes this stiffness may not be objectionable and it may even be desired, but if the excess, mechanically held nitrogen peroxide is removed before applying water to the sheet, the paper will retain in a very large measure practically all of its original softness and flexibility while acquiring improved wet strength properties.

The step of treating the paper with water following the nitrogen peroxide treatment produces a two fold result; the inter-fiber wet-strength bonding material is precipitated, regenerated, or in some manner developed, and the action of the nitrogen peroxide present in the paper is terminated. Usually the paper is immersed in a stream of water or is passed through a series of water baths. Preferably the paper is washed with copious quantities of water until substantially free of acid to prevent any acidic deterioration.

Papers made from well bleached pulps in addition to developing wet strength properties are improved in color by the nitrogen peroxide treatment. Sized and unsized paper may be processed equally well but in some cases the sizing effect is somewhat adversely affected by the nitrogen peroxide.

The following examples are given to illustrate the invention:

Example 1

A sheet of bleached kraft paper was placed in a large glass chamber, the air was displaced with substantially dry nitrogen peroxide gas, and additional nitrogen peroxide was introduced in a slow stream. After the paper had remained in contact with the gas at room temperature for about 20 minutes it was removed and washed in water until free of acid by passing it through 3 tanks of running water. The paper was then dried. The product had a wet tensile strength of 6.9 pounds per inch while the wet tensile strength of the untreated paper was 1.0 pound per inch. The dry tensile strength of the product was 20.1 pounds per inch as compared to 13 pounds per inch for the untreated paper. The wet bursting strength of the product was 18 points Mullen and the dry value was 36 points while the untreated paper had a wet Mullen too low to be measured and a dry Mullen of 24.5 points. The general appearance, flexibility, feel, porosity, and absorptiveness were unimpaired. The treated paper withstood severe abrasion while wet without disturbance of the surface fibers. Scotch tape firmly pressed against the dried treated paper and stripped therefrom failed to lift any fibers from the sheet.

In a modified process a sheet of the same paper was left in the gas chamber for only 5 minutes, and then allowed to stand in the room for an interval of 15 minutes before it was washed. An increase in wet Mullen and tensile properties not quite as large as the above was obtained.

Example 2

A sheet of 55-pound paper, 25 x 38—500 basis weight, made from bleached chemical wood pulp was immersed in liquid nitrogen peroxide for 1 minute at a temperature just below its boiling point, e. g. about 70% F. The paper was removed from the bath and allowed to drain momentarily, then air was drawn through the paper for about 2 minutes until substantially all the mechanically held nitrogen peroxide was evaporated; the paper was then immersed in running water until free of acid, and dried. The treated paper had a wet bursting strength of 25 points Mullen and a dry bursting strength of 63 points. Corresponding values for the untreated paper were 6 points wet and 39 points dry. Wet and dry tensile were markedly increased, and the sheet remained soft, porous, and unchanged in appearance from its original condition.

Example 3

A sheet of paper made from a well beaten bleached sulfate pine pulp was immersed in a 30% solution of nitrogen peroxide in carbon tetrachloride at room temperature for 20 minutes then was withdrawn and allowed to drain momentarily. After removing the carbon tetrachloride and the the mechanically held nitrogen peroxide with a stream of dry air, the paper was washed thoroughly in water and dried. The product had a wet Mullen test of 21 points and a dry Mullen of 40 points as compared to 3 points wet and 42 points dry for the untreated paper.

According to another modification of the invention a transparent, greaseproof, glassine-like sheet may be obtained. In this case paper is saturated with liquid nitrogen peroxide, and while in this condition it is subjected to pressure, such as by passing it through the nip of two press rolls, following which it is freed of excess nitrogen peroxide by a stream of air and is then washed with water. The resulting sheet is more or less transparent depending largely upon the degree of pressure exerted and in addition to having wet strength has marked greaseproof properties.

In addition to improving wet strength properties, the process of our invention also improves the dry strength of paper in some respects. This is particularly true in papers made from lightly and moderately beaten pulps. Thus in Example 1, the dry tensile strength of the sheet which was made from a lightly beaten kraft pulp, was 13 pounds per inch, whereas the dry tensile of the same paper after it was treated was 20.1 pounds per inch. The dry bursting strength of a treated lightly-beaten sheet is from 40% to 100% higher than that of a similar but untreated sheet. A sheet made from unbeaten cellulosic fibers and having little strength can be transformed by this process into a sheet showing considerable toughness, both when dry and when wet.

In the preferred form of our invention commercially dry paper is contacted with substantially dry nitrogen peroxide for a time sufficient to yield improved wet strength properties but insufficient to deleteriously alter the dry properties, then is freed of substantially all the unreacted, that is, mechanically held nitrogen peroxide, and finally is washed with water until free of acid. Little or no acid parchmentizing takes place and the sheet is substantially unaltered in softness, flexibility, porosity, and absorptiveness.

