(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 199524384 B2
(10) Patent No. 702265

(54) Title

Dual surface treated filler material, method for its preparation and use in papermaking

(51)6 International Patent Classification(s)
D21H 017/69 D21H 021/16
C09C 001/02

(21) Application No: 199524384 (22) Application Date: 1995.05.16

(87) WIPO No: WO95/32335

(30) Priority Data

| (31) Number | (32) Date | (33) Country |
|---|---|---|
| 246448 | 1994.05.20 | US |

(43) Publication Date : 1995.12.18
(43) Publication Journal Date : 1996.01.25
(44) Accepted Journal Date : 1999.02.18

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(56) Related Art

US 5244542
US 3873336
GB 1425114

OPI DATE 18/12/95 APPLN. ID 24384/95
AOJP DATE 25/01/96 PCT NUMBER PCT/US95/06013

AU9524384

(PCT)

(51) International Patent Classification 6 :
D21H 17/69, C09C 1/02, D21H 21/16

A1

(11) International Publication Number: WO 95/32335

(43) International Publication Date: 30 November 1995 (30.11.95)

(21) International Application Number: PCT/US95/06013

(22) International Filing Date: 16 May 1995 (16.05.95)

(30) Priority Data:
246,448 20 May 1994 (20.05.94) US

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(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

**Published**
*With international search report.*

(54) Title: DUAL SURFACE TREATED FILLER MATERIAL, METHOD FOR ITS PREPARATION AND USE IN PAPERMAKING

(57) Abstract

An inorganic filler composition and a method for the use thereof wherein the inorganic filler has been pre-treated with an anionic treating agent and a cationic polymer to produce a dual treated inorganic filler. The surface-treated inorganic filler materials of the present invention are particularly suitable for use in papermaking processes where sizing and other properties, such as strength and optical performance are important.

# DUAL SURFACE TREATED FILLER MATERIAL, METHOD FOR ITS PREPARATION AND USE IN PAPERMAKING

## Field of the Invention

The present invention relates to a composition and a method for using that composition to improve the papermaking process and the quality of the paper products produced therefrom. More particularly, the present invention relates to the use of sizing agents. Even more specifically, the present invention relates to surface treated inorganic filler materials that are particularly suitable in papermaking processes where sizing and other properties, such as, strength and optical performance are important.

## Background of the Invention

Sizing agents are typically used in the papermaking process in order to slow down or resist the passage of liquids through the paper. Sizing agents are generally used in the papermaking process as either internal sizing agents or surface treating sizing agents. An internal sizing agent is added to the wet-end of the papermaking process, while surface sizing agents are added at the size press and effect the surface sizing properties of the sheet.

In the early development of cellulose reactive type sizing agents, excessive amounts of the sizing agent were required to control sizing. Two synthetic sizes presently in use are alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). Both impart sizing to the paper by means of a chemical reaction (covalent bonding) with the hydroxyl groups of cellulose fiber. However, the excessive use of cellulose reactive type sizing agents results in increased wet-end deposits, press picking, and, in coefficient of friction problems with the paper surface. These problems adversely impact paper production and quality of the final paper product. Therefore, the excessive use of sizing materials continues to be a problem for papermakers both from an economic and technical point of view.

Equally important to the control of sizing in the papermaking process, is the type of filler material that is used. Inorganic base fillers, such as, for example, clay, titanium dioxide, and calcium carbonate are known to have a detrimental effect on sizing. Filler and fines present in the wet-end papermaking process, absorb the sizing agent, thus rendering it ineffective in controlling sizing.

Studies of alkaline papers filled with various types of calcium carbonate reveal an inverse correlation between the specific surface area (ssa) of the filler and sizing values of the sheet. In other words, the higher the surface area of the filler material the more detrimental is its effect on sizing. Also, in circumstances where increasing the filler content of the paper would be advantageous both to the papermaking process and the final

product, sizing problems can occur which negatively affect sheet quality, machine performance, and production efficiency.

