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SIZED MINERAL FILLED PAPER AND METHOD OF MAKING SAME

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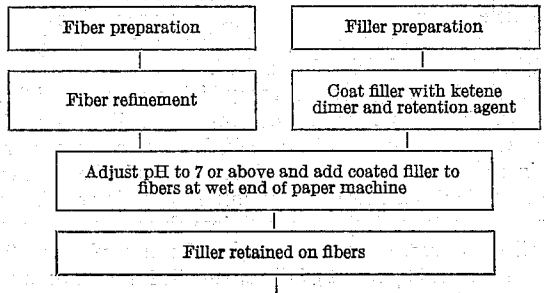
This invention relates to a process for simultaneously sizing and filling paper under alkaline conditions, and more particularly to a process for applying sizing and filling to paper under alkaline conditions in the wet end of the papermaking process. This is a continuation of our similarly entitled, previous and copending application Serial No. 449,262, filed August 11, 1954. This invention relates specifically to the preferred embodiment of that application in which a mineral filler is coated both with a particular sizing agent and a retention agent under alkaline conditions and is mixed with the furnish prior to the formation of the paper web.

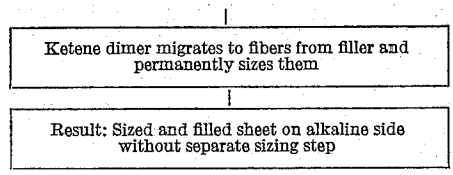
In our process any mineral filler or loading agent may be used. Without limitation thereto, the mineral fillers or loading agents are exemplified by clay, calcium carbonate, magnesium carbonate, titanium dioxide, talc, or mixtures thereof.

According to the invention the finely divided mineral filler or loading agent is pretreated in an aqueous dispersion or emulsion of a sizing agent. Said sizing agent is adsorbed or absorbed from said aqueous dispersion or emulsion by the fine particles of the mineral filler. The sizing agent coats the fine particles of mineral filler, either upon the entire surface of said particles, or on one or more spots of the respective fine particles. Said coatings on the particles are stable and adherent to said particles and said coatings remain on said particles in the aqueous suspension of the cellulose fibers. At least part of the coatings migrate from the pre-coated particles to the cellulose fibers in the finished paper web.

The pre-treated or pre-coated and finely divided mineral filler is mixed with an aqueous suspension of cellulose fibers. The resultant aqueous mixture or blend is supplied to the wire screen of a Fourdrinier machine or other web-making machine, and the resultant paper web is dried and treated in any suitable manner. During the drying period, the sizing material migrates sufficiently to the cellulose fiber from the pre-coated particles to produce a sheet of paper which has satisfactory sizing. In some cases, the partial migration of the sizing to the cellulose fibers is completed after the drying, while the finished paper sheet is kept during a few days at 20° C.–30° C., such as during a period of 3 or 4 days.

A flow diagram of a preferred embodiment of our invention is a follows:





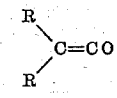
The improved process of the invention does not require the use of alum or other acidic agent, in order to precipitate or seat the sizing material. Indeed, from consideration of the previously mentioned disadvantages of alum, it is preferred to avoid the use of alum in this invention. The omission of alum is however not necessary to achieve successful sizing with the sizing agents used in this invention. However, the results which are obtained when alum is used, are somewhat less satisfactory than when alum is not used.

The invention gives equally good results when an inert filler like clay is used, or when an alkaline filler like calcium carbonate is used. As has been previously stated, there has been no satisfactory process for making a white and sized paper, which contained calcium carbonate filler, in which the sizing was provided by sizing material which was in an acidic aqueous suspension of cellulosic fibers, prior to the formation of the paper web from said aqueous suspension. However, the present invention provides very excellent sizing in paper which contains calcium carbonate filler. Indeed, the preferred practice according to the invention is to use an alkaline aqueous suspension of the cellulose fibers for the purpose of making the paper web on the wire screen of the web-making machine, whether the filler is calcium carbonate or other alkaline filler or an inert filler, such as clay.

The initial paper web and the finished paper contain particles of mineral filler which carry adsorbed or absorbed sizing material. Part of the sizing material migrates to the cellulose fibers, but part of said sizing material remains on the particles of mineral filler or loading agent. As a result, a finished paper which has a sufficient degree of sizing can be easily made, even when such paper has a large proportion of mineral filler. This is very different from former processes, in which the sizing in the aqueous suspension of the cellulose fibers becomes decreasingly effective when the proportion of added mineral filler is increased.

