

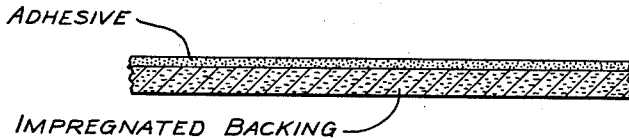
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METHOD OF MANUFACTURING UNIFIED PAPER CONTAINING TITANIA

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(Impregnant - Elastomer and Orthotitanic  
Acid or Water Soluble Low Polymer of  
Orthotitanic Acid)

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2,947,658

**METHOD OF MANUFACTURING UNIFIED PAPER CONTAINING TITANIA**

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This invention relates to improved method of manufacturing papers and in particular to novel papers having improved wet strength, delamination resistance and tear strength.

Very often in the employment of paper it is necessary that the paper having high tear strength such as for backings of normally tacky and pressure-sensitive adhesive tapes, artificial leather, gasket material, etc. Papers used as backings for normally tacky and pressure-sensitive tapes, in addition to high tear strength, must also have high delamination resistance, so that the roll of tape may be unrolled without splitting or delaminating the paper web by means of forces set up by adhesion of the adjacent plies of the tape in roll form.

Prior to the present invention various techniques have been used for improving the characteristics of paper such as wet strength, tear strength and delamination resistance. One of the most common methods for improving the delamination resistance of paper, such as that used as backings for normally tacky and pressure-sensitive tapes, comprises the incorporation into raw paper extensible materials of a more or less rubbery nature termed "impregnants." Such impregnants allow the sheet to retain a major portion of the characteristic flexibility and yet bind the fibers when a roll of pressure-sensitive tape is unwound. In employing the aforementioned impregnating method, however, it is not always possible to obtain uniform dispersion of the impregnant throughout the paper.

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 processes, steps, combinations, improvements and compositions pointed out in the appended claims.

The invention consists in the novel processes, steps, combinations and improvements, and compositions herein shown and described.

It is an object of this invention to provide improved method of manufacturing papers having the characteristics of high delamination resistance, high tear strength and high wet tensile strength with adequate flexibility and elongation. Another object of this invention is to provide a novel method of manufacturing paper backed adhesive tape, and particularly pressure-sensitive tape, having improved unified paper backings, and which have a high resistance to delamination, high tear strength, high wet tensile strength and adequate elongation and flexibility. A still further object of this invention is to provide novel methods for the production of improved papers having the characteristics set forth in accordance with the foregoing objects.

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The drawing is a diagrammatic representation of the product of this invention.

It has been found that the foregoing objects may be realized by producing paper by the beater impregnation method containing elastomeric impregnant utilizing water soluble solutions of reactive titania in the paper pulp. By reactive titania is meant monomeric orthotitanic acid of the structure  $Ti(OH)_4$  or a low polymer  $[Ti(OH)_4]_n$ .

In accordance with the present invention, it has been found that the incorporation of a water-soluble solution of reactive titania to a dilute paper stock (slurry of pulp) containing an impregnant latex followed by subsequent precipitation of the impregnant onto the paper fibers and drying of said pulp to form a paper sheet, results in the formation of a paper sheet having improved wet tensile strength, delamination resistance and tear strength and adequate elongation and flexibility.

More particularly, it has been found that the presence of reactive titania in a paper stock containing a water base impregnant effects uniform distribution of the impregnant throughout the formed paper resulting in a paper having the characteristics of high delamination resistance, high tear strength, high wet tensile strength and adequate flexibility and elongation.

The water soluble reactive titania solutions useful in accordance with this invention can be prepared from a water soluble orthotitanic ester in the presence of a suitable screener to delay hydrolysis of the orthotitanate, thus producing a highly reactive form of monomeric or low polymer orthotitanic acid. These stabilized solutions are disclosed in copending application Serial No. 576,498, filed April 5, 1956, by Paul Lagally. The orthotitanates disclosed in the copending application Serial No. 576,498 are those which are relatively stable in aqueous medium and which require a hydrolyzing agent, such as an acid or an alkali, for hydrolysis thereof. Examples of the preferred orthotitanates of this type are those of the chelated kind.

The water soluble reactive titania solutions useful in accordance with this invention can be prepared from a water-soluble orthotitanic ester in the presence of a suitable screener as illustrated by esters containing:

(1) Two, three or four ligands containing basic nitrogen. Chelated esters of this type are, for example, isopropyl-tri-triethanolamine orthotitanate, di-isopropyl-di-triethanolamine orthotitanate, di-isopropyl-di-diethanolamine orthotitanate, tetra cyanoethyl-diethanolamine orthotitanate.

