SANITARY THIN PAPER AND PROCESS FOR PRODUCING THE SAME

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ABSTRACT

A sanitary thin paper is provided which has an excellent pliability together with an excellent smoothness. Such a paper can be obtained by incorporating a fatty acid ester-based compound and a fatty acid amide-based compound internally and/or externally.
Fig. 1

(a)

MACHINE DIRECTION

(b)

APEX

L

APEX

APEX
Fig. 2

Fig. 3

PAPER SAMPLE

MOVEMENT=2 cm
MOVEMENT SPEED=0.1 cm/second
SANITARY THIN PAPER AND PROCESS FOR PRODUCING THE SAME

FIELD OF THE INVENTION

The present invention relates to a sanitary thin paper for example for a domestic use and a for producing the same, and provides a particularly soft and smooth sanitary thin paper, including tissue paper or toilet paper.

BACKGROUND OF THE INVENTION

In response to a recent change in life style, a trend toward a soft and smooth sanitary thin paper becomes apparent in consumers. Especially in the field of tissue paper, such a trend is marked.

In order to ensure a softness, addition of a quaternary ammonium salt is considered to be effective as disclosed in Patent Reference 1. Also as disclosed in Patent Reference 2, a polysiloxane substance is attempted to be added.

However, a comfortable texture to the touch can not be obtained if only a softness is imparted but no smoothness is associated. In order to obtain the "smoothness" by which the texture is affected, it is proposed to add a lubricant, but it is difficult to find a suitable lubricant.


SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

A main objective of the invention is to provide a sanitary thin paper which is highly excellent both in terms of softness and smoothness as well as a process for producing the same.

Means to Solve the Problems

To solve the problems described above, the invention is established as follows.

(Invention of claim 1)

A sanitary thin paper which employs a pulp as a raw material and contains a fatty acid ester-based compound and a fatty acid amide-based compound internally or externally.

(Invention of claim 2)

The sanitary thin paper according to claim 1 wherein the softener components including said fatty acid ester-based compound and said fatty acid amide-based compound are contained in an amount, on dried mass basis, of 0.002 to 10 parts by mass per 100 parts by mass of said pulp raw material.

(Invention of claim 3)

The sanitary thin paper according to claim 1 or claim 2 wherein said fatty acid ester-based compound is contained internally and said fatty acid amide-based compound is contained either internally or externally, and wherein a polyester-based compound is contained, and said polyester-based compound is contained externally.

(Invention of claim 4)

The sanitary thin paper according to claim 3 wherein a polyester-based compound represented by General Formula (1):

\[
\begin{align*}
R_1 & \quad C \quad O \quad O \quad (R_{O_a})_b \quad R_3 \\
\end{align*}
\]

wherein \(R_1\) is HO— or HO(R_{O_a})a—, \(R_2\) is an alkylene group having 2 to 3 carbon atoms, only a single type of \(R_{O_a}\) may be present or two or more types of \(R_{O_a}\) are attached randomly or as a block, "a" is 1 to 200, all "a"s may be same or different in an identical molecule, b is 2 to 100, and \(R_3\) is a hydrogen atom or a group represented by General Formula (2):

\[
\begin{align*}
O & \quad C \quad OH \\
\end{align*}
\]

is contained as said polyester-based compound.

(Invention of claim 5)

The sanitary thin paper according to claim 3 or claim 4 wherein said polyester-based compound is added in an amount, on dried mass basis, of 0.05 to 30.0% by mass based on said pulp raw material.

(Invention of claim 6)

The sanitary thin paper according to any one of claims 1 to 5 wherein the basis weight (gsm) per 1 ply is 10 to 35 g/m².

(Invention of claim 7)

The sanitary thin paper according to any one of claims 1 to 6 wherein the crepe is formed at a paper making stage, and the crepe is formed in such a shape that the apex distance in the machine direction of the crepe is 0.1 mm or less, and the length in the width direction of the crepe is 0.5 mm or less.

(Invention of claim 8)

The sanitary thin paper according to any one of claims 7 wherein the number of the pulp fibers each of which has a distance of 1 μm or more from the adjacent pulp fiber in the section in the width direction of the paper is 50% or more of the number of all pulp fibers.

(Invention of claim 9)

The sanitary thin paper according to claim 7 or 8 wherein the area ratio of the voids excluding the area occupied by the pulp fibers in the width direction of the paper is 50% or more.
A process for producing a sanitary thin paper comprising adding a fatty acid ester-based compound and a fatty acid amide-based compound to a wet paper as a pulp raw material internally, and then adding a polyester-based compound to said wet paper externally on-line.

A process for producing a sanitary thin paper comprising adding a fatty acid ester-based compound and a fatty acid amide-based compound to a wet paper as a pulp raw material internally and/or externally, and then adding externally on line a polyester-based compound to said pulp wet paper or a dry paper obtained by drying the same.

