United States Patent Office 2,967,797
Patented Jan. 10, 1961

2,967,797

METHOD OF FORMING PAPER CONTAINING TITANOUS HYDROXIDE AND PRODUCT THEREOF

Joseph R. Weschler, New Brunswick, N.J., and Paul Lagally and Herta Lagally, State College, Pa., assignors, by mesne assignments, to Johnson & Johnson, New Brunswick, N.J., a corporation of New Jersey

No Drawing. Filed Dec. 10, 1956, Ser. No. 627,108

7 Claims. (Cl. 162—158)

This invention relates to a novel method for producing improved papers and in particular to papers having improved wet strength.

In many uses of paper it is essential that the paper possess a high wet strength, such as packaging paper for meat, hand towels, garbage bags, sandpaper backings, adhesive tape backings, etc. Paper used for the aforementioned purposes often comes in contact with moistures and must be sufficiently resistant thereto so as not to rapidly deteriorate in use.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the methods and paper pointed out in the appended claims.

The invention consists in the novel method and paper herein described.

It is an object of this invention to provide a novel method for forming in a simple manner improved papers having the characteristics of high wet tensile strength. Another object of this invention is to provide improved papers having the characteristics of high wet tensile strength.

It has been found that the foregoing objects may be realized by forming paper from paper pulp utilizing water soluble trivalent titanium salts in the paper pulp. More particularly, it has been found that the incorporation of a water soluble trivalent titanium salt and hydrolysis thereof, followed by subsequent formation of a paper web and drying thereof to form a paper sheet, results in the formation of a paper sheet having improved wet tensile strength.

Examples of suitable water soluble trivalent titanium salts useful in accordance with this invention are titanium trichloride ($TiCl_3$ or $TiCl_3 \cdot 6H_2O$), titanous sulfate ($Ti_2(SO_4)_3 \cdot 8H_2O$ or $3Ti_2(SO_4)_3 \cdot H_2SO_4 \cdot 25H_2O$) and titanous oxalate ($Ti_2(C_2O_4)_3 \cdot 10H_2O$).

On hydrolysis the trivalent titanium salt is converted to a titanous hydroxide having the formula $Ti(OH)_3$. The exact mechanism involved in the cross-linking of the cellulose fibers to improve the wet strength of the paper is not known and the invention is not to be limited to any theory of action. It appears, however, that the titanous hydroxide ($Ti(OH)_3$) is converted to a different titanium derivative which reacts with the hydroxy groups on the cellulose to effect the desired cross-linking.

Bases useful as hydrolyzing agents in accordance with this invention are alkali hydroxides, such as sodium hydroxide and potassium hydroxide, alkali carbonates, such as potassium carbonate and sodium carbonate, ammonia and organic bases, such as triethanolamine and diethanolamine.

The amount of titanium derivative that is incorporated in the paper pulp will vary depending upon the particular salt that is used. The retention of small amounts of $Ti(OH)_3$ (up to 10%) is almost quantitative but when

amounts greater than 10% $Ti(OH)_3$ are used, retention is not quantitative. In general, the titanium salt is added in such an amount that the range of concentration of $Ti(OH)_3$ will vary between 1 to 45% and preferably 1 to 20%.

Preferably, the hydrolyzing agent is added in such amount to give a final pH of 6.5–7.5 to the paper pulp containing an aqueous solution of trivalent titanium salt. The resulting mixture having the desired pH is then stirred and the desired sheet is formed resulting in a paper of high wet strength.

The following examples are now given illustrating improved papers formed in accordance with the invention. These examples are for the purpose of illustrating the invention more specifically but the invention is not limited thereto. Unless otherwise indicated, the percentages or parts given are by weight.

Example I

To a quantity of semi-bleached kraft pulp (600 cc. Schopper-Reigler freeness) to give a 30 pound (24" x 36" x 480) basis weight sheet was added an amount of 20% aqueous $TiCl_3$ solution to give about 20% $Ti(OH)_3$ based on the weight of pulp. Hydrolysis of the $TiCl_3$ was carried out by addition of dilute NH_4OH to a pH of 7. The sheet was then formed and dried. The wet tensile was found to be 3.6#/in. before heating and 5.1#/in. after heating 1 minute at 350° F. A control sheet made without $TiCl_3$ had a wet tensile of .1#/in. before heating and .6#/in. after heating 1 minute at 350° F.