(2) Less than two ligands containing basic nitrogen and in addition other ligands containing electron-donating groups. Water-soluble esters of this type are, for example, tri-cyanoethyl-mono-triethanolamine orthotitanate, tri-ethylene glycol - mono - triethyleneglycol - mono-triethanolamine orthotitanate.

As indicated heretofore, orthotitanates which are relatively stable in aqueous medium and of the type indicated by the preferred esters require the addition of a suitable hydrolyzing agent for the hydrolysis thereof to occur. Moreover, the hydrolyzing agent must be of such nature that it will not form a stable titanium complex with the hydrolyzed product.

Examples of acids which are not useful as hydrolyzing agents because they form stable titanium complexes are—

- (1) hydroxy acids containing a hydroxy group in the alpha or beta position such as lactic acid or tartaric acid;
- (2) lower aliphatic dicarboxylic acids such as oxalic acid and malonic acid and
- (3) hydro-fluoric acid.

Specific examples of acids which may be used as a hydrolyzing agent are:

Acid	Formula
Hydrochloric	HCl
Hydrobromic	HBr
Perchloric	HClO <sub>4</sub>
Sulfuric	H <sub>2</sub> SO <sub>4</sub>
Phosphoric	H <sub>3</sub> PO <sub>3</sub>
Boric	H <sub>3</sub> BO <sub>3</sub>
Formic	HCOOH
Acetic	CH <sub>3</sub> COOH
Trifluoroacetic	CF <sub>3</sub> COOH
Perfluorobutyric	C <sub>3</sub> F <sub>7</sub> COOH
Cyanoacetic	CH <sub>2</sub> CNCOOH
Chloroacetic	CH <sub>2</sub> ClCOOH
Trichloroacetic	CCl <sub>3</sub> COOH
Maleic Fumaric	(CH=CHCOOH) <sub>2</sub>
Succinic	(CH <sub>2</sub> COOH) <sub>2</sub>
Polyacrylic	(CH <sub>2</sub> CHCOOH) <sub>n</sub>
Thioglycolic	CH <sub>2</sub> SHCOOH
Thiomalic	CH <sub>2</sub> SHCOOH
Carboxymethyl-mercapto-succinic	$\begin{array}{c} \text{CH}_2\text{COOH} \\   \\ \text{S} \\   \\ \text{CH}_2\text{COOH} \end{array}$
Toluene sulfonic	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H
Sulfanilic	NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H

In addition to acids, bases may be used as hydrolyzing agents for certain of the orthotitanates. Examples of suitable bases for this purpose are sodium hydroxide, potassium hydroxide and nitrogen containing bases such as ammonium hydroxide, ethyl amine, diethyl amine, pyridine, piperidine and cyclohexylamine.

As indicated heretofore, a stabilizer is employed for controlling the hydrolysis of the orthotitanate and for preventing the precipitation of the hydrolyzed product from the aqueous solution. The stabilizer contains electron donating groups for temporarily screening the orthotitanic acid or ester to prevent polymerization thereof and subsequent precipitation from solution. Hence, any compound exhibiting the required electron donating qualities for effectuating the desired screening effect may be used as the stabilizer.

Typical compounds which may be used as stabilizers include hydroxyaldehydes and hydroxy-ketones and corresponding semiacetals of the aldehydes and ketones. Examples of such compounds are the monosaccharides such as glucose, fructose, mannose, xylose, threose, erythrose, rhamnose; the polysaccharides such as lactose and cellobiose, sugars with straight chains or as substances having oxide rings such as methyl glucoside may also be used. Also, suitable as stabilizers for this purpose are water soluble alcohols as represented by those having straight chain or cyclic structure such as ethylene glycol, diethylene glycol, diethylene glycol, triethylene glycol, sorbitol, mannitol and inositol. Also, operable are water soluble amides such as urea, dimethylformamide; hydroxy-alkyl derivatives of amines containing tertiary nitrogen such as triethanolamine and hydroxyalkyl-alkylenepolyamines such as tetrahydroxyethyl ethylene diamine.