Effects of the Invention

According to the invention, the excellence is experienced not only in terms of softness but also in terms of smoothness. The reasons for this excellence may be explained as described below. Thus, since a fatty acid ester-based compound enters between fibers to loosen the fibers, it gives a bulkiness, which is experienced as a softness by a consumer. A fatty acid amide-based compound not only serves to enhance the bulkiness but also gives a moisture-retaining wetness/smoothness. Both of these fatty acid ester-based compound and fatty acid amide-based compound are also known to be preferable especially if they are cationic.

When such a pulp paper is combined externally with a polyester-based compound, a thin film of the polyester can be formed on the surface of the pulp fiber, which serves to reduce the friction between fibers on a superficial layer upon touch to a skin. Accordingly, a resultant sanitary thin paper is porous, moistening, soft, and its surface is smooth.

As described above, it is preferable to add a polyester-based compound externally since a thin polyester film is intended to be formed on the pulp fiber surface. A fatty acid ester-based compound is added internally since it is intended to enter between the fibers to loosen the inter-fiber binding. On the contrary, a fatty acid amide-based compound may be added externally, although it exerts a higher effect when added internally.

On the other hand, the smoothness was found to be related greatly to the crepe morphology. Thus, as shown in FIG. 1, it was found to be preferable that the apex distance L in the machine direction of the crepe (paper) is 0.1 mm or less, and the widthwise length W of the crepe is 0.5 mm or less. An apex distance L of the machine direction of the crepe which is short and 0.1 mm or less gives a smoothness. On the other hand, a widthwise length W of the crepe exceeding 0.5 mm the smoothness upon wiping a skin with a sanitary thin paper while moving in the machine direction is affected adversely.

BEST MODE FOR CARRYING OUT THE INVENTION

The embodiments of the invention are described below. Also as discussed above, a sanitary thin paper may for example be a tissue paper or a toilet paper. It may be used as a cosmetic paper.
esterification reaction accompanied with de-methanol reaction. A polyester-based compound represented by General Formula (1) in which a repeating unit having “a” of 1 and a repeating unit having “a” of several tens to a hundred and several tens can be produced for example by reacting a dihydroxy ester of terephthalic acid, isophthalic acid, phthalic acid and the like with a polyethylene glycol having a certain molecular weight and conducting an transesterification reaction accompanied with de-ethylen glycol reaction. In General Formula (1), “b” is 2 to 100, more preferably 2 to 30. A “b” exceeding 100 results in a too high viscosity of the polyester-based compound represented by General Formula (1), which may lead to a difficulty in handling.

The weight mean molecular weight of a polyester-based compound represented by General Formula (1) is preferably 1,000 to 200,000, more preferably 10,000 to 50,000. A weight mean molecular weight of a polyester-based compound less than 1,000 may lead to an insufficient softness imparting effect. A weight mean molecular weight of a polyester-based compound exceeding 200,000 may result in a too high viscosity of the polyester-based compound, which may lead to a difficulty in handling. The weight mean molecular weight of a polyester-based compound can be determined by a gel permeation chromatography using a monodisperse polyethylene glycol having a known molecular weight.

While in an inventive sanitary thin paper a polyester-based compound represented by General Formula (1) may be added at a content (in an amount to be added) which is not limited particularly, preferably it is added externally in an amount, on dried mass basis, of 0.05 to 30.0% by mass based on said pulp raw material, more preferably 0.5 to 5.0% by mass. An amount of the polyester-based compound represented by General Formula (1) less than 0.05% by mass may lead to an insufficient softness imparting effect. An amount of the polyester-based compound represented by General Formula (1) exceeding 30.0% by mass results in a higher softness imparting effect, but also poses a problem including stickiness.

The invention may contain a water-soluble polyurethane resin represented by General Formula (3) if necessary. Such a water-soluble polyurethane resin can be added in an amount, on dried mass basis, of 0.05 to 7% by mass based on the pulp raw material. The weight ratio of a polyester-based compound and the water-soluble polyurethane resin is 100/1 to 55/45, preferably 100/1 to 70/30. Thus, one whose major component is an inventive polyester-based compound is preferred. The process for addition may be an external procedure such as spray application, offset application and the like.

wherein \( R_1 \) is a polyalkylene ether glycol chain having a molecular weight of 400 to 5000, \( R_2 \) is the formulae:

![Chemical structure](image)

and \( Z \) is an integer of 3 to 300.

In the invention, the addition of a polyester-based compound mentioned above enables an addition to pulp fibers while not being affected by the hydrogen bond of the pulp raw material, possibly undergoing coating on each pulp fiber, resulting in a smoothness.