The preferred sizing materials are selected from the class of dimers of aliphatic ketenes, in which the original ketenes have hydrocarbon groups containing from six to twenty carbon atoms inclusive.

The ketenes are compounds of the general formula



in which at least one R stands for an aliphatic hydrocarbon group and the other R stands for an aliphatic hydrocarbon group or hydrogen. The aliphatic hydrocarbon group or groups may be straight chain or branched chain or staturated or unsaturated. In other words the ketenes may be either keto or aldo alkyl or alkylene ketenes. The ketenes, the dimers of which are used as sizing materials in accordance with the present invention have hydrocarbon groups containing from 6 to 20 carbon atoms.

The ketenes and their dimers are well-known. They are described, for example, in Thorpe's "Dictionary of Applied Chemistry," vol. VII (published in 1946), pages 102–106; the "Journal of the American Chemical Society" vol. 69 (published in 1947), pages 2444–2448. Ketenes are also described in Gilman's "Organic Chem-

istry," vol. 1, second edition, published in 1943, pages 662–665.

The above mentioned ketenes, which have from six to twenty carbon atoms in their hydrocarbon groups are designated as the higher aliphatic ketenes for the purposes of this disclosure.

As stated above one R may be a hydrocarbon group and the other R may be hydrogen or both R's may be hydrocarbon groups and these hydrocarbon groups may be identical or different from each other.

For example, the ketene may be derived from oleic acid of which the formula is

$$CH_3(CH_2)_7CH{:}CH(CH_2)_7.COOH$$

The symbol R in the ketene formula would then represent $CH_3(CH_2)_7CH{:}CH(CH_2)_6$. This ketene and its dimer can be prepared as above described in the cited technical literature, and this dimer containing unsaturated hydrocarbon groups can be used.

The other unsaturated fatty acids are well known. The ketenes derived from these unsaturated acids can be dimerized and used in this invention.

Examples of ketenes having saturated hydrocarbon groups the dimers of which are usable in the present invention are hexyl, decyl, tetradecyl, hexadecyl and eicosanyl ketenes, to name only a few species of the group described above.

The use of emulsions which includes said higher aliphatic ketene dimers is disclosed in Downey U.S. Patent No. 2,627,477 issued February 3, 1953, which refers to the formation of emulsions of said dimers in water by means of soap, synthetic detergents and other agents.

Many of the original ketenes of this class are disclosed in British Patent No. 522,204, accepted June 12, 1940.

The general formula of a ketene dimer of this class may be $RCH_2COCR{:}C{:}O$ as stated in the "Journal of the American Chemical Society," vol. 69, page 2444, although a more probable configuration is



In the above formula, "R" represents the radical of a saturated straight-chain or branched chain hydrocarbon, or a radical which is unsaturated at one or more parts of its chain.

The fine particles of the mineral filler are immersed in said aqueous dispersion or emulsion of the dimer. The fine particles of the mineral filler absorb or adsorb the dimer, so that the dimer forms a coating on the entire surface of each particle of the mineral filler or upon one or more spots of each said particle. In order to provide said adsorption or absorption, the particles should be free from any coating which repels the dimer.

One example of making an aqueous emulsion of a dimer is stated below:

In the following, the term "unit" refers to any unit of weight such as a pound or kilogram or the like.

Sixty units of the dimer of monohexadecyl ketene and twelve units of an emulsifying agent are mixed and heated to a temperature of 55° C. This operation, like all the operations disclosed herein, is performed under ordinary atmospheric pressure of approximately 760 millimeters of mercury. In this example, the emulsifying agent is polyoxyethylene sorbitan trioleate, which is known commercially as "Tween 85."

This emulsifying agent is an oily liquid at 25° C., with a specific gravity of 1.00 to 1.05 at 25° C. It is dispersible in distilled water. This "Tween 85" is fully described at page 587 of "Handbook of Material Trade Names" by Zimmerman & Lavine, published in 1953 by Industrial Research Service.