What is required is an inorganic base filler material that can be employed in the papermaking process without detrimentally affecting the papermaking process, nor the physical properties of the final sheet.

It is therefore an object of the present invention to provide a method for improving the sizing of paper. Another object of the present invention is to provide an inorganic base filler composition that is capable of use in the papermaking process to improve sizing. A further object of the present invention is to provide an inorganic base filler composition that improves the quality of the final paper product without adversely affecting sizing. These and other objects will become apparent as provided in the detailed specification that follows.

Prior Related Art

German Patent Application 2,316,097 discloses a filler for use in papermaking comprising a calcium carbonate coated with an anionic synthetic polymer resin such that the coated filler has a "0" (zero) charge. The coated filler is suggested to minimize the loss of strength normally seen due to using filler in papermaking. The preferred anionic resins are water based polymers, such as, for example styrene-butadiene copolymer.

U.S. Pat. No. 4,610,801 teaches the preparation of a mineral slurry that remains pumpable by adding cationic materials to the mineral slurry such that the treated slurry does not settle or exceed a viscosity of 500

c.p.s.m., and upon dilution, exerts a flocculative action. The treated slurry is alleged to be useful as a coagulant in sewage disposal or papermaking.

U.S. Pat. No. 5,147,507 discloses a method for improving papermaking by, reducing the sizing required, maintaining the sizing content over time, improving the handling properties of a formed web by adding to a papermaking furnish from about 5 to about 50 weight percent of a filler material which has been surface treated with from about 0.1 to about 10.0 weight percent of a cationic polymer which has been made cationic by treating with at least one polyamino-amide and a polyamine polymer which have been reacted with an epoxidized halohydrin compound to form tertiary and quaternary amine groups on the cationic polymer.

## Summary of the Invention

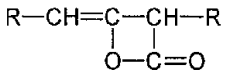
What has been discovered is an inorganic filler composition and a method for the use thereof wherein the inorganic filler has been pre-treated with an anionic treating agent and a cationic polymer to produce a dual treated inorganic filler that is particularly useful in papermaking processes where sizing, strength and optical performance is important.

## Detailed Description of the Invention

In one aspect of the invention, what has been found to be novel and unanticipated by the prior art is a dual treated inorganic filler, such as for example, calcium carbonate, either ground limestone or synthetically produced as precipitated calcium carbonate. The dual treated inorganic filler is particularly useful in a papermaking process where sizing,

strength and optical performance are important.

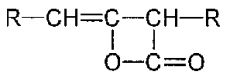
Accordingly, in a first embodiment the invention provides a dual treated mineral filler comprising a mineral filler surface treated with first an anionic treating agent and subsequently a cationic polymer, wherein said anionic treating agent is selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

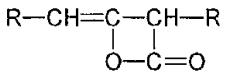
Another aspect of the invention provides a method for producing a dual treated inorganic filler by surface treating the inorganic filler with first and anionic chemical agent and then, a cationic polymer. When the dual surface treated inorganic filler of the present invention is subsequently used in a papermaking process, sizing properties are improved without adversely affecting strength, and optical performance.

In a further embodiment, the invention provides a method for improving sizing comprising adding to a papermaking system an inorganic filler material surface treated first with from 0.1 weight percent to 1.0 weight percent of an anionic agent and secondly with from 0.1 weight percent to 10 weight percent, based on the weight of the inorganic filler material, of a cationic polymer, wherein said anionic agent is selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



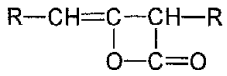
where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

In a still further embodiment, the invention provides an improved paper comprising cellulose fibers and a mineral filler treated with first an anionic treating agent and subsequently a cationic polymer, wherein said anionic agent wherein said anionic agent is selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