In the invention, it is preferred to add as fatty acid ester-based compounds both of cationic fatty acid ester-based compounds and anionic fatty acid ester-based compounds. In addition, (a) either one or both of these fatty acid ester-based compounds are added internally, (b) a fatty acid anide-based compound is added internally or externally. The addition of an additive may be accomplished externally, for example by spray application, offset application and the like. On the other hand, an internal addition, thus, mixing into a paper making raw material prior to the paper making may be employed.

A chemical solution may be added in an amount, on dried mass basis, of 0.002 to 10 parts by mass per 100 parts by mass of said pulp raw material. The ratio of (a)/(b) is preferably 0.1 to 500.

A fatty acid ester-based compound of (a) permeates into a fiber when depositing onto the fiber to allow for a hydrogen bond between the insides of the lumens (voids) upon drying whereby preventing a crush, resulting in a further bulky soft paper. Nevertheless, in the absence of the cationic property, it is not fixed readily in a fiber by itself, posing a difficulty in exerting its effect.

A fatty acid ester-based compound may for example be a compound made from a C6-C24 alcohol and a C7-C25 fatty acid. Such a C6-C24 alcohol may be a straight alcohol, branched alcohol, saturated alcohol and unsaturated alcohol. Among these various alcohols, a C10-22 alcohol is preferred, with laurel alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol and oleoyl alcohol being particularly preferred. Any one of such alcohol may be used, or a mixture of two or more may be used.
A fatty acid amide-based compound of (b) coats the surface of each individual fiber to impart a bulkiness together with a lubricity on the surface, whereby improving the paper surface smoothness.

An inventive fatty acid amide compound can be obtained by reacting a polyalkylene polyamine and a carboxylic acid.

A polyalkylene polyamine employed in the invention contains at least three amino groups in its molecule and is represented by the following formula:

$$\text{H}_n\text{N}-(\text{R}^1-\text{NH}-\text{R}^2-\text{NH})_n-\text{R}^3-\text{NH}_2$$  \hspace{1cm} (4)

wherein each $\text{R}^1$ is independently a C1-4 alkyl group, and $n$ is an integer of 1 to 3.

Examples of $\text{R}^1$ in Formula (4) shown above are methylene group, ethylene group, trimethylene group, tetramethylene group and butylene group. Different $\text{R}^1$s may be present in one molecule, and two or more polyalkylene polyamines may be employed. A preferred $\text{R}^1$ is an ethylene group. A number of carbons in the alkylene group exceeding 4 leads to a difficulty in handling. If an amide compound obtained from such a compound is used, a bulky and soft paper can be employed.

A carboxylic acid employed in the production of an amide compound is a C10-24 carboxylic acid. Such a carboxylic acid may be a saturated carboxylic acid, unsaturated carboxylic acid, straight carboxylic acid or branched carboxylic acid. Nevertheless, at least 40% by mass should correspond to a carboxylic acid having at least one of an unsaturated bond or a branched chain.

A C10-24 carboxylic acid may for example be any of following compounds: a single fatty acid such as capric acid, lauric acid, myristic acid, palmitic acid, palmitoleic acid, isopalmitic acid, stearic acid, oleic acid, linoleic acid, linoleic acid, isostearic acid, arachic acid, behenic acid, erucic acid, lignoceric acid and the like; and a natural fat-derived mixed fatty acid such as coconut oil fatty acid, palm oil fatty acid, beef tallow fatty acid, lard fatty acid, soybean oil fatty acid, rapeseed oil fatty acid, tallow oil fatty acid, olive oil fatty acid, cocoa butter fatty acid, sesame oil fatty acid, corn oil fatty acid, sunflower oil fatty acid, cotton seed oil fatty acid and the like, as well as hydrogenated derivatives thereof. Any one of these may be used alone, or a mixture of two or more may be used. Among these, a C12-22 carboxylic acid is preferred, with a C14-C18 carboxylic acid being preferred especially. A carboxylic acid having less than 10 carbon atoms yields an amide compound which shows only a poor bulkiness and softness improving effect, while one whose number of carbons exceeds 24 may lead to a difficulty in handling of resultant amide compound.

Among those listed above, an unsaturated bond-carrying carboxylic acid (single fatty acid) may for example be oleic acid, linolic acid, linoleic acid, erucic acid and palmitoleic acid, and a branched chain-carrying carboxylic acid may be isopalmitic acid and isostearic acid. Any of these fatty acids may contain other fatty acids as impurities, and such fatty acid can also be employed. A natural mixed fatty acid containing 40 to 100% by mass of unsaturated carboxylic acids may for example be a soybean oil fatty acid, palm oil fatty acid, olive oil fatty acid, cocoa butter fatty acid, sesame oil fatty acid, corn oil fatty acid, sunflower oil fatty acid, cotton seed oil fatty acid, cotton seed oil fatty acid, beef tallow fatty acid, lard fatty acid and the like. Among the carboxylic acids having at least either one of unsaturated bonds and branched chains or mixtures thereof, those especially preferred are soybean oil fatty acid, oleic acid and erucic acid.

