Patented Apr. 17, 1951 2,549,177

UNITED STATES PATENT OFFICE

2,549,177

SIZED PAPER, COMPOSITION THEREFOR, AND METHOD OF MAKING SAME

Paul B. Davidson, Wilkinsburg, Pa., assignor to Strathmore Paper Company, Springfield, Mass., a corporation of Massachusetts

No Drawing. Application March 21, 1949, Serial No. 82,702

13 Claims. (Cl. 117—156)

1

This invention concerns the art of paper making, and is more particularly addressed to a paper and process of making the same in which the paper is excellently adapted to the demands made upon papers which require a treatment in the wet condition or may be subjected to wetting while in service; such as "blueprint" papers.

One feature of the invention is the provision of a sizing liquor capable of inducing high wet strengths in paper.

Another feature of the invention is the provision of a paper having wet tensile strength in excess of 900 grams and wet rub value above 5.

Another feature of the invention is the provision of a paper having the stated strength values and being dimension-fast, that is, being highly resistant to change of dimensions as a result of prior wetting.

A further feature is the production of a paper having the stated wet strength values, satisfactory dry strength values, and satisfactory resistance to the penetration and spreading of liquids applied to the paper such as writing and printing inks, and light-sensitive coatings.

A further feature of the invention is a process of producing such a paper by reacting papermaker's sizing starch with glyoxal in the presence of the paper fibers.

A further feature is a process of producing such a material by employment of existing papermaking machines, through use of an improved sizing liquor, with a completion of the procedure during the normal drying procedure.

With these and other features in view, as will appear in the course of the following description and claims, illustrative examples of practice are set forth for indicating the properties of the paper produced and the procedure of making the same.

These examples will be set out illustratively with the employment of a basic stock or paper material which is presently accepted in the industry as being adapted for blue-print paper. By way of comparison, when this stock was tub-sized in the usual way with a 10 per cent dispersion of an oxidized or chlorinated starch, designed for this type of sizing, and then dried by heating, the wet tensile strength was about 460 grams. By way of further comparison, when samples of this same paper were tub-sized with a 10 per cent dispersion of the same modified starch, previously cooked with 5.8 per cent of formaldehyde (based upon the dry weight of starch in the system), and then dried by heating, the wet tensile strength was about 590 grams. While this is a significant increase in wet strength, it is not sufficient to satisfy the demands for a blueprint paper, where a wet tensile strength in excess of 900 grams, and preferably in excess of 1200 grams, is required.

2

According to this invention, a size for samples of this paper was prepared by cooking the starch with glyoxal (5 per cent of the dry weight of the starch): this was applied in the same manner as the formaldehyde-treated or un-treated starch; and then subjected to drying and heating, whereupon it was found that the wet tensile strength was 1160 grams. On another lot of paper, treated in the same way, the increase in wet tensile strength was from 450 grams for the starch-sized paper to 1340 grams for the starch-glyoxal-sized paper.

In addition to this great increase of wet tensile strength, it was discovered that the resistance to wet abrasion, or the so-called wet-rub value, was greatly increased. For comparison, the starch-sized paper gave a value of 2 rubs, the starch-fomaldehyde-sized paper gave a wet rub of 2, while the starch-glyoxal-sized paper gave a wet rub of 17.

The testing methods employed were modifications of the TAPPI standards but are believed more severe. Wet tensile strength was determined by T–456M44, but immersing the whole paper strip in water at 21° C. for a half-hour, and then mounting the wet strip in the jaws of the standard strength tester, and making the test as prescribed for dry tensile strength, by T–404–M–44. Wet rub testing consisted of soaking pieces of the paper in water at 21° C. for one minute, and then rubbing with the thumb until roughness is felt to have been developed on the surface of the paper.

The dry tensile strength is not decreased by the treatment, and in most cases is improved with other dry properties.