In yet a further embodiment, the invention provides an improved paper comprising cellulose fibers and a calcium carbonate filler surface treated with from 0.1 weight percent to 1.0 weight percent of an anionic agent and from 0.1 weight percent to 10 weight percent, based on the weight of the filler material, of a cationic polymer wherein said anionic agent is selected from the group consisting of glassy sodium phosphates, carboxymethylolestearic acid and fatty acids, cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

**Anionic Chemical Agents**

Anionic chemical agents found to be effective for first treating the inorganic filler are selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates, sodium polyacrylic acid or other inorganic or organic dispersing agents. Glassy sodium phosphates include, but are not limited to, sodium tetraphosphate, tetrasodium pyrophosphate, sodium hexametaphosphate and amido long chain polyphosphate. From these, tetrasodium phosphate is preferred. Sodium polyacrylic acids, including polyacrylates with a molecular weight of less than about 4000, are especially preferred. A suitable polyacrylate is manufactured by Rhone-Poulenc, Marietta, Georgia, under the trade name of Collids-211. The glassy sodium phosphates are preferred and tetrasodium phosphate is especially preferred.

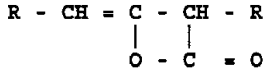
The level of anionic chemical agent required to improve the optical and physical performance of paper made according to the present invention is from about 0.01 weight percent to about 1.0 weight percent based on the weight of the inorganic filler. The preferred

level of anionic chemical agent is from about 0.1 weight percent to about 0.5 weight percent.

Cationic Polymers

The second component necessary to produce the dual treated inorganic filler of the present invention is a cationic polymer. The use of from about 0.1 percent to about 10.0 percent, preferably, from about 0.25 percent to about 2 percent by weight of the cationic polymer, based on the weight of the inorganic filler, improves the sizing performance without adversely affecting optical and physical properties, particularly opacity, and tensile strength of the resulting paper in which the filler is utilized.

Cationic polymers found to be effective for surface treating the inorganic filler are dimers of the general formula:



where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl. Specific dimers are octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl-, eikosyl-, dokosyl-, tetrakosyl-, phenyl, benzyl-beta-naphthyl-, and cyclohexyl- dimer. Other utilizable dimers produced from mining acids, naphthenic acid, delta-9, 10-decylenic acid, palmitoline acid, oleic acid, ricine oleic acid, linoleate, linoleic acid, olestearic acid and the like, as well as dimers manufactured from natural fatty acid mixtures, such as are obtained from coconut oil, babassu oil, palm seed oil, palm oil, olive oil, peanut oil, rape seed oil, beef suet and

lard, and the like, including mixtures of the above.

The polymer is made cationic by treating the dimer with a polyamino-amide and/or polyamine polymer reacted with an epoxidized halohydrin compound, such as epichlorohydrin, thereby forming tertiary and quaternary amine groups on the dimer surface. It is preferred that the cationic charge on the dimer be derived primarily from quaternary amine groups. A suitable polymer of this type is manufactured by Hercules, Inc., Wilmington, Delaware, under the tradename Hercon.

Inorganic Base Fillers

Inorganic fillers suitable for use in the present invention are selected from the group consisting of calcium carbonate, either ground natural limestone or synthetically produced as precipitated calcium carbonate (PCC), titanium dioxide, talc and silica/silicate fillers. The above mentioned fillers, if used untreated, have a detrimental effect on sizing, but when treated with first an anionic treating agent and then a cationic polymer material according to the present invention become readily utilizable and in fact improve the papermaking process and the resulting paper product.

For all types of fillers, it has been discovered that the amount of cationic polymer required to be added to the filler material-containing slurry is directly correlated with the surface area of the filler material.