A fatty acid amide-based compound in this embodiment can be obtained by reacting a polyalkylene polyamine represented by Formula (4) shown above with a carboxylic acid mentioned above. Such a carboxylic acid is employed in an amount of 1.5 to 2.5 moles, preferably 1.8 to 2.2 moles per 1 mole of a polyalkylene polyamine. An amount less than 1.5 moles makes it impossible to obtain a sufficiently bulky soft paper, while an amount exceeding 2.5 moles leads to a difficulty in handling of the resultant amide compound.

While an amide compound described above can be used as it is as an additive, it can be handled more easily when used as a salt by neutralizing with an inorganic acid or organic acid. Such an inorganic acid may for example be hydrochloric acid, sulfuric acid, carbonic acid, nitric acid, phosphoric acid and the like. Examples of the organic acid are formic acid, acetic acid, propionic acid, acetyl chloride, butyric acid, oxalic acid, malonic acid, itaconic acid, adipic acid, seuccinic acid, sebamic acid, citric acid, hydroxybenzoic acid, malic acid, hydroxymalonic acid, lactic acid, sulicylic acid, hydroxovaleric acid, aspartic acid, glutamic acid, taurine, sulfamic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid and the like. Among these, organic acids are preferred, with formic acid, acetic acid and lactic acid being particularly preferred.

The amount of an acid to form a salt can be selected appropriately depending on the purpose by measuring the entire amine value of a product obtained by the reaction described above. Preferably, an inorganic acid or an organic acid equivalent to the entire amine value is added to form a salt of the amide compound.

An amide compound thus obtained or a salt thereof can easily be handled, and can produce a bulky soft paper. Also when adding this compound to a pulp slurry formed by dispersing a pulp fiber in water at a certain rate, foaming can advantageously be inhibited.

Since the use of a chemical solution may reduce the paper strength, it is preferable that a paper strength agent such as a starch, polyacrylamide-based superficial paper strength agent, a polyvinyl alcohol and the like is added internally, with a starch being preferred especially.

While in this embodiment a fatty acid ester-based compound and a fatty acid amide-based compound are added internally to a pulp wet paper to which then a polyester-based compound is added online externally or a fatty acid ester-based compound and a fatty acid amide-based compound are added internally and/or externally and then a polyester-based compound is added online externally to a pulp wet paper or dry paper, other appropriate moisturizing agent or lubricant can be added in a separate step.

Such a moisturizing agent may for example be polyethylene glycol, glycerin, 1,3-butyleneglycol, 1,2-pentanediol, erythritol, sorbitol, xylitol, maltitol, propylene glycol, dipropylene glycol, diglycerin, sodium pyrolidone carbonate, lactic acid, sodium lactate and the like.
A lubricant may for example be a polysiloxane such as silicone oil, silicone powder and the like. If necessary, a polyester-based compound described above can be converted into a microparticle for example by means of emulsification whereby being used as a powder particle. A silicone powder consisting of powder particles whose mean particle size is 0.1 to 30 μm is especially preferred. Alternatively, an aggregated powder of the powder particle mentioned above whose mean particle size is 10 to 100 μm is also preferred.

As a pulp raw material for an inventive sanitary thin paper, a pulp fiber whose NBKP content is 30 to 80% by mass and whose LBKP is 20 to 70% by mass is employed preferably in a major part. While the pulp raw material can contain 5% by mass or less, preferably 10% by mass or less of a waste paper pulp if necessary, one containing 100% by mass of virgin pulp is more preferable in view of softness and the like.

On the other hand, a sanitary thin paper in this embodiment has an area ratio of the void excluding the area occupied by a pulp fiber F in the widthwise section of a paper shown schematically in FIG. 2 (thus an area ratio of the non-hatched region excluding a pulp fiber F in a unit area S in FIG. 2) which is 50% or more. A higher area ratio results in a softer touch. An excessively high area ratio results in a reduced strength and a reduced firmness.

Particularly, the number of the pulp fibers each of which has a distance of 1 μm or more from the adjacent pulp fiber in the section in the width direction of the paper is 50% or more of the number of all pulp fibers. And most preferably the number of those of 5 μm or more is 50% or more. Similarly in this case a higher rate of the number results in a softer touch. An excessively high rate of the number results in a reduced strength.

As discussed in Examples shown below, no conventional examples involve a product having a morphology according to the invention.

An MMD as an index of the surface characteristics are preferably 9.0 or less, especially 8.5 or less for a tissue paper, and 13 or less, especially 11 or less for a toilet paper.