In addition to the aforementioned stabilized water-soluble reactive titania solutions, water-soluble reactive titania solutions can also be used which are prepared from certain water-soluble orthotitanate esters by neutralization of an aqueous solution of the ester to give a product which is not stable for long periods of time but for short intervals, long enough to be used on a practical basis. Examples of orthotitanates which may be used for this purpose are:

Tetra-triethanolamine orthotitanate  
 Tetra-diethanolamine orthotitanate  
 Isopropyl-tri-triethanolamine orthotitanate  
 Diisopropyl di-triethanolamine orthotitanate  
 Dicyanoethyl-di-triethanolamine orthotitanate

Tri-triethanol sulfide Triethanolamine orthotitanate  
 Tetra-aminoethanolamine orthotitanate  
 Tetra-diethylethanolamine orthotitanate

In general, the procedure used in accordance with this invention involves addition of reactive titania solution to a slurry of pulp (dilute stock containing cellulose fibers) and water base impregnant in water, followed by precipitation of the impregnant onto the fibers and subsequent formation of the paper sheet; or addition of a water-soluble orthotitanate ester to the stock followed by hydrolysis of the ester by a suitable hydrolyzing agent to reactive titania, followed by precipitation of the impregnant onto the fibers and subsequent formation of the paper sheet. The addition of the reactive titania alone imparts wet strength to the sheet but the effect may be further increased by heating after formation and drying.

The amount of titania used will vary depending upon the structure of the orthotitanate used for making the reactive titania. In general, the range of concentration of Ti(OH)<sub>4</sub> will vary between 1 to 45%, and preferably 1 to 20%, based on the weight of the dry pulp.

Sheets produced in accordance with this invention by beater impregnation from a pulp containing elastomeric materials have been found to exhibit improved delamination resistance, high tear strength, high wet tensile strength and adequate flexibility and elongation. Any conventional elastomeric impregnant commonly used for unifying paper sheets may be used as exemplified by the following:

(1) Copolymers of a diene and acrylonitrile containing at least 60% by weight of the diene, such as a copolymer of 60% butadiene and 40% acrylonitrile.

(2) Copolymers of a diene and styrene and styrene homologues containing at least 40% of the diene, such as a copolymer of 50% butadiene and 50% styrene; and

(3) Copolymers of a diene and an acrylic acid, containing at least 50% of the diene, such as a copolymer of 60% butadiene and 40% of acrylic acid. In general, the impregnant is in an amount from 2 to 150% by weight based on the amount of dry pulp.

As will be understood by those skilled in the field, in impregnating the cellulosic fibers with an elastomeric impregnant by the heater impregnation method, there is involved the coagulation of precipitation of the elastomeric impregnant on the paper fibers. Although the impregnants in accordance with the present invention may be coagulated by the commonly used techniques utilizing the addition of aluminum sulfate, an acid, or an acid colloidal polymer, such methods are not preferred. In all of these cases coagulation required the use of acidic media at some step. The amount of elastomeric polymer that can be incorporated by these methods is limited.

The preferred precipitating agents for precipitating the elastomeric impregnants are those poly-N-basic compounds disclosed in U.S. Patent 2,745,744, patented May 15, 1956. These flocculating agents are produced by reacting formaldehyde with guanidine carbonate at a molar ratio at least one to one, although at least two to one is preferred. The chemical structure of the desired product is not fully understood, but the action of the material in flocculating particles of polymer onto pulp fiber is believed to be due to the presence of a multiplicity of positively charged amino groups linked together into a polymeric electrolyte so that each polymer molecule has many positive charges distributed along its length. Also effective is the polymeric electrolyte made by the treatment of polyvinyl pyridine with any lower alkyl halide having an alkyl group of from one to eight carbon atoms, e.g. (Fuoss—Jour. Poly. Sci. 3, 246-63 (1948)).

In order to illustrate the invention more specifically the following examples are given hereinbelow. Unless otherwise indicated, the percentages or parts given are by weight.

The following Examples I-IV disclose the preparation

of stabilized water soluble orthotitanate solutions which may be used as the source of reactive titania in accordance with the present invention.

#### EXAMPLE I

284.0 grams of tetra isopropyl orthotitanate (1 mole) are mixed with 298.4 grams of triethanolamine (2 moles). 120 grams of this mixture (containing .206 mole di-isopropyl-di-triethanolamine titanate) are dissolved in 300 ml. water, and 100 ml. of a 50% solution of methyl glucoside are added. In order to neutralize this mixture, 20 ml. conc. HCl are added. Diluting with water to 600 ml. does not produce hydrolysis sufficient to precipitate insoluble titania.

#### EXAMPLE II

120 grams of a mixture of 1 mole tetra isopropyl orthotitanate and two moles triethanolamine (containing .206 moles di-isopropyl-di-triethanolamine titanate) are dissolved in 200 ml. water 200 ml. of a 50% solution of urea are added. The resulting mixture is neutralized with 25 ml. conc. HCl and diluted with water to 600 ml.