Example II

In the same manner as described in Example I, a quantity of $TiCl_3$ calculated to give about 20% $Ti(OH)_3$ based on the dry weight of pulp when neutralized with dilute KOH gave 3.3#/in. wet tensile before heating and 4.9#/in. after heating 1 minute at 350° F.

Example III

To a quantity of semi-bleached kraft pulp to give a 50#(24" x 36" x 480) basis weight sheet was added an amount of 20% aqueous $TiCl_3$ to give 6% $Ti(OH)_3$ based on the weight of pulp. Hydrolysis of the $TiCl_3$ was carried out by addition of dilute NaOH to a pH of 7. The sheet was then formed and dried. The wet tensile was found to be 4.4#/in. before heating and 7.8#/in. after heating 1 minute at 350° F. A control sheet made without $TiCl_3$ had a wet tensile of .7#/in. before heating and 1.6#/in. after heating 1 minute at 350° F.

Example IV

In the same manner as described in III, a quantity of $TiCl_3$ to give 18% $Ti(OH)_3$ when neutralized with triethanolamine gave 12.6#/in. wet tensile before heating.

Example V

To a quantity of semi-bleached kraft pulp to give an 80# (24" x 36" x 480) basis weight sheet was added an amount of 20% aqueous $TiCl_3$ to give about 7.5% $Ti(OH)_3$ when hydrolyzed with dilute NH_4OH. After sheet formation and drying the wet tensile was found to be 8.3#/in. and after heating 1 minute at 350° F. 13.9#/in. A control made without any $Ti(OH)_3$ gave 1.4#/in. wet tensile before heating and 2.4#/in. after heating 1 minute at 350° F.

Example VI

To a semi-bleached kraft pulp of 610 cc. Schopper-Riegler freeness was added an amount of 20% aqueous $TiCl_3$ to give about 9.0% $Ti(OH)_3$ based on dry weight of pulp. Hydrolysis of the $TiCl_3$ was carried out by addition of dilute NH_4OH. After stirring till the mixture

was colorless, 23% of a butadiene-acrylonitrile latex based on the weight of finished sheet (24" x 36" x 480=70#) was added. After mixing, the latex was precipitated with a resin made from guanidine nitrate formaldehyde. The sheet was then formed in a standard sheet mold.

As an illustration of the improved physical properties obtained we give below the results obtained in comparison with the results when no $Ti(OH)_3$ was used.

	Wet tensile, #/in.
Control	1.2
Example VI	4

Example VII

To a quantity of semi-bleached kraft pulp (600 cc. Schopper-Riegler freeness) to give a 30#

(24" x 36" x 480)

basis weight is added an amount of 20% aqueous titanous sulfate solution to give about 20% $Ti(OH)_3$ based on the weight of the pulp. Hydrolysis of the titanous sulfate is carried out by addition of dilute NH_4OH to a pH of 7. The sheet is then formed and dried. The wet tensile strength is considerably improved over a sheet made without titanous sulfate.

Example VIII

To a quantity of semi-bleached kraft pulp (600 cc. Schopper-Riegler freeness) to give a 30#

(24" x 36" x 480)

basis weight is added an amount of 20% aqueous titanous oxalate solution to give about 20% $Ti(OH)_3$ based on the weight of the pulp. Hydrolysis of the titanous oxalate is carried out by addition of dilute NH_4OH to pH of 7. The sheet is then formed and dried. The wet tensile strength is found to be considerably improved over a sheet made without titanous oxalate.

The invention in its broader aspects is not limited to the specific method and paper described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

It is claimed:

1. The method of forming a paper sheet having improved wet strength comprising the steps of mixing with a slurry of paper pulp including cellulose fibers, a water soluble trivalent titanium salt, hydrolyzing said salt to form $Ti(OH)_3$, forming a paper web from said pulp and drying said web to form a paper sheet.

2. The method according to claim 1 wherein the trivalent titanium salt is hydrolyzed by the addition of a base to the pulp.

3. The method according to claim 1 wherein the trivalent titanium salt is selected from the group consisting of titanium trichloride, titanous sulfate and titanous oxalate.

4. The method according to claim 3 wherein the trivalent titanium salt is titanium trichloride.

5. The method according to claim 3 wherein the trivalent titanium salt is titanous sulfate.

6. The method according to claim 3 wherein the trivalent titanium salt is titanous oxalate.

7. A paper sheet having improved wet tensile strength formed in accordance with the method of claim 1.

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