One hundred and twenty-eight units of water, which may be distilled water or tap water, are slowly added to the above mentioned mixture at 55° C.–60° C. The initial emulsion which is thus formed has a yellow color, and is an emulsion of water in oil. When about half the water has been added, the emulsion becomes an emulsion of oil in water, and the original yellow color changes to a white color. This emulsion can be used for the purposes of this invention. Other emulsions which can be used are described in said U.S. Patent No. 2,627,477.

In this example, there are sixty units of the dimer in an emulsion whose total weight is 200 units. Hence, the weight of the dimer is 30% of the total weight of the emulsion. This is a convenient concentration of the dimer in the emulsion, but this ratio is not a sharply critical factor.

It has been proposed, as disclosed in said U.S. Patent No. 2,627,477, to apply small proportions of the dimers of higher alkyl ketenes, to the surface of a paper web, for sizing purposes. However, tests have shown that if said small proportions of the higher alkyl ketene dimers are included in the aqueous suspension of cellulose fibers from which a paper web is formed, the sizing is unsatisfactory. In order to obtain any appreciable degree of sizing by adding said dimers directly to the aqueous suspension of the cellulose fibers, it is necessary to use large quantities of said dimers, which makes the process too expensive.

The aqueous blend or mixture from which the initial paper web is formed, may consist solely of water, cellulose fibers or cellulose pulp suspended in the water, and the final mixture of pre-coated particles and water. The cellulose fiber or cellulose pulp may be of any type, either uncooked cellulose fiber or cooked cellulose pulp, or a mixture of cooked fibers, or a mixture of uncooked cellulose fibers and cooked cellulose fibers.

For best results, it is desirable to avoid all use of alum in the aqueous suspension of the cellulose fibers, and in the aqueous blend which is supplied to the wire screen of the web-making machine.

It is preferred to mix the pre-treated or dimer pre-coated particles of mineral filler with the aqueous suspension of the cellulose fibers, after the cellulose fibers have been fully mechanically worked in the aqueous suspension, as by beating or otherwise, in order fully to hydrate and swell the cellulose fibers and to produce thin fibrils on their surfaces, before the dimer-coated particles of filler are mixed with said aqueous suspension.

The invention is not limited to a process in which all of the filler is thus pre-treated with a higher aliphatic ketene dimer. Only a part of the added mineral filler may be precoated with the selected dimer or mixture of dimers, and the remainder of the filler may be added in ordinary uncoated form to the aqueous suspension of the cellulose fibers. It is sufficient if the finished paper web contains 0.1 percent or more of the selected dimer or mixture of dimers, calculated upon the air-dry weight of the dimer and the air-dry weight of the finished paper, if such proportion of the dimer is supplied in the form of a coating on some of the fine particles of mineral filler.

Usually, from 0.25 percent to 0.50 percent of the dimer is sufficient, based upon the air-dry weight of the cellulosic fiber and of the dimer if said percentage of the dimer is supplied in the form of a pre-coating on the particles of mineral filler. A greater proportion of the dimer in the form of a pre-coating may be used, if a higher degree of sizing is required.

If the finished paper has a very high percentage of filler by weight, the percentage of pre-coating dimer may be increased, because the filler itself, in some cases, may retain so much of the absorbed or adsorbed dimer of the pre-coating that there will be insufficient dimer left free to migrate to and size the cellulose fiber. However, in ordinary cases, the above mentioned range of about 0.1 percent to 0.50 percent of dimer supplied as a pre-coating on the mineral filler, as calculated on the air-dry weight

of the cellulose fiber of the finished paper and upon the air-dry weight of the dimer, gives excellent results. The quantity of coated mineral filler in the finished paper may range from about 1.0% to about 50%.

As previously mentioned, the invention is applicable to papers whose filler is calcium carbonate or other alkaline filler, without limitation to such fillers, which may be clay, titanium dioxide, etc. In fact, this invention provides the first really satisfactory process of sizing paper which has an alkaline filler, other than by methods in which the paper web is sized by a surface sizing method.

Paper which has a considerable percentage of calcium carbonate and which is well-sized, and which has a very high degree of whiteness, can thus be produced according to this invention. When such paper is tested by the conventional spot test, such paper will of course show a surface pH value which is above 7.

Non-acid paper whose pH value is 7 or above, shows much less deterioration upon ageing than acidic paper.