In order to produce the dual surface treated inorganic filler of the present invention, the inorganic filler is first treated an anionic chemical agent and then, a cationic

polymer in order to produce the dual surfaced treated inorganic filler of the present invention. The anionic and cationic treating agents are typically added to a slurry containing the inorganic filler by any means known in the art. The anionic chemical agent may be added in wet or dry form, while the cationic treating agent are typically added in solution form. One effective means of surface treating the filler is by adding the treating agents while agitating the slurry, at room temperature of 25 degrees Centigrade. When the dual surface treated inorganic filler of the present invention is subsequently used in a papermaking process, sizing performance is improved.

When the present invention is practiced utilizing clay as the inorganic base filler, it has been discovered that surface treating the clay with a level of from about 1.0 to about 2.0 weight percent of a cationic polymer material of the aforesaid type, is effective in producing a filler clay having a substantially reduced sizing demand.

Sizing was tested by the Hercules Size Test (HST) to measure penetration of liquid through the handsheets. HST is the test method used to determine the degree of sizing of paper in the instant invention. The test was performed on a Hercules sizing tester model KA or KC and the test method employed is TAPPI Method T-530 PM-89 (revised 1989).

The following examples are intended to further illustrate the novel and unobvious aspects of the surface treated inorganic base filler and the method of using the same of the present invention. However, they should not be

taken, nor are they intended, to limit the scope of the present invention in any aspect whatsoever, except, as defined in the attached claims.

EXAMPLE I

A $CaCO_3$ slurry at 17.5% solids and pH of 8.0 was treated with the below described cationic or anionic and cationic materials. Treatment levels are calculated on a dry weight basis of the calcium carbonate present (dry wt. % based on the filler). For the dual treatment, to the calcium carbonate slurry, while stirring, was first added the anionic treating agent. After stirring five minutes the cationic material was added and stirring continued another five minutes. The treated $CaCO_3$ fillers were then incorporated into paper handsheets for further evaluation in the following manner: Turbulent-pulse former handsheets ($74g/m^2$) were prepared from a furnish of 75% bleached hardwood and 25% bleached softwood kraft pulps beaten to 400 Canadian standard freeness (CSF) at pH 7.0 in distilled water. Shear speed on the turbulent-pulse former was set at 1250 RPM utilizing a pulp furnish having a consistency of 0.12 percent. Hercon-85, a synthetic sizing agent (alkyl ketene dimer) was added to the pulp at levels of from 0.25 to 0.75 percent. The filler was added to the furnish to achieve a filler content range of from about 15 to about 25 percent in the finished sheets. A high molecular weight anionic polyacrylamide retention aid (accurac-171) was added in an amount corresponding to 0.05 percent. Distilled water was used throughout the process of preparing the handsheets. The sheets were pressed using one nip at a pressure of 25 P.S.I.

and dried on a rotating chrome-plated drum at a temperature of 125° Centigrade. All sheets were conditioned at 50% R.H., and 23°C.

The sizing values obtained on sheets filled with anionic/cationic dual treatment $CaCO_3$ were found to improve sizing to exceed the values obtained on sheets produced using a single cationic treatment.

TABLE I. HST Comparison of Single Vs. Dual Treatment Using Two Different Anionic Agents at Varying Levels.

| Treatment Type | | 16% Filler Target | | 24% Filler Target | |
|---|---|---|---|---|---|
| | | % Filler | HST | % Filler | HST |
| No Treatment | | 16.9 | 48 | 25.8 | 3 |
| (anionic) | (cationic) | | | | |
| 0 (Zero) | 0.5% Hercon-85 | 15.8 | 348 | 24.5 | 72 |
| 0.1% Colloids-211 + | 0.5% Hercon-85 | 15.6 | 421 | 23.7 | 182 |
| 0.3% Colloids-211 + | 0.5% Hercon-85 | 15.2 | 424 | 23.8 | 303 |
| 0.5% Colloids-211 + | 0.5% Hercon-85 | 15.0 | 397 | 23.3 | 294 |
| 0.1% TSPP + | 0.5% Hercon-85 | 15.6 | 357 | 23.4 | 120 |
| 0.5% TSPP + | 0.5% Hercon-85 | 15.2 | 389 | 24.2 | 170 |

EXAMPLE II

In the same manner as described in Example I, a $CaCO_3$ slurry at approximately 17-18% solids and pH -8 was treated with the materials mentioned below (treatment levels calculated based on dry weight) allowing 5 minutes of mixing time for each addition. Paper handsheets were then produced using the resulting surface-treated $CaCO_3$ slurries with target filler levels of 16% and 24% and target dry sheet weights of 0.6g (74 $g/m^2$).