In a test for such surface characteristics, a frictional texture tester KESSE manufactured by KATO TECH CO., LTD. can be employed. For the measurement, as shown in FIG. 3, a friction probe consisting of a piano wire of 0.5 mm in diameter and having a contact length of 5 mm was brought into contact with a paper sample under a load of 10 g while applying to the paper sample a tension of 20 g/cm in the direction of the movement with moving over a distance of 2 cm at a rate of 0.1 cm/sec whereby measuring a friction coefficient. The mean deviation of the friction coefficient (the change in the surface thickness by the movement of the friction probe, thus, the friction coefficient divided by the friction distance (movement distance=2 cm)) is designated as MMD.

A softness of 1.5 or less, especially 1.4 or less for a tissue paper, and 3.5 or less, especially 2.5 or less for a toilet paper is preferred.

In order to obtain a sanitary thin paper in this embodiment, various factors may be selected. Thus, the ratio between LBKP and NBKP as pulp raw material, the types of the pulps (fiber coarseness, types and ages of source wood materials and the like), freeness, paper moisture, calender gap/pressure/material, chemical solution addition and its quantity and the like may vary appropriately. Preferably, the pulp contains no waste pulp.

In addition, tensile strength, aspect ratio, crepe morphology (crepe rate, crepe height), moisture content, density, addition of paper strengthening agents, addition of chemical solutions as well as their quantities may also vary appropriately. Desired surface characteristics can be obtained also by varying pulp incorporation, calender condition, paper moisture, doctor blade tip angle, blade angle, balance between adhesion/peeling strength, crepe rate, addition of chemical solutions and their quantities and the like appropriately.

In obtaining a crepe morphology according to the invention, the effects of the addition of the additives are of important. Thus, it is preferable to add both of a cationic fatty acid ester-based compound (chemical solution) and an anionic fatty acid ester-based compound (chemical solution).

A softener component including a fatty acid ester-based compound and a fatty acid amide-based compound is discussed below.

A softener added to a sanitary thin paper is preferably a cationic surfactant. Such a cationic surfactant is not limited particularly, and preferably an amine compound having in its molecule at least one C6-26 saturated or unsaturated hydrocarbon group or a neutralized or quaternized derivative thereof as well as a mixture thereof. More specifically, such a preferred amine compound or a neutralized or quaternized derivative thereof has in its molecule at least one, preferably one or two, most preferably two C6-26, preferably C14-22 saturated or unsaturated hydrocarbon group such as an alkyl or alkenyl group. Such a hydrocarbon group may have in its chain an ester group, reversed ester group, amide group, reversed amide group, ether group. Such a hydrocarbon group can be introduced for example by using a fatty acid obtained by hydrogenating or partially hydrogenating a beef tallow-derived non-hydrogenated fatty acid or unsaturated moiety employed usually in an industrial field, a fatty acid or a fatty acid ester obtained by hydrogenating or partially hydrogenating a plant-derived non-hydrogenated fatty acid or fatty acid ester or unsaturated moiety derived from palm or coconut.

In addition, a compound represented by General Formula (5):

\[
\begin{align*}
R^1 &\quad R^5 \quad \text{X} \\
R^2 &\quad \text{CH}_3
\end{align*}
\]

wherein \(R^2\) is a C6-24 alkyl group or a C6-24 alkenyl group, each of \(R^4\) and \(R^5\) is one selected from \((EO)_n(PO)_m\), a C1-24 alkyl group and a C1-24 alkenyl group, and \(R^4\) and \(R^5\) are same or different, \(\text{X}^+\) is an anion, wherein \(E\) is an ethylene group and \(P\) is a propylene group, and the total of

[0052] [0053] [0054] [0055] [0056] [0057] [0058] [0059] [0060] [0061] [0062] [0063] [0064] [0065]
m and n is 1 to 60, where m and n denote mean addition mole numbers, is also employed preferably.

[0066] Particularly contemplated here is a C6-24 alkyl group-carrying trimethylmonooalkylammonium halide and/or a C6-24 alkyl group-carrying dimethyldialkylammonium halide.

[0067] Also contemplated is an alkyl group and/or an alkenyl group-carrying imidazoline ring-carrying quaternary ammonium salt. Such an imidazoline ring-carrying quaternary ammonium salt may be a compound represented by General Formula (6):

\[
\begin{align*}
R^1 & \quad N \quad R^2 \\
X^- & \quad \text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]

wherein R\(^2\) is a C6-24 alkyl group or a C6-24 alkenyl group, R\(^1\) is a C1-24 alkyl group or a C1-24 alkenyl group and X\(^-\) is an anion.

[0068] In the invention, an alkoxylated fatty acid ester can be employed.

[0069] A cationic surfactant which can be employed in the invention may also be an imidazolium salt represented by R1R2R3R4N+:X\(^-\), wherein R1 is selected from an alkyl group having about 12 to about 18 carbon atoms, or an aromatic aryl or alkaryl group having about 12 to about 18 carbon atoms; each of R2, R3 and R4 is independently of one another selected from a hydrogen atom, an alkyl group having about 1 to about 18 carbon atoms, or an aromatic aryl or alkaryl group having about 12 to about 18 carbon atoms; X\(^-\) is an anion selected from chloride, bromide, iodide, acetate, phosphate, nitrate, sulfate, methyl sulfate, ethyl sulfate, tosylate, lactate, glycolate as well as mixtures thereof. The alkyl group may contain an ether bond or hydroxy or amino group-substituted form (for example, the alkyl group can contain polyethylene glycol and polypropylene glycol moieties).

[0070] Another useful cationic surfactant is an aminoamidine in which R1 in the structure shown above is converted into R5CO—(CH\(_2\)\(_n\))— wherein R5 is an alkyl group having about 12 to about 18 carbon atoms; n is an integer of about 2 to about 6, preferably about 2 to about 4, more preferably about 2 to about 3). Non-limiting examples of such a cationic emulsifier are stearamide propyl PG-dimonomium chloride phosphate, stearamide propyldimethyl dimonium ethosulfate, stearamide propyldimethyl (myristyl acetate) ammonium chloride, stearamide propyldimethyl ceteryl ammonium tosylate, stearamide propyldimethyl ammonium chloride, stearamide propyldimethyl ammonium lactate as well as mixtures thereof.

[0071] Non-limiting examples of a quaternary ammonium salt cationic surfactant are cetyltrimmonium chloride, cetlylammonium bromide, laurylammonium chloride, laurylammonium bromide, stearylaminium chloride, stearylaminium bromide, cetlyldimethyl ammonium chloride, cetlyldimethyl ammonium bromide, lauryldimethyl ammonium chloride, stearyldimethyl ammonium chloride, cetlytrimethyl ammonium chloride, cetlytrimethyl ammonium bromide, lauryltrimethyl ammonium chloride, lauryltrimethyl ammonium bromide, stearyltrimethyl ammonium chloride, stearyltrimethyl ammonium bromide, lauryldimethyl ammonium chloride, stearyldimethyl dimethyldialkylammonium chloride, dicetylaminium chloride, dicetylaminium bromide, dilaurylaminium chloride, dilaurylaminium bromide, distearylaminium chloride, distearylaminium bromide, dihydrogenated tallow dimethyl ammonium chloride, dihydrogenated tallow dimethyl ammonium chloride, dihydrogenated tallow dimethyl ammonium chloride, dihydrogenated tallow dimethyl ammonium chloride. Examples of a quaternary ammonium salt derived from the tallow and coconut origins are ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, ditallow dimethyl ammonium nitrate, di(coconut alkyl) dimethyl ammonium chloride, di(coconut alkyl) dimethyl ammonium chloride, tallow ammonium chloride, coconut ammonium chloride, stearamide propyl PG-dimonomium chloride phosphate, stearamide propyldimethyl dimonium ethosulfate, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride as well as mixtures thereof.

[0072] An additional quaternary ammonium salt is one whose C12-C22 alkyl carbon chain is derived from a tallow fatty acid or coconut fatty acid. The term “tallow” generally means an alkyl group derived from a tallow fatty acid in which C12-C18 alkyl chains coexist (usually a hydrogenated tallow fatty acid). The term “coconut” generally means an alkyl group derived from a coconut fatty acid in which C12-C18 alkyl chains coexist (usually a hydrogenated tallow fatty acid). Examples of a quaternary ammonium salt derived from the tallow and coconut origins are ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, ditallow dimethyl ammonium nitrate, di(coconut alkyl) dimethyl ammonium chloride, di(coconut alkyl) dimethyl ammonium chloride, tallow ammonium chloride, coconut ammonium chloride, stearamide propyl PG-dimonomium chloride phosphate, stearamide propyldimethyl dimonium ethosulfate, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride, stearamide dimethyl (myristyl acetate) ammonium chloride as well as mixtures thereof.

[0073] A preferable cationic surfactant useful here includes dilauryl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dimyristyl dimethyl ammonium chloride, dipalmityl dimethyl ammonium chloride, dipalmityl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride as well as mixtures thereof.

[0074] Otherwise, a softener may for example be a polyethylene polyamine higher fatty acid amide-type cationic surfactant, imidazoline-type cationic surfactant and a quaternary ammonium salt-type cationic surfactant such as an alkylimidinium ammonium chloride, with a polyethylene polyamine higher fatty acid amide-type cationic surfactant being especially because of a higher softening effect.