Since alum and other acid agents can be omitted according to this invention, it is also possible to dissolve a soluble alkali, such as sodium carbonate, in the water of the aqueous suspension of the cellulose fibers, thus rendering the paper alkaline and thus improving its ageing characteristics. Such sized paper can have clay or other filler which is inert to acids. Such paper will also show a surface pH value above 7 when it is tested by a conventional spot test.

By eliminating the use of alum and acidic agents, it is possible to beat or otherwise mechanically work the aqueous suspension of the cellulosic fibers under alkaline conditions, and thus obtain all the known benefits of such alkaline beating or working without decreasing such benefits by the subsequent addition of alum to said aqueous suspension.

The dried paper web which is thus made, can be finished for use as an uncoated printing paper, or said paper web can be coated so as to provide a more expensive and better coated paper for printing purposes. In either case, a dried paper web made according to this invention is substantially uniformly sized throughout, with both cellulose fiber and mineral filler particles in close association with the higher alkyl ketene dimer, which is distributed throughout the entire thickness of the sheet in a substantially uniform manner, and which has migrated to the cellulose fibers on intimate combination with the fibers.

If sizing material is applied to the surface of a pre-formed paper web, the greatest concentration of the sizing material is at the surface of the pre-formed paper web to which the sizing composition is applied. Hence, it is a marked improvement to distribute the sizing uniformly or substantially uniformly throughout the entire thickness of the paper, closely combined with the cellulose fibers by absorption, adsorption or reaction.

At ordinary room temperature of 20°–30° C. the preferred dimers range from oily liquid to solid and wax-like consistency. These physical properties depend upon the degree of unsaturation of the fatty acids which are used to make the initial ketenes.

The particles of filler, pre-coated in whole or in part with the selected dimer material, may be used mainly as a sizing agent, with some provision of filler material.

In such case, the filler has a dual function, namely, to apply the dimer initially to the cellulose fiber, and also to act as a loading agent. The percentage of filler may be low, if it applies sufficient dimer to the cellulose fiber to supply the desired sizing quality. Additional uncoated filler can be added, to serve the ordinary function of a filler, after the sizing requirement has been met.

In the practice of our process, an important improvement resides in the fact that the particles of filler are initially coated with said dimer material and they are then coated with manno-galactan plant mucilage, or with a coating composition which includes a plant mucilage, in order to provide better retention of the particles in the initial paper web and in the finished paper. The use of manno-galactan to improve retention of mineral filler is claimed broadly in our copending application Serial No. 449,261, filed August 11, 1954, and now abandoned and in a continuation-in-part thereof Serial No. 515,238, filed June 13, 1955, now Patent No. 2,949,397.

This also avoids the use of alum or other acidic agent for the purpose of retaining filler and for sizing purposes.

As previously noted, the use of alum is highly objectionable for many reasons.

The most common manno-galactans are present in or are derived from or are modified products of the gums of the following:

(*a*) Locust bean gum, also designated as carob bean gum or carob gum. The botanical name of its source is *Ceratonia siliqua* L.

It has about 83% by weight of manno-galactans. It has been used in the paper industry for various purposes, such as a size and binder and finishing agent. It has never been used for the purposes of this invention.

This product is sold under the commercial name of locust bean gum and "Lycoid" gums. It is a substantially anhydrous powder.

As above noted, the coating need not be a pure manno-galactan. The coating medium can be a mixture of manno-galactan plant mucilage and starch.

(*b*) Guar gum. This is derived from a legume whose botanical name is *Cyamposis psoralioides* or *Cyamposis tetragonaloba* (*psoralioides*). It is sold commercially as guar gum or as "Burtonite No. 7," in the form of a substantially anhydrous powder.

Other plant mucilages which have little commercial importance at the present time and which have at least 50% by weight of one or more manno-galactans, and which can be used herein, are found in or are derived from the seeds of the following sources:

(*c*) Flame tree—this is a class which includes the following:

Nutysia floribunda, family *Loranthaceae.*

Brachychiton aerifolius, family *Sterculiaceae.*

The Indian rhododendrum, whose botanical name is *R. aboreum.*

(*d*) The huisache shrub, whose botanical name is *Vachellia farnesiana.*

(*e*) The Kentucky coffee tree, whose botanical name is *Gymnocladus dioica.*

(*f*) The mesquite, whose botanical name is, *Proscopis* juliflora.