#### EXAMPLE III

To 10 grams of a mixture of one mole tetra isopropyl-orthotitanate and four moles triethanolamine (0.0131 mole tetra-triethanolamine titanate) are added 3.9 grams triethanolamine (0.026 moles) .20 ml. of water are added and, after neutralization, the obtained solution is diluted with water to 50 mls. The obtained mixture remains stable.

Without adding an excess of triethanolamine, a neutralized aqueous solution of tetra-triethanolamine titanate precipitates insoluble titania quickly.

#### EXAMPLE IV

To 2.82 grams (0.0176 mole) triethanolamine are added 5.0 grams (0.0176 mole) tetra-isopropyl orthotitanate. The mixture containing mono-triethanolamine tri-isopropyl orthotitanate (0.0176 mole) is cooled and 20 mls. of a 50% aqueous solution of methylglucoside are added. The resulting solution is titrated with 5.395 N HCl (HCl:water=1:1). 1.7 ml. are needed to reach pH 7.

In the absence of methylglucoside of another proper stabilizer, it is impossible to dissolve mono-triethanolamine orthotitanate in water or to neutralize the obtained mixture.

The following Example V serves to describe the preparation of a preferred precipitating agent for precipitating the elastomeric polymer in accordance with the present invention.

#### EXAMPLE V

One hundred and twenty-one grams of commercial guanidine carbonate, one hundred grams of commercial thirty-seven percent formaldehyde are mixed and heated with occasional stirring, on an electric hot plate.

The initial hydrogen ion concentration of the mixture was equivalent to a pH of about 8.5. At the end of four hours of heating, the reaction vessel contained a viscous (when hot) transparent mass and the pH had fallen to about 7.5. Water was added and stirred to dissolve the reaction product. All during the heating, there was evolution of carbon dioxide from the reaction, and it was to facilitate the escape of this material that water was added. After additional heating for one and one-half hours at the boiling point of the solution, the pH was about 7.2 as measured with pH paper, and heating was discontinued.

The product obtained was an almost colorless solution containing thirty-seven percent solids. The viscosity of this thirty-seven percent solution was not substantially greater than water. The dry reaction product was a transparent, very slightly colored solid, softening below eighty degrees centigrade.

The following Examples VI to XXI serve to describe the preparation by beater impregnation of unified paper

sheets containing elastomeric impregnants in accordance with this invention.

#### EXAMPLE VI

To a semi-bleached kraft pulp of 600 cc. Schopper-Riegler freeness basis weight including elastomer (24" x 36" x 480=70 lbs.) was added 23% butadiene-acrylonitrile (65:35) latex based on the weight of finished sheet (70#—480). To this was added an amount of stabilized tetra triethanolamine titanate of Example III to give 9.3% Ti(OH)<sub>4</sub> based on dry weight of pulp. After mixing, the latex was precipitated with the guanidine-formaldehyde precipitating agent of Example V. 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 titanate was used.

	Wet Tensile, Pounds/Inch	Delamination Resistance, Ounces
Control.....	1	20
Ex. VI.....	3.8	29

#### EXAMPLE VII

To a semi-bleached kraft pulp of 650 cc. Schopper-Riegler freeness basis weight including elastomer (24" x 36" x 480=70 lbs.) was added 23% butadiene-acrylonitrile (65:35) latex based on the weight of finished sheet. To this was added an amount of tetratriethanolamine titanate to give 9.3% Ti(OH)<sub>4</sub> based on the weight of dry pulp. The titanate was then neutralized to pH 7 with dilute hydrochloric acid. The latex was then coagulated with the same reagent as used in Example VI. The sheet was then formed in a standard T.A.P.P.I. sheet mold.

As an illustration of improved physical properties obtained, we give below the results obtained in comparison with the results when no titanate was used.

	Wet Tensile, Pounds/Inch	Delamination Resistance, Ounces
Control.....	1.4	21
Ex. VII.....	3.5	30

#### EXAMPLE VIII

In the same manner described as in Example VII, a sheet basis weight including elastomer (24" x 36" x 480=70 lbs.) containing 34% butadiene-acrylonitrile latex (65:35) and 7.8% Ti(OH)<sub>4</sub> from tetratriethanolamine titanate based on dry weight of pulp gave a 10 ounce increase in delamination resistance and an increase in wet tensile over a control containing no titanate.

#### EXAMPLE IX

In the same manner as described in Example VII, a sheet, basis weight including elastomer (24" x 36" x 480=70 lbs.) containing 45% butadiene-acrylonitrile (65:35) latex and 2.2% Ti(OH)<sub>4</sub> from tetra-triethanolamine titanate gave an increase in delamination resistance of 12 ounces over a control containing no titanate.