[0075] Such a polyethylene polyamine higher fatty acid amide-type cationic surfactant may for example be a polyethylene polyamine higher fatty acid amide (e1), a polyoxyalkylene polyethylene polyamine higher fatty acid amide (e2), a polyethylene polyamine higher fatty acid amide urea condensate (e3), a polyoxyalkylene polyethylene polyamine higher fatty acid amide urea condensate (e4), (e1) to (e4) epichlorohydrin adduct (e5), a polyethylene polyamine
higher fatty acid amide alkyl chloride quaternized salt (e6),
a polyethylene polyamine higher fatty acid amide
monochloroacetic acid adduct amphoteric compound (e7)
and a polyethylene polyamine higher fatty acid amide partial
imidazolinium salt (e8) and the like.

[0076] A polyethylene polyamine as a constituent of these
(e1) to (e8) may for example be diethylene triamine, triethy-
ylene tetramine, tetraethylene pentamine and the like.
Among these, diethylene triamine and triethylene tetramine
are preferred.

[0077] A polyoxyalkylene group constituting (e2) or (e4)
is a group to which an alkylene oxide is added. Such an
alkylene oxide may for example be ethylene oxide, propyl-
ene oxide and butylene oxide. Among these, ethylene oxide
and a combination of ethylene oxide with propylene oxide
(block or random addition) are preferred. The mixing weight
ratio when using a combination of ethylene oxide with
propylene oxide is preferably 1:0.1 to 1.0. The molar
number of the alkylene oxide to be added is usually 1 to 10
moles, preferably 1 to 5 moles.

[0078] While a higher fatty acid as a constituent of these
(e1) to (e8) is usually one derived from a natural fatty acid
such as a palm oil, beef tallow, rapeseed oil, rice bran oil,
fish oil and the like, a synthetic higher fatty acid produced
by a petroleum chemical process may also be employed.
Among these, a higher fatty acid having an iodine value of
50 or less and 12 to 24 carbon atoms is preferred.

[0079] Another constituent of these (e1) to (e8), namely a
polyethylene polyamine or a polyoxyalkylene polyethylene
polyamine is present in a molar ratio to a higher fatty acid
usually of 1:1.0 to 2.5, preferably 1:1.2 to 1.8. Among (e1)
to (e8) listed above, those preferred are (e1) to (e5).

EXAMPLES

[0080] Examples of the invention are described below.

[0081] Samples for a tissue paper and a toilet paper were
evaluated while comparing between the types of additives
added. The results are shown in Table 1. The additives
employed were included in Table 1.

[0082] The evaluation was made by measuring an MIU
value related to the friction coefficient using a KES test
machine manufactured by KATO TECH CO., LTD. A
smaller value reflects a smoother texture.

[0083] Also under an electron microscope observation, the
fiber fluffiness on the surface of the paper was observed,
since only MIU values are insufficient for the evaluation.

[0084] Based on these results, an inventive product was
evaluated in a sensory test to be excellent both in terms of
“softness” and “smoothness”. A total fluff length of 0.1 mm
or longer and a large total number of fluffs of 0.1 mm or
longer, as observed here, reflect a higher smoothness. This
is because of the presence of a large number of long fluffs
on the paper surface, as assumed from the fluffs illustrated.

Example 2

[0085] A commercially available tissue paper and an
inventive tissue paper were compared in various profiles.
Each was tested as a 2-ply (two sheets make a unit) sample.
The results are shown in Table 2.

[0086] The softener employed here are listed below. The
results are shown in Table 2.

[0087] The softener employed here are listed below. Soft-
ener A: Nonionic fatty acid ester (NIPPON PMC, SFS1001)
Softener B: Cationic fatty acid ester (NIPPON PMC,
SFS1002) Softener C: Cationic fatty acid ester (NIPPON
PMC, SFS1004) Softener D: Cationic fatty acid amide
(NO, bulk agent J)

[0088] The sensory test was on the basis of 5-point
evaluation. A % void area and a % fiber number were measured
by stacking 6 samples whose top and bottom were covered
with OHP sheets, which was cut by a sharp shaving blade at
an angle of 90°, and the sectional view of a sample after
cutting was taken as a x1000 SEM photograph, which then
was evaluated.

[0089] Based on these results, an inventive product was
evaluated in a sensory test to be excellent both in terms of
“softness” and “smoothness”.

[0090] The invention can be applied as a sanitary thin
paper for example for a domestic use including tissue paper
or toilet paper and a process for producing the same,
especially as a soft and smooth sanitary thin paper.

BRIEF DESCRIPTION OF THE DRAWINGS

[0091] FIG. 1 shows a schematic view of a crepe in a
sanitary thin paper, (a) a surface, (b) a B-B view on arrow.

[0092] FIG. 2 is a widthwise sectional view of a paper.

[0093] FIG. 3 is a schematic view of an MMD testing
process.

TABLE 1

<table>
<thead>
<tr>
<th>Internal addition (inner)</th>
<th>Fatty acid ester-containing softener (SEIKO PMC CORPORATION, TFS301)</th>
<th>Wet paper strengthening agent (SEIKO PMC Corporation, WSS47)</th>
<th>Polyester-based compound (NICCA CHEMICAL, <em>(A-POLE</em>) ES-500)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight (gsm)</td>
<td>g/m²</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Experiment 1</td>
<td>Experiment 2</td>
<td>Experiment 3</td>
<td>Experiment 4</td>
</tr>
<tr>
<td>12.0</td>
<td>15.0</td>
<td>16.0</td>
<td>21.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>0.6</td>
<td>0.6</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>0.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>
TABLE 1-continued

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Unit</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoothness (MIU vertical)</td>
<td></td>
<td>0.9</td>
<td>0.8</td>
<td>0.7</td>
<td>1.2</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Smoothness (MIU lateral)</td>
<td></td>
<td>0.7</td>
<td>0.6</td>
<td>0.7</td>
<td>0.9</td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Total length of fluffs of 0.1 mm or longer</td>
<td>Mm/mm</td>
<td>250</td>
<td>350</td>
<td>250</td>
<td>300</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Total number of fluffs of 0.1 mm or longer</td>
<td>Fluffs/mm</td>
<td>2000</td>
<td>2800</td>
<td>2000</td>
<td>2400</td>
<td>1200</td>
<td>800</td>
</tr>
</tbody>
</table>

TABLE 2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Commercial product</th>
<th>Company B</th>
<th>Company C</th>
<th>Company D</th>
<th>Company E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 11</td>
<td>Applicant</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>Experiment 12</td>
<td>Company A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment 13</td>
<td>Company B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment 14</td>
<td>Company C</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Experiment 15</td>
<td>Company D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment 16</td>
<td>Company E</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. A sanitary thin paper which employs a pulp as a raw material and contains a fatty acid ester-based compound and a fatty acid amide-based compound and also contains a polyester-based compound.

2. The sanitary thin paper according to claim 1 wherein the softer components including said fatty acid ester-based compound and said fatty acid amide-based compound are contained in an amount, on dried mass basis, of 0.002 to 10 parts by mass per 100 parts by mass of said pulp raw material.

3. The sanitary thin paper according to claim 1 wherein said fatty acid ester-based compound is contained internally and said fatty acid amide-based compound is contained internally and/or externally, and wherein a polyester-based compound is contained, and said polyester-based compound is contained externally.

4. The sanitary thin paper according to claim 3 wherein a polyester-based compound represented by General Formula (1):

\[
\begin{align*}
R_1 &\quad \quad O \quad \quad C\quad \quad O \quad \quad (R_2O)_n \quad R_3 \\
\end{align*}
\]

wherein \(R_1\) is HO— or HO(R_2O)_n—, \(R_2\) is an alkylene group having 2 to 3 carbon atoms, only a single type of \(R_2O\) may be present or two or more types of \(R_2O\) are attached randomly or as a block, “a” is 1 to 200, all “a”s may be same or different in an identical molecule, b is 2 to 100, and \(R_3\) is a hydrogen atom or a group represented by General Formula (2):

\[
\begin{align*}
\end{align*}
\]

is contained as said polyester-based compound.
5. The sanitary thin paper according to claim 3 or claim 4 wherein said polyester-based compound is added in an amount, on dried mass basis, of 0.05 to 30.0% by mass based on said pulp raw material.

6. The sanitary thin paper according to claim 1 wherein the basis weight (gsm) per 1 ply is 10 to 35 g/m².

7. The sanitary thin paper according to claim 1 wherein a crepe is formed at a paper making stage, and the crepe is formed in such a shape that the apex distance in the machine direction of the crepe is 0.1 mm or less, and the length in the width direction of the crepe is 0.5 mm or less.

8. The sanitary thin paper according to claim 7 wherein the number of the pulp fibers each of which has a distance of 1 μm or more from the adjacent pulp fiber in the section in the width direction of the paper is 50% or more of the number of all pulp fibers.

9. The sanitary thin paper according to claim 7 or claim 8 wherein the area ratio of the voids excluding the area occupied by the pulp fibers in the width direction of the paper is 50% or more.

10. A process for producing a sanitary thin paper comprising adding a fatty acid ester-based compound and a fatty acid amide-based compound to a wet paper as a pulp raw material internally, and then adding a polyester-based compound to said wet paper externally on-line.

11. A process for producing a sanitary thin paper comprising adding a fatty acid ester-based compound and a fatty acid amide-based compound to a wet paper as a pulp raw material internally and/or externally, and then adding externally on line a polyester-based compound to said pulp wet paper or a dry paper obtained by drying the same.

* * * * *