(*g*) Palo verde, whose botanical names are *torreyanum, Cercidium torreyanum* and *Cercidium floridum.*

Whenever a "unit" is mentioned herein, this refers to any unit of weight, such as a kilogram, pound, or other unit of weight.

Thus, as one example, one unit of said locust bean gum is mixed with 100 units of water, and the mixture is heated to 91° C. with stirring, and the mixture is then additionally heated at 91° C., with stirring, for five minutes, and it may optionally then be cooled to 20° C.–30° C. All of the operations described herein are carried out under ordinary atmospheric pressure of about 760 millimeters of mercury, and the heating and mixing operations described herein are performed with little or no loss of water. All measurements of pH and viscosity are made at 25° C.

The resultant product has a pH of 6.0 and a viscosity of 2960 centipoises.

If the ratio of said locust bean gum is increased to 1.5 units, the resultant colloidal dispersion has a pH of 6.0 and a viscosity of 17,600 centipoises.

The invention is not limited to a pH of 6.0 or above, in the colloidal dispersion.

Thus, as later described, we can use a colloidal dispersion of a product which is known commercially as "Star gum No. 709." This product is a mixture of locust bean gum and starch which is water-soluble or water-dispers-

ible. When one unit of said "Star gum" is colloidally dispersed in 100 units of water, the resultant dispersion has a pH of 9.0, and a viscosity of 1600 centipoises. It is sufficient if the coated particles are electrostatically attracted to the cellulose fibers in aqueous suspension.

Cellulose fibers are negatively charged in aqueous suspension. Mineral fillers are also negatively charged in aqueous suspension. The pre-coating of the particles of mineral filler positively charges the pre-coated particles of mineral filler in aqueous suspension, or at least lowers the negative charges of the uncoated particles, so that the pre-coated particles are attracted to the cellulose fibers in aqueous suspension and then retained by the cellulose fibers.

As above noted, in order to be effective for purposes of filler retention, the swelled and colloidally dispersed coating composition must have a sufficient concentration of the organic colloidal material relative to water, so that the colloidal material can coat the particles of mineral filler. If the mineral filler is thus intimately contacted with a sufficiently concentrated swelled and colloidal dispersion of the coating ingredient or ingredients, the weight of the coating ingredient or ingredients may be a small percentage of the weight of the uncoated mineral filler. If the ingredient is a swelled and colloidally dispersed manno-galactan, and the coating composition has a sufficiently high concentration of such manno-galactan relative to water, there is a marked improvement in filler retention if the air-dry weight of such swelled and colloidally dispersed manno-galactan in the mixture of water and colloid and mineral filler, is as low as one unit of said manno-galactan per 2,000 units of the filler particles. Another important factor, which may even be the controlling factor, is that the mixture is free from cellulose fiber, which attracts the manno-galactan, so that the manno-galactan coats the mineral filler.

For the purpose of retaining the pre-treated or pre-coated mineral filler in the initial paper web and in the finished paper, the preferred ratio in such mixture is from one unit to 100 units of manno-galactan, per 2,000 units of mineral filler, as calculated upon the air-dry weight of such manno-galactan and filler.

In most cases, as little as 10 units of manno-galactan is adequate, per 2000 units of mineral filler. As above noted, the weight of the manno-galactan is calculated upon its air-dry weight or substantially its air-dry weight and the weight of the filler is calculated on its air-dry weight. The ratio of manno-galactan to filler depends to some extent upon the cellulose material and the degree of beating thereof, which are factors in the retention of the filler. However, on an average, the air-dry weight of the manno-galactan may be one-half percent of the air dry weight of the mineral filler.

If desired, the suspension of mineral filler coated with dimer can, either before or after the subsequent treatment with manno-galactan, be concentrated as by filtration, sedimentation or evaporation for convenience in storing or shipping. This concentration can be carried to the point at which the product is a paste containing as little as about 30% by weight of water without destroying the ability of the filler to be redispersed in water to a dilution suitable for addition to the cellulose fiber suspension.

If more of the manno-galactan is added beyond the amount which is required for good retention of the filler, the effect of the excess manno-galactan is chiefly to increase the strength of the finished paper. It is old and well-known to use the manno-galactans for increasing the strength of the finished paper, especially when the finished paper is wetted with water. The above ratios are calculated upon the use of locust bean gum as the manno-galactan.