#### EXAMPLE X

In the same manner as described in Example VII, a sheet, basis weight including elastomer (24" x 36" x 480=70 lbs.) containing 9.3% Ti(OH)<sub>4</sub> from tetratriethanolamine titanate and 23% butadiene-styrene (50:50) latex (GR-S) gave an increase in delamination resistance of 5 ounces over a control containing no titanate.

#### EXAMPLE XI

To a semi-bleached kraft pulp of 650 cc. Schopper-Riegler freeness basis weight including elastomer

(24" x 36" x 480=70 lbs.) was added 23% butadiene-acrylonitrile (65:35) latex based on the weight of finished sheet added with mixing. To this was added an amount of methyl glucoside stabilized mono-triethanolamine triisopropyl orthotitanate of Example IV to give 17.2%  $Ti(OH)_4$  based on the weight of the dry pulp. The titanate was then neutralized to pH 7 with dilute hydrochloric acid. The latex was then coagulated with the same guanidine-formaldehyde agent as used in Example VI. The sheet was then formed in a standard T.A.P.P.I. sheet mold.

## EXAMPLE XII

To a semi-bleached kraft paper of 650 cc. Schopper-Riegler freeness basis weight including elastomer (24" x 36" x 480=70 lbs.) was added 23% butadiene-acrylonitrile (65:35) latex based on the weight of the finished sheet added with mixing. To this was added an amount of methyl glucoside stabilized diisopropyl di-triethanolamine orthotitanate of Example I to give 18.8%  $Ti(OH)_4$  based on the weight of the dry pulp. The titanate was then neutralized to pH 7 with dilute hydrochloric acid. The latex was then coagulated with the same guanidine-formaldehyde agent as used in Example VI. The sheet was then formed in a standard T.A.P.P.I. sheet mold.

Additional samples of paper sheets were prepared in the same manner as in Example XII using different Hycar (butadiene-acrylonitrile copolymer 65:35) as the elastomeric impregnant and different titanate solutions. These examples are summarized in below Table II.

Table II

No.	Type of Latex	Percent Rubber	Titanate Used	Based on Pulp Percent $Ti(OH)_4$
XIII.....	Hycar....	23	Tetra-diethanolamine Titanate.	19
XIV.....	do.....	23	Di-diethanolamine Di-isopropyl Titanate.	23
XV.....	do.....	23	Di-triethanolamine Di-isopropyl Titanate.	18.8
XVI.....	do.....	23	Dicyanoethyl Di-triethanolamine Titanate.	17.7
XVII.....	do.....	23	Dicyanoethyl Triethanolamine Isopropyl Titanate.	22.2
XVIII.....	do.....	23	Tetra-aminoethanolamine Titanate.	15.5
XIX.....	do.....	23	do.....	11.7
XX.....	do.....	23	Tetra-diethanolmethylamine Titanate.	11.6
XXI.....	do.....	23	Tetra-diethylethanolamine Titanate.	11.1

The unified papers of the present invention containing elastomeric impregnants, as exemplified by those prepared in accordance with Examples VI and XXI are particularly useful as backings of normally tacky and pressure-sensitive adhesive tapes.

In forming a novel normally tacky and pressure-sensitive tape comprising a unified backing and a coat of adhesive on at least one side as shown in the accompanying drawing, a unified sheet is coated in a conventional manner with any normally tacky and pressure-sensitive adhesive. An example of such adhesive is one having the following recipe:

	Parts
Crude rubber .....	100
Rosin dehydrogenated .....	90
Aluminum hydrate .....	90
Mineral oil .....	30
Antioxidant .....	2

The invention in its broader aspects is not limited to the specific steps, processes, compositions, combinations and improvements shown and 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.

What is claimed is:

1. The method of forming a unified paper sheet having improved characteristics of wet tensile strength, tear strength and delamination resistance and adequate flexibility and elongation comprising the steps of mixing with a slurry of paper pulp including cellulose fibers, a latex of an elastomeric impregnant and a solution of reactive titania selected from the group consisting of monomeric orthotitanic acid and water soluble low polymers of orthotitanic acid, precipitating said elastomeric impregnant onto said fibers, subsequently forming a paper web and drying said web to form a paper sheet.

2. The process according to claim 1, wherein the elastomeric impregnant is selected from the group consisting of diene-acrylonitrile copolymers, diene-styrene and styrene homolog copolymers and diene-acrylic acid copolymers.

3. The process according to claim 1, wherein the elastomeric impregnant is a butadiene-acrylonitrile copolymer.

4. The process according to claim 1, wherein the elastomeric impregnant is a butadiene-styrene copolymer.

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