The wet strength papers of this invention are similar to cloth and can be used in water, dried, and reused several times without disintegrating. They are useful as toweling, drapery substitutes, filtering material, twisting paper, disposable sheet material, impregnating papers, etc. The fact that the wet strength developing agent can be applied in gaseous or liquid form affords a wide range of operating conditions.

Where an interval of contact of the paper with the nitrogen peroxide is specified in the claims, it is understood to mean that time which the paper is within the gas chamber or peroxide bath; it does not include, for example, an interval during which a roll of nitrogen peroxide treated paper is allowed to stand before it is treated with water.

We claim:

1. Process of imparting wet strength properties to paper which comprises exposing a web or sheet of paper to nitrogen peroxide and then treating the paper with an excess of water to produce partial gelatinization of the surface of the fibers and limiting the time of exposure of the paper to the nitrogen peroxide in relation to the concentration of nitrogen peroxide used, to a degree such that the carboxyl content of the cellulose in the paper is less than 1% and the nitrogen content of the cellulose is less than 0.2%.

2. Process of claim 1 wherein the paper has not materially lost dry strength, porosity, or softness, and the time of exposure of the paper to the nitrogen peroxide is less than one hour.

3. Process of imparting wet strength properties to paper without materially decreasing the dry strength, porosity or softness of the paper, which comprises exposing a web or sheet of paper to nitrogen peroxide, removing mechanically-held nitrogen peroxide from the paper, immersing the paper in water and limiting the time of exposure

of the paper to the nitrogen peroxide in relation to the concentration of nitrogen peroxide used, to a degree such that the carboxy content of the cellulose in the paper is less than 1% and the nitrogen content of the cellulose is less than 0.2%.

4. Process of improving the wet strength of paper which comprises contacting paper in web or sheet form with an atmosphere containing substantial proportions of gaseous nitrogen peroxide for an interval from 15 minutes to 4 hours, treating said paper with an excess of water and limiting the time of exposure of the paper to the nitrogen peroxide in relation to the concentration of nitrogen peroxide in the said atmosphere to a degree such that the carboxyl content of the cellulose in the paper is less than 1% and the nitrogen content of the cellulose is less than 0.2%.

5. Process of improving the wet strength of paper without materially impairing its softness, porosity or dry strength properties which comprises contacting paper in web or sheet form with gaseous nitrogen peroxide for from 5 to 60 minutes, and treating said paper with an excess of water whereby the cellulose in the paper has a carboxyl content of less than 1% and a nitrogen content of less than 0.2%.

6. Process of improving the wet strength of paper without materially impairing its softness, porosity, or dry strength properties which comprises contacting paper in web or sheet form with liquid nitrogen peroxide for about one minute, removing the mechanically held nitrogen peroxide from said paper, and treating said paper with an excess of water, whereby the cellulose in the paper has a carboxyl content of less than 1% and a nitrogen content of less than 0.2%.

7. Process for increasing the wet strength of paper which comprises treating paper with a solution of nitrogen peroxide in an inert solvent, removing excess solution from the paper, and thereafter washing the paper with water, and limiting the time of exposure of the paper to the nitrogen peroxide in relation to the concentration of nitrogen peroxide used, to a degree such that the carboxyl content of the cellulose in the paper is less than 1% and the nitrogen content is less than 0.2%.

8. Process of imparting wet strength and greaseproof properties to paper which comprises immersing paper in liquid nitrogen peroxide, subjecting said paper to pressure while still saturated with liquid nitrogen peroxide, removing mechanically held nitrogen peroxide, treating said paper with water and limiting the time of exposure to nitrogen peroxide to a degree such that the carboxyl content of the cellulose in the paper is less than 1% and the nitrogen content of the cellulose is less than 0.2%.

9. Paper having improved wet strength properties and substantially unchanged softness, porosity and absorptiveness, said wet strength properties produced by exposing paper to nitrogen peroxide and then treating the paper with an excess of water and limiting the time of exposure of the paper to the nitrogen peroxide in relation to the concentration of nitrogen peroxide used, to a degree such that the carboxyl content of the cellulose in the paper is less than 1% and the nitrogen content of the cellulose is less than 0.2%.

HERMAN C. N. HECKEL.
ARTHUR C. SALISBURY.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,699,779	Cochran	Jan. 22, 1929
1,850,808	Redd	Mar. 22, 1932
1,917,400	Staud et al.	July 11, 1933
1,934,956	Wait	Nov. 14, 1933
2,018,244	Alm	Oct. 22, 1935
2,232,990	Yackel et al.	Feb. 25, 1941
2,338,587	Kenyon et al.	Jan. 4, 1944
2,423,707	Kenyon et al.	July 8, 1947
2,448,892	Kenyon et al.	Sept. 7, 1948

OTHER REFERENCES

Frantz, "Absorbable Cotton, Paper and Gauze," Annals of Surgery, July 1943, pages 116, 117, 125, 126.