Without limitation thereto, some specific examples of the conjoint and successive use of dimers and manno-galactans are stated below:

Example No. 1

One hundred units of finely divided calcium carbonate were suspended in three hundred units of water. This suspension was mixed with an aqueous emulsion of the dimer of mono-hexadecyl ketene. This emulsion had six units of said dimer, 1.2 units of said "Tween 85," and 12.8 units of water. Said emulsion of said dimer was prepared as above described. These ingredients were mixed while said ingredients were at 20° C.–30° C. Locust bean gum to the amount of 0.7 units, calculated upon its air-dry weight, was colloidally dispersed in substantially 66.7 units of distilled water at substantially 90° C., in the above stated manner.

The aqueous suspension of the calcium carbonate was initially mixed with the aqueous emulsion of the dimer, at 20° C.–30° C., during a mixing period of 5 minutes or more, in order to coat the particles of filler with the dimer. This mixture was then mixed with the aqueous colloidal dispersion of the swelled locust bean gum, at 20°–30° C., by adding the dispersion of the locust bean gum to the initial mixture, in order to provide the second coating of locust bean gum.

The aqueous suspension of the cellulosic fibers had 1,000 units of pre-worked cellulosic fibers, calculated on the air-dry weight of said cellulosic fibers, which had previously been fully swelled and hydrated and provided with surface fibrils in said aqueous suspension. Said aqueous suspension of the cellulosic fibers had 95% of water. Enough crude commercial sodium carbonate or soda ash had been dissolved in said water to give it a pH value between 10 and 12.5. These ingredients were intermixed at 20°–30° C.

The resultant aqueous blend or mixture was formed into a paper web on the wire screen of the web-making machine, and the initial paper web was pressed in the usual manner and it was dried in the usual manner on a drum which was heated by steam.

The finished sheet had excellent sizing on both sides. The finished sheet had substantially nine percent by weight of the calcium carbonate filler, calculated on the air-dry weight of said finished sheet, by recirculating the drainage water to the inlet end of the Fourdrinier.

Example No. 2

One hundred units of finely divided clay were suspended in substantially one hundred and twenty-five units of water.

An aqueous emulsion of a mixture of said higher dimers of ketenes derived from stearic and oleic acids was made separately, as above described. This aqueous emulsion had ten units of the mixture of dimers, and substantially thirty-three units of water, together with sufficient emulsifying agent.

A colloidal dispersion of one unit of locust beam gum was made separately in substantially one hundred units of water, in the manner above described.

Said aqueous emulsion of the dimers was mixed with the aqueous suspension of the filler clay, while said ingredients were at 20°–30° C. The colloidal dispersion of the locust bean gum was then stirred into said mixture, while said ingredients were at 20°–30° C.

This provided a final mixture which had the following: 100 units of finely divided filler clay; 10 units of the mixed higher alkyl ketene dimers; one unit of locust bean gum; 258 units of water.

As above noted, the emulsion of the mixed higher organic ketene dimers was mixed with the suspension of the filler clay, prior to the addition of the colloidal dispersion of the locust bean gum. In this initial mixture, the concentration of the emulsified dimers was sufficient to cause their absorption or adsorption by the finely divided filler clay.

A considerable part of the locust bean gum was adsorbed on the particles previously coated with the higher aliphatic ketene dimers. The clay filler was thus pre-

coated with both the dimers and the locust bean gum.

This final mixture was added, with stirring, to the aqueous suspension of the pre-beaten cellulosic fiber, while both said ingredients were at 20°–30° C. This aqueous suspension of the pre-beaten cellulosic fiber had 1,000 units of the beaten cellulosic fiber, calculated on the dry weight thereof. This aqueous suspension of the pre-beaten or pre-worked cellulose fibers had about 5% of fiber, air-dry and had enough dissolved crude sodium carbonate to give it a pH value of 10. The cellulose fiber had been pre-beaten in water having said pH value of 10.

The resultant complete aqueous blend or mixture was supplied to the wire screen of the web-making machine to form an initial web, which was pressed and dried in the usual manner. The resultant paper was well-sized on both sides.

Example No. 3

In this example, the dimer was the dimer of monohexadecyl ketene.