It was found that increasing anionic treatment while holding cationic treatment constant, resulted in higher sizing values.

TABLE II. HST Comparison of Single Vs. Dual Treatment Using Varying Anionic Agent Levels and Varying AKD Levels.

| Treatment Type | | 16% Filler Target | | 24% Filler Target | |
|---|---|---|---|---|---|
| | | % Filler | HST | % Filler | HST |
| No Treatment | | 15.1 | 38 | 23.2 | 3 |
| (anionic) | (cationic) | | | | |
| 0 (Zero) | 0.5% Hercon-85 | 15.0 | 100 | 22.9 | 7 |
| 0 (Zero) | 0.75% Hercon-85 | 14.9 | 159 | 22.2 | 21 |
| 0.2% Colloids-211 + | 0.25% Hercon-85 | 15.3 | 100 | 22.8 | 10 |
| 0.2% Colloids-211 + | 0.5% Hercon-85 | 15.4 | 309 | 23.1 | 62 |
| 0.3% Colloids-211 + | 0.25% Hercon-85 | 15.0 | 154 | 23.3 | 13 |

EXAMPLE III

In the same manner as described in Example I, a $CaCO_3$ slurry at approximately 17-18% solids and pH ~8 was treated with the materials mentioned below (treatment levels calculated based on dry weight) allowing 5 minutes of mixing time for each addition. Paper handsheets were then produced using the resulting surface-treated $CaCO_3$ slurries following 2 days and again after 10 days of filler storage. Target filler level was 16% and target bone dry sheet weights were 0.6g (74 $g/m^2$).

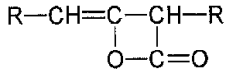
The sizing values obtained on sheets filled with anionic/cationic dual treatment $CaCO_3$, were found to exceed the values obtained on sheets produced using a single cationic treatment after both 2 days and 10 days of filler storage time. Moreover, the dual treatment showed less sizing loss (lower % HST reduction) than the single treatment.

TABLE III. HST Comparison of Single Vs. Dual Treatment After Extended Filler Slurry Storage. (16% Filler Target)

| Treatment Type | | Treated Filler Age (days) 2 % Filler | HST | 10 Filler | HST | % Reduction |
|---|---|---|---|---|---|---|
| No Treatment | | 17.0 | 17 | 16.7 | 10 | 41 |
| (anionic) | (cationic) | | | | | |
| 0 (Zero) | 0.5% AKD | 17.0 | 176 | 16.3 | 75 | 57 |
| 0.3% Colloids-211 + | 0.5% AKD | 16.5 | 307 | 16.0 | 223 | 27 |

**The claims defining the invention are as follows:**

1. A method for improving sizing comprising adding to a papermaking system an inorganic filler material surface treated first with from 0.1 weight percent to 1.0 weight percent of an anionic agent and secondly with from 0.1 weight percent to 10 weight percent, based on the weight of the inorganic filler material, of a cationic polymer, wherein said anionic agent is selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



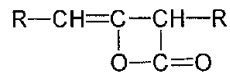
where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

2. A method as claimed in claim 1, wherein the cationic polymer is a cationized dimer of an acid selected from octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl-, eikosyl-, dokosyl-, tetrakosyl-, phenyl, benzyl-beta-naphthyl-, cyclohexyl-, naphthenic acid, delta-9, 10-decylenic acid, palmitoline acid, oleic acid, ricine oleic acid, linoleate, linoleic acid, olestearic acid and fatty acids.