In these comparisons, the "starch" sizings were prepared by suspending 1200 grams of the oxidized or chlorinated starch in 4800 ml. of water, and dispersing the starch by cooking for ten minutes at between 80° C. and 85° C. The system was then diluted to 12 liters with water, therewith cooling to a temperature of about 40 degrees to 45 degrees C., and used in a pilot plant having a sizing press which accommodates rolls of paper twelve inches wide and about eleven inches in diameter. The speed of this sizing press was adjusted so that the degree of sizing (as measured by the amount of wet size dispersion soaked up by the paper) was the same as that produced on commercial machines during commercial runs.

In preparing the starch-formaldehyde or starch-glyoxal sizes, the starch was suspended and dispersed as before but, after dispersion, the formaldehyde or glyoxal was added, and the cooking continued for an additional five minutes before the size was diluted to twelve liters, therewith cooled, and then employed in the size press as before.

In general, the operation can be employed with paper-maker's starches of various sources such as potato, wheat, corn, tapioca, etc. In practice, the original starch must have been treated in such a manner that, when cooked at above the gelation temperature of the starch, that is to say at a temperature of between about 70° C. and 80° C., the modified or solubilized starch must have lost its identity of granules and also be capable of producing a fluid or free flowing (Saybolt viscosity below 40 seconds) sizing dispersion at the temperatures normally maintained for the sizing operation, i. e. between 40° C. and 60° C. (104–140 degrees F.). This free flowing property of the dispersion is required so as to allow the material to soak into the paper and permit the excess to be removed from the surface by squeeze rolls while leaving the paper essentially with its original surface characteristics. The general molecular starch structure does not appear changed: and the herein-described glyoxal reaction occurs with the various modified forms. Such treatment of the raw starch to produce a fluidly dispersable material is accomplished in practice by one of several procedures, for example, by a chlorination or oxidizing operation, by dextrinization, by enzyme conversion, etc. Such procedures of preparing satisfactory fluid dispersions of starch are described, for example, in "Paper Trade Journal" for February 19, 1942, at page 107 et seq., for February 17, 1938, at page 27 et seq. and for December 3, 1942, at page 30 et seq. It will be understood that the words "starch dispersion" refer to a starch size, of components used by paper-makers for surface or "tub" sizing operations, present in the form of free flowing aqueous dispersion: and that "paper-maker's modified starch" is employed in its normal meaning of a starch converted for paper-maker's use and capable of forming a fluid dispersion as distinguished from a jelly or paste or suspension of separate particles.

It has been found that glyoxal reacts with these various so-called "modified starches" in substantially the same fashion. For example, Table I shows the behavior with diastase-converted starch and with chlorinated starch, the starch being present at 10 per cent (dry weight) concentration in the sizing liquor in each case.

Table I

	Wet Rub	Wet Tensile
10% diastase converted starch	2	690
10% diastase converted starch+1.6% glyoxal	6	940
10% diastase converted starch+4.8% glyoxal	18	1,360
10% chlorinated starch	3	803
10% chlorinated starch+4.8% glyoxal	23	1,670

Similar results have been obtained with starch which has been slightly dextrinized by roasting, as referred to in the aforesaid publications:

Table II

	Wet Rub	Wet Tensile
10% dextrin size	2	700
10% dextrin size+1.6% glyoxal	3	790
10% dextrin size+4.8% glyoxal	9	1,010

For Tables I and II, identical papers were used for tub-sizing, being Strathmore blueprint paper #6386.

It has been found that the concentration of glyoxal, for sizing blueprint papers to obtain high wet tensile strength and wet rub values, depends upon the effective starch concentration in the liquor. Assuming a 10 per cent (dry weight) starch concentration, as a standard, a concentration of less than 2 per cent of glyoxal produces a greater increase of values than can be obtained with formaldehyde, for example, but does not produce the high and optimum values which are desirable for blueprint papers. On the other hand, a concentration of more than 5 per cent of glyoxal in such liquors leaves the paper with so much unchanged glyoxal that a reducing environment results: so that the reducing effects, in the presence of the photographic blueprint and negative sensitizing coatings, tend to cause a premature change of color, for example, what is called "silvering." This difficulty is not present, however, when the paper is to be used for printing. Thus, the desirable range of concentration of glyoxal, for a 10 per cent starch solution, is between 0.2 per cent and 0.5 per cent, or from one-fiftieth to one-twentieth of the concentration of the starch itself for photographic papers. At these values, the following wet strengths can be expected:

Table III

	Wet Rub	Wet Tensile
10% chlorinated starch+5% glyoxal	17	1,160
Do	22	1,320
Do	27	1,440
10% chlorinated starch+4% glyoxal	23	1,410
Do	21	1,360
10% chlorinated starch+3% glyoxal	10	1,080
Do	15	1,130

While it has been found that a 10 per cent concentration of starch in the sizing liquor is a desirable one, changes of this ratio of dispersion can be used, for specific cases. It has been found that if the starch dispersion is too dilute (say 5 per cent or less concentration of starch in the system) then there is a lesser reaction between the glyoxal and the starch, and lesser strength values develop. The commercial preparation of a surface or tub-size comprises the dispersion of about 15 to 35 per cent of modified starch in the original water, by cooking, and then dilution of the same to a proper viscosity for application on the commercial machine. When the glyoxal is cooked into the starch, at such concentrations the particular percentage of starch present appears to have no appreciable effect upon the wet tensile strength, and only a slight effect upon the wet abrasion or "wet rub" value. By way of comparison, employing a bond paper, rather than a blueprint paper, the following values were obtained with different starch concentrations:

Table IV

Starch cooked with 3% glyoxal	Wet Strengths	
	Rub	Tensile
1,200 gm. starch in 3 liters water (28.6%)	16	900
1,200 gm. starch in 4 liters water (23.0%)	14	860
1,200 gm. starch in 5 liters water (19.4%)	13	920
1,200 gm. starch in 6 liters water (16.7%)	12	890

Likewise, the time of cooking of the starch and glyoxal does not appreciably change the wet strength developed in the paper. For example,

after the cooking for dispersion had been completed, an additional cooking time in the presence of glyoxal, of five minutes, gave a wet tensile strength of 1440 grams, while cooking for ten minutes gave 1320 grams, and for fifteen minutes gave 1350 grams. That is, other factors appear to have a greater influence, including minor variations in the preliminary cooking for dispersion: but in each of these instances of timing, it will be noted that the final wet tensile strength was above 1300 grams. Indeed, it is believed that the major part of the strength is developed during the final drying and heating operation, and that the preliminary coupling, or like reaction, occurring in the preparation of the sizing solution, is relatively lesser in importance. Thus, the cooking occurring while the glyoxal is being distributed in the dispersed starch, within a couple minutes, may be sufficient in some instances for developing adequate strengths.

In practice, it has been found to make little difference in the final strength properties, whether the glyoxal is added to the water before the starch is suspended therein and the cooking started, or whether the glyoxal is added after the starch has been dispersed in the water by cooking or the like. In the previous tables, the size solution was prepared by adding the glyoxal after the dispersion had been accomplished by cooking. For purpose of comparison, sizing solutions were prepared by adding the selected quantity of technical or commercial glyoxal to 5 liters of water, adding preservative at the same time when preservative is to be used. 1200 grams of the modified starch was then added slowly, with stirring to obtain an even suspension. The system was then heated to above the gelation point of the starch (between 70° C. and 75° C.), a temperature of 80° to 85° being preferably employed: the cooking is carried on at this temperature for between five and ten minutes. The heating can be done by the direct injection of live steam, or by use of a steam-jacketed kettle. The direct injection is preferred, to avoid possible formation of a layer of gelled and less soluble starch material on the hot surface of the kettle. Comparing the results, dependent upon the time of adding the glyoxal:

Table V

	Wet tensile
Glyoxal added after starch is swelled	1300
Glyoxal added after starch is swelled	1240
Glyoxal added before starch is swelled	1170
Glyoxal added before starch is swelled	1250
Glyoxal added before starch is swelled	1230

However, when raw starch is to be dispersed by the enzyme conversion method, the glyoxal must be added after the starch has been dispersed from its suspension form, in order to avoid the action of glyoxal in killing the enzyme. Since a normal procedure is to permit the conversion to proceed to a desired point of viscosity or dispersability of the starch, and then to terminate the conversion by heating, the glyoxal can properly be added just before this heating is begun.

The reaction between glyoxal and the starch, which is believed to occur, takes place in sizing solutions of normal acidity: and will also occur in the presence of weak alkaline salts. Owing to the possibility of an auto-oxidation-reduction reaction of the Cannizzaro type, when strong alkali conditions are present, the solution should not be more alkaline than about pH 9.0. However, the presence of weak alkaline salts such as lithium and sodium carbonates do not cause this reaction to take place to any appreciable degree, nor do these salts change the reactivity of glyoxal toward modified starches in any fashion to impair the wet tensile strength of the sized paper produced thereby.

The glyoxal may be of high chemical purity, but such is not needed: in practice it can be employed in the commercial form, sometimes called a polymer and at times designated as tetrahydroxydioxan. The material used for several of the above examples had a concentration of 30 per cent; but commercial products may vary from this by several per cent, due allowance being made in the amount of material taken.

The technical grade of glyoxal contains an appreciable concentration of formic acid, and exhibits a value of pH 1.3 to pH 2.0. When it is desired to operate under more alkaline conditions, this acid can be neutralized or partly neutralized with such weak alkalies as the lithium carbonate or sodium carbonate stated above, and the resulting glyoxal solution can then be added to the starch dispersion with essentially the same results as though the original glyoxal, without neutralization, had been employed. Some buffering appears to be present from the starch dispersion, but in general the wet rub resistance appears greater when glyoxal solutions, and prepared sizes, are used with a pH above 5.0, as for example:

Table VI

Size prepared with 3% glyoxal, pH Conditions		Wet Strengths	
Glyoxal Solution	Prepared Size	Rub	Tensile
8.6	7.12	15	1,010
7.3	5.7	18	1,080
7.15	7.1	15	1,090
6.5	6.3	12	1,080
1.3	4.0	10	1,080

In preparing the sizes used for Table VI, the starch dispersion was brought to the stated pH value of 7.1 in the third example above, before adding the neutralized glyoxal solution. The results of Table VI were obtained by using specimens from the same lot of paper; except for the first example above, which employed a paper having a somewhat less wet tensile strength in the absence of the glyoxal-starch sizing.

The results of Table VI were obtained by use of chlorinated starch, which when dispersed exhibited a pH of 5.75.

In another series of sizings, using 4 per cent of glyoxal, and adjusting its pH value as noted, results were obtained:

Table VII

pH of glyoxal solution	Wet Strengths	
	Rub	Tensile
6.0	22	1,240
5.3	14	1,210
1.3	16	1,170

In preparing and testing sizing liquors within the presently preferred pH values of about 4 to 6

for the sizing solution, it was found that the following variations may be expected:

Table VIII

Approximate pH of size	Wet Tensile	Average
4	1,140	--------
4	1,230	--------
4	1,300	1,220
5	1,190	--------
5	1,210	1,220
6	1,250	--------
6	1,270	1,260

It has been found that excellent conditions can be produced by employing the sizing solution in a size press formed as a part of a normal paper-making machine. Thus, the paper web is introduced to the sizing solution and is permitted to take up a quantity of the sizing solution which is dependent upon the properties of this sizing liquor, the time of contact, the preliminary condition of the paper stock, etc. Thereafter the water is evaporated away, and then the sized paper is dried.

The temperature at which the sized paper is dried, and therewith apparently a final reaction produced, has some effect upon the final wet strength developed. The temperatures available in a commercial paper-making machine are determined by the practical necessities of obtaining a good rate of production, and by limitations of steam pressure to be employed in the drying drums on the machine. It has been found that temperatures of 121° C. to 134° C. are easily maintainable on the machine which has been used for the work. The drying temperature should be from 110° C. to 150° C., to secure a sufficiently rapid drying and reaction, and to avoid side reaction. In practice, for example, the following values were found, under otherwise identical conditions:

Table IX

Drying Time	Drying Temperature	Wet Rub	Wet Tensile
	°C.		
15 seconds	121	15	1,130
15 seconds	134	17	1,250

Since the drying time on a paper-making machine may be a critical commercial factor, it is interesting that the actual drying time at a given temperature is not so critical for the development of optimum wet strength values as the drying temperature for the given time This is illustrated by the following table:

Table X

[10% size prepared with 3% glyoxal.]

Drying		Wet Strengths	
Temp.	Time	Rub	Tensile
°C.	Sec.		
121	15	15	1,130
121	30	16	1,230
121	60	18	1,260
121	120	18	1,220
134	15	17	1,250
134	30	17	1,330
134	60	18	1,390
134	120	17	1,260

[10% size prepared with 4% glyoxal.]

Drying		Wet Strengths	
Temp.	Time	Rub	Tensile
°C.	Sec.		
121	15	23	1,410
121	30	24	1,370
121	60	25	1,440
121	120	26	1,500
134	15	24	1,390
134	30	34	1,470
134	60	35	1,470
134	120	40	1,410

As a further example of practice, oxidized starch has been cooked with 5 per cent of glyoxal, under the conditions given above, and then diluted and cooled to the proper consistency (ratio of 1200 grams of starch to about 10 liters of water) and then another 5 per cent of glyoxal was added. When this was used as a sizing solution for paper, upon drying and heating as above, corresponding wet strength and wet rub values were obtained, and also the paper was "non-expanding" or "dimension fast" useful for printed maps and other employments where this quality is of primary importance, in that its dimensions were not changed upon wetting, or by successive wetting and drying, within wide ranges of procedures. It appears that this excess glyoxal reacts with the cellulose fibers of the paper itself in some fashion to change their behavior with respect to water, either by making them less subject to the imbibition of water or by causing a tie between the fibers at points of contact. If the residual quantity of unreacted glyoxal, at the end of the drying, causes oxidation-reduction action, it may be removed by leaching.

When penetration resistance to ink, for example, is not of importance, the starch-glyoxal size may be added to the pulp, a waterleaf sheet formed, and this sheet dried and heated as described above. Therewith a paper toweling, for example, may be made which has the stated high increment of wet strengths, and also has improved dry strength values, such as:

Table XI

	Dry tensile, grams
Control experiment (low rosin size)	3297
Oxidized starch size (3% conc.)	3543
Oxidized starch-glyoxal size (10% starch: 3% glyoxal)	5810

It is obvious that the forms of practice stated, and the products, are illustrative: and that the invention may be executed in many ways within the scope of the appended claims.

I claim:

1. A paper having a wet tensile strength in excess of 900 grams and a wet rub value above 5, and characterized in having a sizing predominantly consisting of reaction product of glyoxal and paper-maker's modified starch, said glyoxal being present as one-fiftieth to one-twentieth by weight of the dry weight of starch.

2. A paper having a wet tensile strength above 1200 grams, a wet rub value above 10, and characterized in having a sizing predominantly consisting of the baked reaction product of paper-maker's modified starch with one-fiftieth to one-twentieth its weight of glyoxal on the basis of dry weight of starch.

3. The method of sizing paper, which comprises applying to the fibers a water dispersion of a 5 to

35 per cent of paper-maker's modified starch reacted with 2 to 5 per cent of glyoxal on the basis of the dry weight of starch, drying the water from the paper, and thereafter heating to a temperature of 110° C. to 150° C.

4. The method of sizing paper, which comprises heating a paper-maker's modified starch and glyoxal in water, the starch concentration being from 5 to 35 per cent and the amount of glyoxal being 2 to 5 per cent by dry weight of starch, applying the sizing liquor to the paper, drying, and then heating to a temperature of 110° C. to 150° C.

5. The method of preparing a sizing liquor for paper, which comprises suspending a paper-maker's modified starch in water, cooking for about ten minutes at above the gelation point of the starch for effecting swelling of the starch, adding 2 to 5 per cent of glyoxal based on the dry weight of the starch and adjusting the pH value to between 4 and 9, continuing the cooking for about five minutes, and then diluting and cooling the product.

6. The method of preparing a sizing liquor for paper, which comprises cooking a paper-maker's modified starch in water for about five minutes at about 85° C. for effecting swelling of the starch, and in the presence of about 3 per cent of glyoxal, based on the dry weight of the starch, while maintaining the pH of the liquor between 4 and 9, and then diluting with water and thereby cooling the product to below 70° C.

7. The method of preparing a sizing liquor for paper, which comprises dispersing a paper-maker's modified starch in water at a concentration of 5 to 35 per cent, dissolving commercial glyoxal in water and adjusting to a pH value of 4 to 9 by weak alkaline salt, adding the glyoxal solution to the starch dispersion and heating at a temperature of about 85° C. for about five minutes, the quantity of glyoxal being about 3 per cent based on the dry weight of the starch, and then diluting and cooling the product to below 70° C.

8. A sizing liquor for paper, comprising water and dispersed therein the reaction product of cooking at 80° C. to 85° C. for about five minutes a 5 to 35 per cent dispersion of a paper-maker's modified starch with 2 to 5 per cent of glyoxal based on the dry weight of starch.

9. A tub-sizing liquor for paper, consisting of water and dispersed therein the reaction product of cooking at 80° C. to 85° C. for about five minutes a water dispersion of about 10 per cent paper-maker's modified starch with about 4 per cent of glyoxal based on the dry weight of starch.

10. A sizing liquor for paper, comprising water, dispersed therein about 12 per cent of the reaction product of cooking at 80° C. to 85° C. for about five minutes a water dispersion of paper-maker's modified starch with about 5 per cent of glyoxal based on the dry weight of the starch, and also containing in addition about 5 per cent of glyoxal.

11 A paper having a wet tensile strength in excess of 900 grams and a wet rub value above 5, and characterized in having a sizing coating thereon predominantly consisting of a reaction product of glyoxal and paper-maker's modified starch, said glyoxal being present as one-fiftieth to one-twentieth by weight of the dry weight of starch.

12. The method of sizing paper, which comprises dispersing a paper-maker's modified starch in water at a concentration of 5 to 35 per cent, dissolving commercial glyoxal in water and adjusting to a pH value of 4 to 9 by weak alkaline salt, adding the glyoxal solution to the starch dispersion and heating at a temperature of about 85 degrees C. for about five minutes, the quantity of glyoxal being about 3 per cent based on the dry weight of the starch, diluting and cooling the product to below 70 degrees C., applying the sizing liquor to the paper, drying, and then heating to a temperature of 110 degrees C. to 150 degrees C.

13. A sized paper made in accordance with claim 12, and characterized in having a wet tensile strength in excess of 900 grams and a wet rub value above 5.

PAUL B. DAVIDSON.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,106,164	Bowlby	Jan. 25, 1938
2,222,873	Leach	Nov. 26, 1940
2,258,741	Champion et al.	Oct. 14, 1941
2,354,662	Bryce	Aug. 1, 1944
2,370,266	Smith et al.	Feb. 27, 1945
2,391,621	Powell et al.	Dec. 25, 1945
2,396,937	Bauer et al.	Mar. 19, 1946
2,411,989	Dunham	Dec. 3, 1946
2,412,832	Pfeffer et al.	Dec. 17, 1946
2,413,463	Nichols et al.	Dec. 31, 1946
2,414,858	Davidson	Jan. 28, 1947
2,422,423	Kvalnes	June 17, 1947