Ten units of the dimer were emulsified in substantially thirty-three units of water, together with a suitable emulsifying agent. This emulsion was mixed with one hundred parts of titanium dioxide filler in fine particle form, suspended in substantially two hundred units of water.

A separate colloidal dispersion was made which had 0.8 unit of said locust bean gum, and 1.5 units of modified potato starch, in substantially 200 units of water.

The emulsion of the dimer was mixed with the suspension of the titanium dioxide, while these ingredients were at 20°–30° C., and the mixture was stirred for 5 minutes or more at said temperature, in order to cause the titanium dioxide particles to adsorb or absorb the dimer.

The colloidal dispersion of the locust bean gum and the modified potato starch was added to said previously formed mixture while both said ingredients were at 20°–30° C., with stirring, for 5 or more minutes at 20°–30° C.

The resultant final mixture had ten units of the dimer, one hundred units of finely divided titanium dioxide, 0.8 unit of locust bean gum, 1.5 units of the modified starch, and substantially 433 units of water.

Hence, the particles of titanium dioxide were initially coated with the dimer, and said coated particles of titanium dioxide were then coated with the colloidally dispersed locust bean gum and the modified potato starch.

The final mixture which was thus produced was stirred at 20°–30° C. into a pre-beaten aqueous suspension of cellulose fibers. The water of said suspension had a pH value of 8.2. Said suspension had about 1000 units of pre-beaten cellulose fibers, and about 20,000 units of water.

The complete aqueous mixture or blend was supplied to the wire screen of the web-making machine. The initial paper web and the finished sheet of paper had 7 percent by weight of titanium dioxide filler. When the initial paper web was pressed and dried by heat in the usual manner, it was well-sized on both sides.

Although the preferred practice, as above stated, is to use manno-galactan to promote good retention of the dimer-coated mineral filler particles, it is not necessary to use such manno-galactan in order to ensure sizing. In fact it is possible to produce sized paper having a moderate filler content without use of any retention aid whatever, though such practice is not to be preferred.

As described above the invention embraces the paper product and the method of making it as well as the coated pigment and the method of making it. As appears from the disclosure the coated pigment product may be a pigment the particles being coated with dimer and then with manno-galactan. Useful ratios of dimer and of manno-galactan to pigment have been disclosed. The coated pigment as disclosed may be in the form of a relatively dilute suspension in water or aqueous liquid or may be more highly concentrated to a form suitable for storage or shipment. The coated pigment may be in the form of an aqueous paste which is redispersible in water and products useful for filling paper, if redispersible, and for other purposes such as for filling rubber may be made by drying the coated pigment as by the well known process of spray drying. Such products may consist essentially of the pigment coated with dimer only or of pigment coated with both a dimer and a manno-galactan.

What is claimed is:

1. A method of making sized and mineral filled neutral to alkaline paper which comprises preparing an aqueous suspension of cellulose fibers, mechanically refining said fibers, adjusting the pH of said suspension to at least as high as 7.0, adding to said suspension a finely divided neutral to alkaline mineral filler selected from the group comprising clay, calcium carbonate, magnesium carbonate, titanium dioxide and talc, said mineral filler having at least partly coated thereon a water repellent dimer of an aliphatic ketone containing an aliphatic hydrocarbon group having from 6 to 20 carbon atoms, and a positively charged water swellable organic colloidal retention agent for said mineral filler, said mixture of fibers and mineral filler with said coating materials thereon also having a pH at least as high as 7.0, and thereafter forming said fibers and filler into a paper web; whereby said coated mineral filler is attracted to and is retained by said fibers under neutral to alkaline conditions in the wet end of a paper making process to form a web having a surface pH of at least 7.0, and whereby said dimer substantially uniformly sizes said fibers throughout said web by migrating to said fibers from said filler and thereafter reacting with said fibers.