3. The method of claim 1 or 2, wherein the papermaking system contains a filler material surface treated with from about 0.1 weight percent to 0.5 weight percent of an anionic agent and from 0.1 weight percent to about 10 weight percent, based on the weight of the filler material, of a cationic polymer.

4. The method of any one of claims 1, 2 or 3, wherein the inorganic filler material is finely divided calcium carbonate.

5. A dual treated mineral filler comprising a mineral filler surface treated with first an anionic treating agent and subsequently a cationic polymer, wherein said anionic treating agent is selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

6. A dual treated mineral filler according to claim 5 wherein said cationic polymer is a cationized dimer of an acid selected from octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl-, eikosyl-, dokosyl-, tetrakosyl-, phenyl, benzyl-beta-naphthyl-, cyclohexyl-, naphthenic acid, delta-9, 10-decylenic acid, palmitoline acid, oleic acid, ricine oleic acid, linoleate, linoleic acid, olestearic acid and fatty acids.

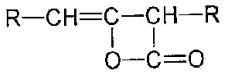
7. The product of claim 5, wherein the filler material is surface treated with from 0.1 weight percent to 1.0 weight percent of an anionic agent and from 0.1 weight percent to 10 weight percent, based on the weight of the filler material, of a cationic polymer.

8. The product of any one of claims 5, 6 or 7, wherein the mineral filler is calcium carbonate.

9. The product of any one of claims 5, 6, 7 or 8, wherein the anionic agent is selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates and sodium polyacrylic acid.

10. The product of claim 6, wherein said dimer is selected from dimers of fatty acids obtained from coconut oil, babassu oil, palm seed oil, palm oil, olive oil, peanut oil, rape seed oil, beef suet or lard.

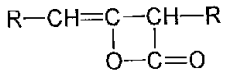
11. An improved paper comprising cellulose fibers and a mineral filler treated with first an anionic treating agent and subsequently a cationic polymer, wherein said anionic agent wherein said anionic agent is selected from the group consisting of glassy sodium phosphates, carboxymethyl cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

12. An improved paper according to claim 11, wherein said cationic polymer is a cationized dimer of an acid selected from and octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl-, eikosyl-, dokosyl-, tetrakosyl-, phenyl, benzyl-beta-naphthyl-, cyclohexyl-, naphthenic acid, delta-9, 10-decylenic acid, palmitoline acid, oleic acid, ricine oleic acid, linoleate, linoleic acid, olestearic acid and fatty acids.

13. An improved paper comprising cellulose fibers and a calcium carbonate filler surface treated with from 0.1 weight percent to 1.0 weight percent of an anionic agent and from 0.1 weight percent to 10 weight percent, based on the weight of the filler material, of a cationic polymer wherein said anionic agent is selected from the group consisting of glassy sodium phosphates, carboxymethylolestearic acid and fatty acids, cellulose, silicates, polyacrylates and sodium polyacrylic acid and mixtures thereof, and said cationic polymer is a cationized dimer of the general formula:



where R is a hydrocarbon group selected from the group consisting of alkyl with at least 8 carbon atoms, cycloalkyl with at least 6 carbon atoms, aryl, aralkyl and alkaryl.

14. An improved paper according to claim 13, wherein said cationic polymer is a cationized dimer of an acid selected from octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl-, eikosyl-, dokosyl-, tetrakosyl-, phenyl, benzyl-beta-naphthyl-, cyclohexyl-, naphthenic acid, delta-9, 10-decylenic acid, palmitoline acid, oleic acid, ricine oleic acid, linoleate, linoleic acid, olestearic acid and fatty acids.

15. A method for improving sizing, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

16. A dual treated mineral filter, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

17. An improved paper comprising cellulose fibres and a mineral filler, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

**Dated 24 December, 1998**
**Minerals Technologies Inc.**

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