2. A method of making sized and mineral filled neutral to alkaline paper which comprises preparing an aqueous suspension of cellulose fibers, mechanically refining said fibers, adjusting the pH of said suspension to at least as high as 7.0, adding to said suspension a finely divided neutral to alkaline mineral filler selected from the group comprising clay, calcium carbonate, magnesium carbonate, titanium dioxide and talc, said mineral filler having at least partly coated thereon a water repellent dimer of an aliphatic ketene containing an aliphatic hydrocarbon group having from 6 to 20 carbon atoms, and a positively charged water swellable organic colloidal retention agent for said mineral filler selected from the group consisting in locust bean gum, carob bean gum, guar gum, and modified starch, said mixture of fibers and mineral filler with said coating materials thereon also having a pH at least as high as 7.0, and thereafter forming said fibers and filler into a paper web; whereby said coated mineral filler is attracted to and is retained by said fibers under neutral to alkaline conditions in the wet end of a paper making process to form a web having a surface pH of at least 7.0, and whereby said dimer substantially uniformly sizes said fibers throughout said web by migrating to said fibers from said filler and thereafter reacting with said fibers.

3. A method of making sized and mineral filled neutral to alkaline paper which comprises preparing an aqueous suspension of cellulose fibers, mechanically refining said fibers, adjusting the pH of said suspension to at least as high as 7.0, adding to said suspension a finely divided neutral to alkaline mineral filler selected from the group comprising clay, calcium carbonate, magnesium carbonate, titanium dioxide and talc, said mineral filler having at least partly coated thereon a water repellent dimer of an aliphatic ketene containing an aliphatic hydrocarbon group having from 6 to 20 carbon atoms, and a positively charged water swellable organic colloidal retention agent for said mineral filler comprising plant mucilage, said mixture of fibers and mineral filler with said coating materials thereon also having a pH at least as high as 7.0, and thereafter forming said

fibers and filler into a paper web; whereby said coated mineral filler is attracted to and is retained by said fibers under neutral to alkaline conditions in the wet end of a paper making process to form a web having a surface pH of at least 7.0, and whereby said dimer substantially uniformly sizes said fibers throughout said web by migrating to said fibers from said filler and thereafter reacting with said fibers.

4. A method of making sized and mineral filled neutral to alkaline paper which comprises preparing an aqueous suspension of cellulose fibers, mechanically refining said fibers, adding to said suspension finely divided calcium carbonate having at least partly coated thereon a water repellent dimer of an aliphatic ketene containing an aliphatic hydrocarbon group having from 6 to 20 carbon atoms, and a positively charged water swellable organic colloidal retention agent for said calcium carbonate, said mixture of fibers and calcium carbonate with said coating materials thereon having a pH at least as high as 7.0, and thereafter forming said fibers and calcium carbonate into a paper web; whereby said coated calcium carbonate is attracted to and is retained by said fibers under neutral to alkaline conditions in the wet end of a paper making process to form a web having a surface pH of at least 7.0, and whereby said dimer substantially uniformly sizes said fibers throughout said web by migrating to said fibers from said calcium carbonate and thereafter reacting with said fibers.

5. A method of making sized and mineral filled neutral to alkaline paper which comprises preparing an aqueous suspension of cellulose fibers, mechanically refining said fibers, adding to said suspension finely divided calcium carbonate having at least partly coated thereon a water repellent dimer of an aliphatic ketene containing an aliphatic hydrocarbon group having from 6 to 20 carbon atoms, and a positively charged water swellable organic colloidal retention agent for said calcium carbonate comprising plant mucilage, said mixture of fibers and calcium carbonate with said coating materials thereon having a pH at least as high as 7.0, and thereafter forming said fibers and calcium carbonate into a paper web; whereby said coated calcium carbonate is attracted to and is retained by said fibers under neutral to alkaline conditions in the wet end of a paper making process to form a web having a surface pH of at least 7.0, and whereby said dimer substantially uniformly sizes said fibers throughout said web by migrating to said fibers from said calcium carbonate and thereafter reacting with said fibers.

6. A sized mineral-filled paper product comprising cellulose paper fibers, a water repellent dimer of an aliphatic ketene containing an aliphatic hydrocarbon group having from 6 to 20 carbon atoms uniformly distributed through said paper product and sizing the fibers in said product, a mineral filler uniformly distributed through said fibers selected from the group comprising clay, calcium carbonate, magnesium carbonate, titanium dioxide, and talc, and a positively charged water swellable organic colloidally dispersible retention agent coating at least a part of the surface of both said mineral filler and said fibers, and said dimer also coating at least a part of the surface of both said mineral filler and said fibers.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,992,964 July 18, 1961

Tyrrell H. Werner et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 10, line 21, for "ketone" read -- ketene --.

Signed and sealed this 9th day of January 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents