

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21H	A2	(11) International Publication Number: WO 96/24719 (43) International Publication Date: 15 August 1996 (15.08.96)
(21) International Application Number: PCT/US96/01145 (22) International Filing Date: 22 January 1996 (22.01.96) (30) Priority Data: 08/381,250 31 January 1995 (31.01.95) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: TROKHAN, Paul, Dennis; 1356 Warvel Road, Hamilton, OH 45013 (US). PHAN, Dean, Van; 6512 Tylers Crossing, West Chester, OH 45069 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, 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, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), 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). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: SOFT TISSUE PAPER CONTAINING AN OIL AND A POLYHYDROXY COMPOUND		
(57) Abstract Tissue paper having an enhanced bulk and tactile softness through incorporation of an effective amount of a polyhydroxy compound and an oil is disclosed. Preferably, from about 0.05 % to about 2.0 % of the polyhydroxy compound, on a dry fiber weight basis, and from about 0.05 % to about 2.0 % of an oil, on a dry fiber weight basis, are incorporated in the tissue paper. These nonionic compounds have high rates of retention when applied to wet tissue paper webs according to the process described herein. Tissue embodiments of the present invention may further comprise a quantity of strength additive, such as starch, to increase paper strength.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

SOFT TISSUE PAPER CONTAINING AN OIL AND A POLYHYDROXY COMPOUND

FIELD OF THE INVENTION

This application relates to tissue papers, in particular pattern densified tissue papers, having an enhanced tactile sense of softness. This application particularly relates to tissue papers treated with certain oils and water-soluble polyhydroxy compounds.

BACKGROUND OF THE INVENTION

Paper webs or sheets, sometimes called tissue or paper tissue webs or sheets, find extensive use in modern society. These include such staple items as paper towels, facial tissues and sanitary (or toilet) tissues. These paper products can have various desirable properties, including wet and dry tensile strength, absorbency for aqueous fluids (e.g., wettability), low lint properties, desirable bulk, and softness. The particular challenge in papermaking has been to appropriately balance these various properties to provide superior tissue paper.

Although somewhat desirable for towel products, softness is a particularly important property for facial and toilet tissues. Softness is the tactile sensation perceived by the consumer who holds a particular paper product, rubs it across the skin, and crumples it within the hand. Such tactile perceivable softness can be characterized by, but is not limited to, friction, flexibility, and smoothness, as well as subjective descriptors, such as a feeling like velvet, silk or flannel. This tactile sensation is a combination of several physical properties, including the flexibility or stiffness of the sheet of paper, as well as the texture of the surface of the paper and the frictional properties of the sheet of paper.

Stiffness of paper is typically affected by efforts to increase the dry and/or wet tensile strength of the web. Increases in dry tensile

strength can be achieved either by mechanical processes to insure adequate formation of hydrogen bonding between the hydroxyl groups of adjacent papermaking fibers, or by the inclusion of certain dry strength additives. Wet strength is typically enhanced by the inclusion of certain wet strength resins, that, being typically cationic, are easily deposited on and retained by the anionic carboxyl groups of the papermaking fibers. However, the use of both mechanical and chemical means to improve dry and wet tensile strength can also result in stiffer, harsher feeling, less soft tissue papers.

Certain chemical additives, commonly referred to as debonding agents, can be added to papermaking fibers to interfere with the natural fiber-to-fiber bonding that occurs during sheet formation and drying, and thus lead to softer papers. These debonding agents are typically cationic and have certain disadvantages associated with their use in softening tissue papers. Some low molecular weight cationic debonding agents can cause excessive irritation upon contact with human skin. Higher molecular weight cationic debonding agents can be more difficult to apply at low levels to tissue paper, and also tend to have undesirable hydrophobic effects on the tissue paper, e.g., result in decreased absorbency and particularly wettability. Since these cationic debonding agents operate by disrupting interfiber bonding, they can also decrease tensile strength to such an extent that resins, latex, or other dry strength additives can be required to provide acceptable levels of tensile strength. These dry strength additives not only increase the cost of the tissue paper but can also have other, deleterious effects on tissue softness.

Examples of cationic debonding agents include conventional quaternary ammonium compounds such as the well known dialkyl dimethyl ammonium salts (e.g., ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated) tallow dimethyl ammonium chloride etc ...). However, as mentioned above, these cationic quaternary ammonium compounds soften the paper by interfering with the natural fiber-to-fiber bonding that occurs during sheet formation and drying. In addition to decreasing tensile strength, these quaternary ammonium compounds also tend to have undesirable

hydrophobic effects on the tissue paper, e.g., resulting in decreased absorbency and wettability.

Mechanical pressing operations are typically applied to tissue paper webs to dewater them and/or increase their tensile strength. Mechanical pressing can occur over the entire area of the paper web, such as in the case of conventional felt-pressed paper. More preferably, dewatering is carried out in such a way that the paper is pattern densified. Pattern densified paper has certain densified areas of relatively high fiber density, as well as relatively low fiber density, high bulk areas. Such high bulk pattern densified papers are typically formed from a partially dried paper web that has densified areas imparted to it by a foraminous fabric having a patterned displacement of knuckles. See, for example, U.S. Patent No. 3,301,746 (Sanford et al), issued January 31, 1967; U.S. Patent No. 3,994,771 (Morgan et al), issued November 30, 1976; and U.S. patent No. 4,529,480 (Trokhan), issued July 16, 1985.

Besides tensile strength and bulk, another advantage of such patterned densification processes is that ornamental patterns can be imprinted on the tissue paper. However, an inherent problem of patterned densification processes is that the fabric side of the tissue paper, i.e. the paper surface in contact with the foraminous fabric during papermaking, is sensed as rougher than the side not in contact with the fabric. This is due to the high bulk fields that form, in essence, protrusions outward from the surface of the paper. It is these protrusions that can impart a tactile sensation of roughness.

The softness of these compressed, and particularly patterned densified tissue papers, can be improved by treatment with various agents such as vegetable, animal or synthetic hydrocarbon oils, and especially polysiloxane materials typically referred to as silicone oils. See Column 1, lines 30-45 of U.S. Patent No. 4,959,125 (Spendell), issued September 25, 1990. These silicone oils impart a silky, soft feeling to the tissue paper. However, some silicone oils are hydrophobic and can adversely affect the surface wettability of the treated tissue paper, i.e. the treated tissue paper can float, thus causing disposal problems in sewer systems when flushed. Indeed, some silicone softened papers can require treatment with other surfactants to offset

this reduction in wettability caused by the silicone. See U.S. Patent No. 5,059,282 (Ampulski et al), issued October 22, 1991.

Tissue paper has also been treated with softeners by "dry web" addition methods. One such method involves moving the dry paper across one face of a shaped block of wax-like softener that is then deposited on the paper surface by a rubbing action. See U.S. Patent No. 3,305,392 (Britt), issued February 21, 1967 (softeners include stearate soaps such as zinc stearate, stearic acid esters, stearyl alcohol, polyethylene glycols such as Carbowax, and polyethylene glycol esters of stearic and lauric acids). Another such method involves dipping the dry paper in a solution or emulsion containing the softening agent. See U.S. Patent No. 3,296,065 (O'Brien et al.), issued January 3, 1967 (aliphatic esters of certain aliphatic or aromatic carboxylic acids as the softening agent). A potential problem of these prior "dry web" addition methods is that the softening agent can be applied less effectively, or in a manner that could potentially affect the absorbency of the tissue paper. Indeed, the '392 patent teaches as desirable modification with certain cationic materials to avoid the tendency of the softener to migrate. Application of softeners by either a rubbing action or by dipping the paper would also be difficult to adapt to commercial papermaking systems that run at high speeds.

Accordingly, it would be desirable to be able to soften tissue paper, in particular high bulk, pattern densified tissue papers, by a process that: (1) uses a "wet web" method for adding the softening agent; (2) can be carried out in a commercial papermaking system without significantly impacting on machine operability; (3) uses softeners that are nontoxic; and (4) can be carried out in a manner so as to maintain desirable tensile strength, absorbency and low lint properties of the tissue paper.

It is an object of this invention to provide soft, absorbent toilet tissue paper products.

It is an object of this invention to provide soft, absorbent facial tissue paper products.

It is an object of this invention to provide soft, absorbent paper towel products.

It is also a further object of this invention to provide a process for making soft, absorbent tissue (i.e., facial and/or toilet tissue) and paper towel products.

These and other objects are obtained using the present invention, as will become readily apparent from a reading of the following disclosure.

SUMMARY OF THE INVENTION

The present invention provides soft, absorbent tissue paper products. Briefly, the soft tissue paper products comprise:

- a) wet-laid cellulosic fibers;
- b) from about 0.01% to about 5% of a water soluble polyhydroxy compound, based on the dry fiber weight of said tissue paper; and
- c) from about 0.01% to about 5% of an oil selected from the group consisting of petroleum-based oils, polysiloxane-based oils, and mixtures thereof, based on the dry fiber weight of said tissue paper;

wherein said tissue paper has a basis weight of from about 10 to about 65 g/m² and a density of less than about 0.60 g/cc, said polyhydroxy compound and said oil having being applied to a least one surface of a wet tissue paper web.

The present invention further relates to a process for making these softened tissue papers. The process includes the steps:

- a) wetlaying an aqueous slurry containing cellulosic fibers to form a web;
- b) applying to said web at fiber consistency of from about 10% to about

80%, total web weight basis, a sufficient amount of a water soluble polyhydroxy compound and an oil to impart a bulk softness to said structure; and

c) drying and creping said web.

Surprisingly, it has been found that these nonionic compounds have high rates of retention even in the absence of cationic retention aids or debonding agents when applied to wet tissue paper webs in accordance with the process disclosed herein. This is especially unexpected because the nonionic oils and polyhydroxy compounds are applied to the wet webs under conditions wherein they are not ionically substantive to the cellulose fibers. Importantly, the wet web process allows the polyhydroxy compounds to migrate to the interior of the paper web where they act to enhance the tissue paper absorbency and softness.

Tissue paper softened according to the present invention has a soft feel. It is especially useful in softening high bulk, pattern densified tissue papers, including tissue papers having patterned designs. The present invention can be carried out in a commercial papermaking system without significantly impacting on machine operability, including speed. The improved softness benefits of the present invention can also be achieved while maintaining the desirable tensile strength, absorbency (e.g., wettability), and low lint properties of the paper.

All percentages, ratios and proportions herein are by weight unless otherwise specified.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of one embodiment of a continuous papermaking machine which illustrates the preferred

process of the present invention of adding treatment chemicals to a pattern densified tissue paper web.

DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims particularly pointing out and distinctly claiming the subject matter regarded as the invention, it is believed that the invention can be better understood from a reading of the following detailed description and of the appended examples.

As used herein, the term "comprising" means that the various components, ingredients, or steps, can be conjointly employed in practicing the present invention. Accordingly, the term "comprising" encompasses the more restrictive terms "consisting essentially of" and "consisting of".

As used herein, the terms tissue paper web, paper web, web, paper sheet and paper product all refer to sheets of paper made by a process comprising the steps of forming an aqueous papermaking furnish, depositing this furnish on a foraminous surface, such as a Fourdrinier wire, and removing the water from the furnish as by gravity or vacuum-assisted drainage, with or without pressing, and by evaporation.

As used herein, an aqueous papermaking furnish is an aqueous slurry of papermaking fibers and the chemicals described hereinafter.

As used herein, the term "consistency" refers to the weight percentage of the cellulosic paper making fibers (i.e., pulp) in the wet tissue web. It is expressed as a weight percentage of this fibrous material, in the wet web, in terms of air dry fiber weight divided by the weight of the wet web.

The first step in the process of this invention is the forming of an aqueous papermaking furnish. The furnish comprises papermaking fibers (hereinafter sometimes referred to as wood pulp). It is anticipated that wood pulp in all its varieties will normally comprise the papermaking fibers used in this invention. However, other cellulose

fibrous pulps, such as cotton liners, bagasse, rayon, etc., can be used and none are disclaimed. Wood pulps useful herein include chemical pulps such as Kraft, sulfite and sulfate pulps as well as mechanical pulps including for example, ground wood, thermomechanical pulps and chemically modified thermomechanical pulp (CTMP). Pulps derived from both deciduous and coniferous trees can be used. Also applicable to the present invention are fibers derived from recycled paper, which may contain any or all of the above categories as well as other non-fibrous materials such as fillers and adhesives used to facilitate the original papermaking. Preferably, the papermaking fibers used in this invention comprise Kraft pulp derived from northern softwoods. The aqueous papermaking furnish is formed into a wet web on a foraminous forming carrier, such as a Fourdrinier wire, as will be discussed hereinafter.

(A) Polyhydroxy compounds

The present invention contains as an essential component from about 0.01% to about 5.0%, preferably from 0.05% to about 2.0%, more preferably from about 0.1% to about 1.0%, of a water soluble polyhydroxy compound, based on the dry fiber weight of the tissue paper.

Examples of water soluble polyhydroxy compounds suitable for use in the present invention include glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycol and polyoxypropylene glycol having a weight-average molecular weight of from about 200 to about 4000, preferably from about 200 to about 1000, most preferably from about 200 to about 600. Polyoxyethylene glycol having an weight average molecular weight of from about 200 to about 600 are especially preferred. Mixtures of the above-described polyhydroxy compounds may also be used. For example, mixtures of glycerol and polyglycerols, mixtures of glycerol and polyoxyethylene glycols, mixtures of polyglycerols and polyoxyethylene glycols, etc. ... are useful in the present invention. A particularly preferred polyhydroxy compound is polyoxyethylene glycol having an weight average molecular weight of about 400. This material

is available commercially from the Union Carbide Company of Danbury, Connecticut under the tradename "PEG-400".

(B) Oils

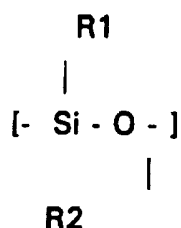
The present invention contains as an essential component from about 0.01% to about 5.0%, preferably from 0.05% to about 2.0%, more preferably from about 0.1% to about 1.0%, by weight of an oil selected from the group consisting of petroleum-based oils, polysiloxane-based oils, and mixtures thereof, based on the dry fiber weight of the tissue paper.

Petroleum-based oils

As used herein, the term petroleum-based oils refers to viscous mixtures of hydrocarbons having from about 16 to about 32 carbon atoms. Preferably, the petroleum-based oil is a petroleum-based turbine oil comprised primarily of saturated hydrocarbons. An example of a preferred petroleum-based turbine oil for use in the present invention is known as "Regal Oil". As used herein, the term "Regal Oil" refers to the compound which is comprised of approximately 87% saturated hydrocarbons and approximately 12.6% aromatic hydrocarbons with traces of additives, manufactured as product number R & O 68 Code 702 by the Texaco Oil Company of Houston, Texas.

Polysiloxane-based oils

In general suitable polysiloxane materials for use in the present invention include those having monomeric siloxane units of the following structure:



wherein, R1 and R2, for each independent siloxane monomeric unit can each independently be hydrogen or any alkyl, aryl, alkenyl, alkaryl, arakyl, cycloalkyl, halogenated hydrocarbon, or other radical. Any of such radicals can be substituted or unsubstituted. R1 and R2 radicals of any particular monomeric unit may differ from the corresponding functionalities of the next adjoining monomeric unit. Additionally, the polysiloxane can be either a straight chain, a branched chain or have a cyclic structure. The radicals R1 and R2 can additionally independently be other silaceous functionalities such as, but not limited to siloxanes, polysiloxanes, silanes, and polysilanes. The radicals R1 and R2 may contain any of a variety of organic functionalities including, for example, alcohol, carboxylic acid, aldehyde, ketone and amine, amide functionalities.

Exemplary alkyl radicals are methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, octadecyl, and the like. Exemplary alkenyl radicals are vinyl, allyl, and the like. Exemplary aryl radicals are phenyl, diphenyl, naphthyl, and the like. Exemplary alkaryl radicals are toyl, xylyl, ethylphenyl, and the like. Exemplary arakyl radicals are benzyl, alpha-phenylethyl, beta-phenylethyl, alpha-phenylbutyl, and the like. Exemplary cycloalkyl radicals are cyclobutyl, cyclopentyl, cyclohexyl, and the like. Exemplary halogenated hydrocarbon radicals are chloromethyl, bromoethyl, tetrafluorethyl, fluorethyl, trifluorethyl, trifluorotoyl, hexafluoroxyl, and the like.

Viscosity of polysiloxanes useful may vary as widely as the viscosity of polysiloxanes in general vary, so long as the polysiloxane is flowable or can be made to be flowable for application to the tissue paper. Preferably the polysiloxane-based oil has an intrinsic viscosity ranging from about 100 to about 1000 centipoises. References disclosing polysiloxanes include U. S. Patent No. 2,826,551, issued March 11, 1958 to Geen; U. S. Patent No. 3,964,500, issued June 22, 1976 to Drakoff; U.S. Patent No. 4,364,837, issued December 21, 1982, Pader, U.S. Patent No. 5,059,282, issued October 22, 1991 to Ampulksi et al.; and British Patent No. 849,433, published September 28, 1960 to Woolston. All of these patents are incorporated herein by reference. Also, incorporated herein by reference is Silicon

Compounds, pp 181-217, distributed by Petrarch Systems, Inc., 1984, which contains an extensive listing and description of polysiloxanes in general.

C. Tissue Papers

The present invention is applicable to tissue paper in general, including but not limited to conventionally felt-pressed tissue paper; pattern densified tissue paper such as exemplified in the aforementioned U.S. Patent by Sanford-Sisson and its progeny; and high bulk, uncompacted tissue paper such as exemplified by U.S. Patent No. 3,812,000, Salvucci, Jr., issued May 21, 1974. The tissue paper may be of a homogenous or multilayered construction; and tissue paper products made therefrom may be of a single-ply or multi-ply construction. Tissue structures formed from layered paper webs are described in U.S. Patent No. 3,994,771, Morgan, Jr. et al. issued November 30, 1976, U.S. Patent No. 4,300,981, Carstens, issued November 17, 1981, U.S. Patent No. 4,166,001, Dunning et al., issued August 28, 1979, and European Patent Publication No. 0 613 979 A1, Edwards et al., published September 7, 1994, all of which are incorporated herein by reference. In general, a wet-laid composite, soft, bulky and absorbent paper structure is prepared from two or more layers of furnish which are preferably comprised of different fiber types. The layers are preferably formed from the deposition of separate streams of dilute fiber slurries, the fibers typically being relatively long softwood and relatively short hardwood fibers as used in tissue papermaking, upon one or more endless foraminous screens. The layers are subsequently combined to form a layered composite web. The layered web is subsequently caused to conform to the surface of an open mesh drying/imprinting fabric by the application of a fluid to force to the web and thereafter thermally predried on said fabric as part of a low density papermaking process. The layered web may be stratified with respect to fiber type or the fiber content of the respective layers may be essentially the same. The tissue paper preferably has a basis weight of between 10 g/m² and about 65 g/m², and density of about 0.60 g/cc or less. Preferably, basis weight will be below about 35 g/m² or less; and density will be about 0.30 g/cc or

less. Most preferably, density will be between 0.04 g/cc and about 0.20 g/cc.

Conventionally pressed tissue paper and methods for making such paper are known in the art. Such paper is typically made by depositing papermaking furnish on a foraminous forming wire. This forming wire is often referred to in the art as a Fourdrinier wire. Once the furnish is deposited on the forming wire, it is referred to as a web. The web is dewatered by pressing the web and drying at elevated temperature. The particular techniques and typical equipment for making webs according to the process just described are well known to those skilled in the art. In a typical process, a low consistency pulp furnish is provided in a pressurized headbox. The headbox has an opening for delivering a thin deposit of pulp furnish onto the Fourdrinier wire to form a wet web. The web is then typically dewatered to a fiber consistency of between about 7% and about 25% (total web weight basis) by vacuum dewatering and further dried by pressing operations wherein the web is subjected to pressure developed by opposing mechanical members, for example, cylindrical rolls.

The dewatered web is then further pressed and dried by a steam heated drum apparatus known in the art as a Yankee dryer. Pressure can be developed at the Yankee dryer by mechanical means such as an opposing cylindrical drum pressing against the web. Vacuum may also be applied to the web as it is pressed against the Yankee surface. Multiple Yankee dryer drums may be employed, whereby additional pressing is optionally incurred between the drums. The tissue paper structures which are formed are referred to hereinafter as conventional, pressed, tissue paper structures. Such sheets are considered to be compacted since the web is subjected to substantial overall mechanical compressional forces while the fibers are moist and are then dried (and optionally creped) while in a compressed state.

Pattern densified tissue paper is characterized by having a relatively high bulk field of relatively low fiber density and an array of densified zones of relatively high fiber density. The high bulk field is alternatively characterized as a field of pillow regions. The densified zones are alternatively referred to as knuckle regions. The densified zones may be discretely spaced within the high bulk field or may be interconnected, either fully or partially, within the high bulk field.

Preferred processes for making pattern densified tissue webs are disclosed in U.S. Patent No. 3,301,746, issued to Sanford and Sisson on January 31, 1967, U.S. Patent No. 3,974,025, issued to Peter G. Ayers on August 10, 1976, and U.S. Patent No. 4,191,609, issued to Paul D. Trokhan on March 4, 1980, and U.S. Patent No. 4,637,859, issued to Paul D. Trokhan on January 20, 1987, U.S. Patent No. 4,942,077 issued to Wendt et al. on July 17, 1990, European Patent Publication No. 0 617 164 A1, Hyland et al., published September 28, 1994, European Patent Publication No. 0 616 074 A1, Hermans et al., published September 21, 1994; all of which are incorporated herein by reference.

In general, pattern densified webs are preferably prepared by depositing a papermaking furnish on a foraminous forming wire such as a Fourdrinier wire to form a wet web and then juxtaposing the web against an array of supports. The web is pressed against the array of supports, thereby resulting in densified zones in the web at the locations geographically corresponding to the points of contact between the array of supports and the wet web. The remainder of the web not compressed during this operation is referred to as the high bulk field. This high bulk field can be further dedensified by application of fluid pressure, such as with a vacuum type device or a blow-through dryer, or by mechanically pressing the web against the array of supports. The web is dewatered, and optionally predried, in such a manner so as to substantially avoid compression of the high bulk field. This is preferably accomplished by fluid pressure, such as with a vacuum type device or blow-through dryer, or alternately by mechanically pressing the web against an array of supports wherein the high bulk field is not compressed. The operations of dewatering, optional predrying and formation of the densified zones may be integrated or partially integrated to reduce the total number of processing steps performed. Subsequent to formation of the densified zones, dewatering, and optional predrying, the web is dried to completion, preferably still avoiding mechanical pressing. Preferably, from about 8% to about 55% of the tissue paper surface comprises densified knuckles having a relative density of at least 125% of the density of the high bulk field.

The array of supports is preferably an imprinting carrier fabric having a patterned displacement of knuckles which operate as the array of supports which facilitate the formation of the densified zones upon application of pressure. The pattern of knuckles constitutes the array of supports previously referred to. Imprinting carrier fabrics are disclosed in U.S. Patent No. 3,301,746, Sanford and Sisson, issued January 31, 1967, U.S. Patent No. 3,821,068, Salvucci, Jr. et al., issued May 21, 1974, U.S. Patent No. 3,974,025, Ayers, issued August 10, 1976, U.S. Patent No. 3,573,164, Friedberg et al., issued March 30, 1971, U.S. Patent No. 3,473,576, Amneus, issued October 21, 1969, U.S. Patent No. 4,239,065, Trokhan, issued December 16, 1980, and U.S. Patent No. 4,528,239, Trokhan, issued July 9, 1985, all of which are incorporated herein by reference.

Preferably, the furnish is first formed into a wet web on a foraminous forming carrier, such as a Fourdrinier wire. The web is dewatered and transferred to an imprinting fabric. The furnish may alternately be initially deposited on a foraminous supporting carrier which also operates as an imprinting fabric. Once formed, the wet web is dewatered and, preferably, thermally predried to a selected fiber consistency of between about 40% and about 80%. Dewatering can be performed with suction boxes or other vacuum devices or with blow-through dryers. The knuckle imprint of the imprinting fabric is impressed in the web as discussed above, prior to drying the web to completion. One method for accomplishing this is through application of mechanical pressure. This can be done, for example, by pressing a nip roll which supports the imprinting fabric against the face of a drying drum, such as a Yankee dryer, wherein the web is disposed between the nip roll and drying drum. Also, preferably, the web is molded against the imprinting fabric prior to completion of drying by application of fluid pressure with a vacuum device such as a suction box, or with a blow-through dryer. Fluid pressure may be applied to induce impression of densified zones during initial dewatering, in a separate, subsequent process stage, or a combination thereof.

Uncompacted, nonpattern-densified tissue paper structures are described in U.S. Patent No. 3,812,000 issued to Joseph L. Salvucci, Jr. and Peter N. Yiannos on May 21, 1974 and U.S. Patent No.

4,208,459, issued to Henry E. Becker, Albert L. McConnell, and Richard Schutte on June 17, 1980, both of which are incorporated herein by reference. In general, uncompacted, non pattern densified tissue paper structures are prepared by depositing a papermaking furnish and a debonding agent on a foraminous forming wire such as a Fourdrinier wire to form a wet web, draining the web and removing additional water without mechanical compression until the web has a fiber consistency of at least 80%, and creping the web. Water is removed from the web by vacuum dewatering and thermal drying. The resulting structure is a soft but weak high bulk sheet of relatively uncompacted fibers. Bonding material is preferably applied to portions of the web prior to creping.

Compacted non-pattern-densified tissue structures are commonly known in the art as conventional tissue structures. In general, compacted, non-pattern-densified tissue paper structures are prepared by depositing a papermaking furnish on a foraminous wire such as a Fourdrinier wire to form a wet web, draining the web and removing additional water with the aid of a uniform mechanical compaction (pressing) until the web has a consistency of 25-50%, transferring the web to a thermal dryer such as a Yankee and creping the web. Overall, water is removed from the web by vacuum, mechanical pressing and thermal means. The resulting structure is strong and generally of singular density, but very low in bulk, absorbency and in softness.

The tissue paper web of this invention can be used in any application where soft, absorbent tissue paper webs are required. Particularly advantageous uses of the tissue paper web of this invention are in paper towel, toilet tissue and facial tissue products. For example, two tissue paper webs of this invention can be embossed and adhesively secured together in face to face relation as taught by U.S. Pat. No. 3,414,459, which issued to Wells on December 3, 1968 and which is incorporated herein by reference, to form 2-ply paper towels.

In the following discussion, wherein reference is made to the several figures, certain preferred embodiments of processes for making the tissue sheet structures of the present invention are described.

In the embodiment illustrated in Figure 1, the papermaking belt 10 travels in the direction indicated by directional arrow B. The papermaking belt 10 passes around the papermaking belt return rolls designated 19a and 19b, impression nip roll 20, papermaking belt return rolls 19c, 19d, 19e and 19f, and emulsion distributing roll 21 (which distributes an emulsion 22 onto the papermaking belt 10 from an emulsion bath 23). In between papermaking belt return rolls 19c and 19d, and also in between papermaking belt return rolls 19d and 19e, are belt cleaning showers 102 and 102a, respectively. The purpose of the belt cleaning showers 102 and 102a is to clean the papermaking belt 10 of any paper fibers, adhesives, strength additives, and the like, which remain attached to the section of the papermaking belt 10 after the final step in the papermaking process. The loop that the papermaking belt 10 travels around also includes a means for applying a fluid pressure differential to the paper web, which in the preferred embodiment of the present invention, comprises vacuum pickup shoe 24a and a vacuum box such as multi-slot vacuum box 24. Associated with the papermaking belt 10 of the present invention, and also not shown in FIG. 1 are various additional support rolls, return rolls, cleaning means, drive means, and the like commonly used in papermaking machines and all well known to those skilled in the art.

The embryonic web 18 is brought into contact with the papermaking belt 10 of the present invention by the Fourdrinier wire 15 when the Fourdrinier wire 15 is brought near the papermaking belt 10 of the present invention in the vicinity of vacuum pickup shoe 24a.

An especially preferred method of continuously applying the polyhydroxy compound and oil to the papermaking belt is via an emulsion distributing roll 21 and emulsion bath 23, illustrated in Figure 1. In this preferred method, the polyhydroxy compound is dissolved into at least one phase of an emulsion 22 comprised of three primary compounds, namely water, oil, and a surfactant, although it is contemplated that other or additional suitable compounds could be used. The emulsion 22 containing the dissolved polyhydroxy compounds and oil is applied to the papermaking belt 10 via the above-mentioned emulsion distributing roll 23. Emulsion 22 can also be

applied to the papermaking belt 10 through cleaning showers 102 and 102a.

An example of an especially preferred emulsion composition contains water, a petroleum-based oil known as "Regal Oil", distearyldimethylammonium chloride, cetyl alcohol and a polyhydroxy compound (such as glycerol). distearyldimethylammonium chloride is sold under the trade name ADOGEN TA 100 by the Witco Corporation of Mapleton, Illinois. Hereinafter, distearyldimethyl-ammonium chloride will be referred to as ADOGEN for convenience. ADOGEN is used in the emulsion as a surfactant to emulsify or stabilize the oil particles (e.g., Regal Oil, Polysiloxane Oil) in the water.

The purpose of the Regal Oil in the composition described above is to serve as a "release emulsion." By "release emulsion," it is meant that it provides a coating on the papermaking belt 10 so the paper formed releases from (or does not stick to) the same after the steps of the present invention have been performed to the paper web.

As referred to herein, the term "surfactant" refers to a surface active agent, one portion of which is hydrophilic, and another portion of which is hydrophobic, which migrates to the interface between a hydrophilic substance and a hydrophobic substance to stabilize the two substances.

As used herein, "cetyl alcohol" refers to a C16 linear fatty alcohol. Cetyl alcohol is manufactured by The Procter & Gamble Company of Cincinnati, Ohio. Cetyl alcohol, like ADOGEN is used as a surfactant in the emulsion utilized in the preferred embodiment of the present invention.

The relative percentages of the composition of the emulsion, in the preferred embodiment of the same are set out in the following table:

Component	Volume		Weight (%)
	(gal.)	(lbs.)	
Water	259	4,320	62.2
REGAL OIL	55	422	6.1
ADOGEN	N/A	24	0.3

18

Cetyl Alcohol	N/A	16	0.2
Glycerol	259	2,160	31.1

The level of polyhydroxy compound and petroleum-based oil or polysiloxane-based oil to be retained by the tissue paper, as a minimum, is at least an effective level for imparting a tactile difference in softness or silkiness to the paper. The minimum effective level may vary depending upon the particular type of sheet, the method of application, the particular type of polyhydroxy compound, petroleum-based oil, or polysiloxane-based oil, surfactant, or other additives or treatments. Without limiting the range of applicable polyhydroxy/petroleum-based oil or polysiloxane-based oil retention by the tissue paper, preferably at least about 0.05% of the polyhydroxy compound, and 0.05% of the petroleum-based oil or polysiloxane-based oil is retained by the tissue paper. More preferably, from about 0.1% to about 2.0% of the polyhydroxy compound, and from about 0.1% to about 2.0% of the petroleum-based oil or polysiloxane-based oil is retained by the tissue paper.

In general, tissue paper having less than about 0.3% petroleum-based oil or polysiloxane-based oil will provide substantial increases in softness and silkiness yet remain wettable even in the absence of sufficient levels of surfactant to impart a wetting effect. Such paper preferably is treated with surfactant and/or starch as described herein.

Tissue paper having in excess of about 0.3% petroleum-based oil or polysiloxane-based oil is preferably treated with a surfactant when contemplated for uses wherein high wettability is desired. The amount of surfactant required to increase hydrophilicity to a desired level will necessarily depend upon the type and level of oil and the type of surfactant. In general, between about 0.1% and about 2.0% surfactant (e.g., Pegosperse®, Igepal® RC-520) retained by the tissue paper is believed to be sufficient to provide sufficiently high wettability for toilet paper and other applications for oil levels less than about 2.0%. However, the benefit of increased wettability is applicable for oil levels well in excess of 2.0%, if a sufficient amount of surfactant is retained by tissue paper.

Analytical and Testing Procedures

Analysis of the amounts of treatment chemicals herein retained on tissue paper webs can be performed by any method accepted in the applicable art. For example, the level of the polyhydroxy compound retained by the tissue paper can be determined by solvent extraction of the polyhydroxy compound with a solvent. In some cases, additional procedures may be necessary to remove interfering compounds from the polyhydroxy species of interest. For instance, the Weibull solvent extraction method employs a brine solution to isolate polyethylene glycols from nonionic surfactants (Longman, G.F., The Analysis of Detergents and Detergent Products Wiley Interscience, New York, 1975, p. 312). The polyhydroxy species could then be analyzed by spectroscopic or chromatographic techniques. For example, compounds with at least six ethylene oxide units can typically be analyzed spectroscopically by the Ammonium cobalthiocyanate method (Longman, G.F., The Analysis of Detergents and Detergent Products, Wiley Interscience, New York, 1975, p. 346). Gas chromatography techniques can also be used to separate and analyze polyhydroxy type compounds. Graphitized poly(2,6-diphenyl-p-phenylene oxide) gas chromatography columns have been used to separate polyethylene glycols with the number of ethylene oxide units ranging from 3 to 9 (Alltech chromatography catalog, number 300, p. 158). The level of polysiloxane-based oil or petroleum-based oil retained by the tissue paper can be determined by solvent extraction of the oil with an organic solvent followed by atomic absorption spectroscopy to determine the level of the oil in the extract

The level of nonionic surfactants, such as alkyl glycosides, can be determined by chromatographic techniques. Bruns reported a High Performance Liquid chromatography method with light scattering detection for the analysis of alkyl glycosides (Bruns, A., Waldhoff, H., Winkle, W., Chromatographia, vol. 27, 1989, p. 340). A Supercritical Fluid Chromatography (SFC) technique was also described in the analysis of alkyl glycosides and related species (Lafosse, M., Rollin, P., Elfakir, c., Morin-Allory, L., Martens, M., Dreux, M., Journal of chromatography, vol. 505, 1990, p. 191). The level of anionic

surfactants, such as linear alkyl sulfonates, can be determined by water extraction followed by titration of the anionic surfactant in the extract. In some cases, isolation of the linear alkyl sulfonate from interferences may be necessary before the two phase titration analysis (Cross, J., Anionic Surfactants - Chemical Analysis, Dekker, New York, 1977, p. 18, p. 222). The level of starch can be determined by amylase digestion of the starch to glucose followed by colorimetry analysis to determine glucose level. For this starch analysis, background analyses of the paper not containing the starch must be run to subtract out possible contributions made by interfering background species. These methods are exemplary, and are not meant to exclude other methods which may be useful for determining levels of particular components retained by the tissue paper.

A. Panel Softness

Ideally, prior to softness testing, the paper samples to be tested should be conditioned according to Tappi Method #T402OM-88. Here, samples are preconditioned for 24 hours at a relative humidity level of 10 to 35% and within a temperature range of 22 to 40 °C. After this preconditioning step, samples should be conditioned for 24 hours at a relative humidity of 48 to 52% and within a temperature range of 22 to 24 °C.

Ideally, the softness panel testing should take place within the confines of a constant temperature and humidity room. If this is not feasible, all samples, including the controls, should experience identical environmental exposure conditions.

Softness testing is performed as a paired comparison in a form similar to that described in "Manual on Sensory Testing Methods", ASTM Special Technical Publication 434, published by the American Society For Testing and Materials 1968 and is incorporated herein by reference. Softness is evaluated by subjective testing using what is referred to as a Paired Difference Test. The method employs a standard external to the test material itself. For tactile perceived softness two samples are presented such that the subject cannot see

the samples, and the subject is required to choose one of them on the basis of tactile softness. The result of the test is reported in what is referred to as Panel Score Unit (PSU). With respect to softness testing to obtain the softness data reported herein in PSU, a number of softness panel tests are performed. In each test ten practiced softness judges are asked to rate the relative softness of three sets of paired samples. The pairs of samples are judged one pair at a time by each judge: one sample of each pair being designated X and the other Y. Briefly, each X sample is graded against its paired Y sample as follows:

1. a grade of plus one is given if X is judged to may be a little softer than Y, and a grade of minus one is given if Y is judged to may be a little softer than X;
2. a grade of plus two is given if X is judged to surely be a little softer than Y, and a grade of minus two is given if Y is judged to surely be a little softer than X;
3. a grade of plus three is given to X if it is judged to be a lot softer than Y, and a grade of minus three is given if Y is judged to be a lot softer than X; and, lastly:
4. a grade of plus four is given to X if it is judged to be a whole lot softer than Y, and a grade of minus 4 is given if Y is judged to be a whole lot softer than X.

The grades are averaged and the resultant value is in units of PSU. The resulting data are considered the results of one panel test. If more than one sample pair is evaluated then all sample pairs are rank ordered according to their grades by paired statistical analysis. Then, the rank is shifted up or down in value as required to give a zero PSU value to which ever sample is chosen to be the zero-base standard. The other samples then have plus or minus values as determined by their relative grades with respect to the zero base standard. The

number of panel tests performed and averaged is such that about 0.2 PSU represents a significant difference in subjectively perceived softness.

B. Hydrophilicity (absorbency)

Hydrophilicity of tissue paper refers, in general, to the propensity of the tissue paper to be wetted with water. Hydrophilicity of tissue paper may be somewhat quantified by determining the period of time required for dry tissue paper to become completely wetted with water. This period of time is referred to as "wetting time". In order to provide a consistent and repeatable test for wetting time, the following procedure may be used for wetting time determinations: first, a conditioned sample unit sheet (the environmental conditions for testing of paper samples are 22 to 24 °C and 48 to 52% R.H. as specified in TAPPI Method T 402), approximately 4-3/8 inch x 4-3/4 inch (about 11.1 cm x 12 cm) of tissue paper structure is provided; second, the sheet is folded into four (4) juxtaposed quarters, and then crumpled by hand (either covered with clean plastic gloves or copiously washed with a grease removing detergent such as Dawn) into a ball approximately 0.75 inch (about 1.9 cm) to about 1 inch (about 2.5 cm) in diameter; third, the balled sheet is placed on the surface of a body of about 3 liters of distilled water at 22 to 24 °C contained in a 3 liter pyrex glass beaker. It should also be noted all testing of the paper through this technique should take place within the confines of the controlled temperature and humidity room at 22 to 24 °C and 48 to 52% relative humidity. The sample ball is then carefully placed on the surface of the water from a distance no greater than 1 cm above the water surface. At the exact moment the ball touches the water surface, a timer is simultaneously started; fourth, the second ball is placed in the water after the first ball is completely wetted out. This is easily noted by the paper color transitioning from its dry white color to a darker grayish coloration upon complete wetting. The timer is stopped and the time recorded after the fifth ball has completely wet out.

At least 5 sets of 5 balls (for a total of 25 balls) should be run for each sample. The final reported result should be the calculated

average and standard deviation taken for the 5 sets of data. The units of the measurement are seconds. The water must be changed after the 5 sets of 5 balls (total = 25 balls) have been tested. copious cleaning of the beaker may be necessary if a film or residue is noted on the inside wall of the beaker.

Another technique to measure the water absorption rate is through pad sink measurements. After conditioning the tissue paper of interest and all controls for a minimum of 24 hours at 22 to 24 °C and 48 to 52% relative humidity (Tappi method #T402OM-88), a stack of 5 to 20 sheets of tissue paper is cut to dimensions of 2.5" to 3.0". The cutting can take place through the use of dye cutting presses, a conventional paper cutter, or laser cutting techniques. Manual scissors cutting is not preferred due to both the irreproducibility in handling of the samples, and the potential for paper contamination.

After the paper sample stack has been cut, it is carefully placed on a wire mesh sample holder. The function of this holder is to position the sample on the surface of the water with minimal disruption. This holder is circular in shape and has a diameter of approximately 4.2". It has five straight and evenly spaced metal wires running parallel to one another and across to spot welded points on the wire's circumference. The spacing between the wires is approximately 0.7". This wire mesh screen should be clean and dry prior to placing the paper on its surface. A 3 liter beaker is filled with about 3 liters of distilled water stabilized at a temperature of 22 to 24 °C. After insuring oneself that the water surface is free of any waves or surface motion, the screen containing the paper is carefully placed on top of the water surface. The screen sample holder is allowed to continue downward after the sample floats on the surface so the sample holder screen handle catches on the side of the beaker. In this way, the screen does not interfere with the water absorption of the paper sample. At the exact moment the paper sample touches the surface of the water, a timer is started. The timer is stopped after the paper stack is completely wetted out. This is easily visually observed by noting a transition in the paper color from its dry white color to a darker grayish coloration upon complete wetting. At the instant of complete wetting,

the timer is stopped and the total time recorded. This total time is the time required for the paper pad to completely wet out.

This procedure is repeated for at least 2 additional tissue paper pads. No more than 5 pads of paper should be run without disposing of the water and post cleaning and refilling of the beaker with fresh water at a temperature of 22 to 24 °C. Also, if new and unique sample is to be run, the water should always be changed to the fresh starting state. The final reported time value for a given sample should be the average and standard deviations for the 3 to 5 stacks measured. The units of the measurement are seconds.

Hydrophilicity characteristics of tissue paper embodiments of the present invention may, of course, be determined immediately after manufacture. However, substantial increases in hydrophobicity may occur during the first two weeks after the tissue paper is made: i.e., after the paper has aged two (2) weeks following its manufacture. Thus, the wetting times are preferably measured at the end of such two week period. Accordingly, wetting times measured at the end of a two week aging period at room temperature are referred to as "two week wetting times." Also, optional aging conditions of the paper samples may be required to try and mimic both long term storage conditions and/or possible severe temperature and humidity exposures of the paper products of interest. For instance, exposure of the paper sample of interest to temperatures in the range of 49 to 82 °C for 1 hour to 1 year can mimic some of potentially severe exposures conditions a paper sample may experience in the trade. Also, autoclaving of the paper samples can mimic severe aging conditions the paper may experience in the trade. It must be reiterated that after any severe temperature testing, the samples must be re-conditioned at a temperature of 22 to 24 °C and a relative humidity of 48 to 52%. All testing should also be done within the confines of the controlled temperature and humidity room.

C. Density

The density of tissue paper, as that term is used herein, is the average density calculated as the basis weight of that paper divided by

the caliper, with the appropriate unit conversions incorporated therein to convert to g/cc. Caliper of the tissue paper, as used herein, is the thickness of the preconditioned (23 \pm 1°C, 50 \pm 2% RH for 24 hours according to a TAPPI Method #T4020M-88) paper when subjected to a compressive load of 95 g/in² (15.5 g/cm²). The caliper is measured with a Thwing-Albert model 89-II thickness tester (Thwing-Albert Co. of Philadelphia, PA). The basis weight of the paper is typically determined on a 4"X4" pad which is 8 plies thick. This pad is preconditioned according to Tappi Method #T4020M-88 and then the weight is measured in units of grams to the nearest ten-thousandths of a gram. Appropriate conversions are made to report the basis weight in units of pounds per 3000 square feet.

D. Lint

Dry lint

Dry lint can be measured using a Sutherland Rub Tester, a piece of black felt (made of wool having a thickness of about 2.4 mm and a density of about 0.2 gm/cc. Such felt material is readily available from retail fabric stores such as Hancock Fabric), a four pound weight and a Hunter Color meter. The Sutherland tester is a motor-driven instrument which can stroke a weighted sample back and forth across a stationary sample. The piece of black felt is attached to the four pound weight. The tissue sample is mounted on a piece of cardboard (Crescent #300 obtained from Cordage of Cincinnati, OH.) The tester then rubs or moves the weighted felt over a stationary tissue sample for five strokes. The load applied to the tissue during rubbing is about 33.1 gm/sq. cm.. The Hunter Color L value of the black felt is determined before and after rubbing. The difference in the two Hunter Color readings constitutes a measurement of dry linting. Other methods known in the prior arts for measuring dry lint also can be used.

Wet lint

A suitable procedure for measuring the wet linting property of tissue samples is described in U.S. Patent No. 4,950,545; issued to Walter et al., on August 21, 1990, and incorporated herein by reference. The procedure essentially involves passing a tissue sample through two steel rolls, one of which is partially submerged in a water bath. Lint from the tissue sample is transferred to the steel roll which is

moistened by the water bath. The continued rotation of the steel roll deposits the lint into the water bath. The lint is recovered and then counted. See col. 5, line 45 - col. 6, line 27 of the Walter et al. patent. Other methods known in the prior art for measuring wet lint also can be used.

Optional Ingredients

Other chemicals commonly used in papermaking can be added to the chemical softening composition described herein, or to the papermaking furnish so long as they do not significantly and adversely affect the softening, absorbency of the fibrous material, and softness enhancing actions of the quaternary ammonium softening compounds of the present invention.

A. Wetting Agents:

The present invention may contain as an optional ingredient from about 0.005% to about 3.0%, more preferably from about 0.03% to 1.0% by weight, on a dry fiber basis of a wetting agent.

Nonionic Surfactant (Alkoxylated Materials)

Suitable nonionic surfactants can be used as wetting agents in the present invention include addition products of ethylene oxide and, optionally, propylene oxide, with fatty alcohols, fatty acids, fatty amines, etc.

Any of the alkoxylated materials of the particular type described hereinafter can be used as the nonionic surfactant. Suitable compounds are substantially water-soluble surfactants of the general formula:



wherein R_2 for both solid and liquid compositions is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups; primary, secondary and branched chain alkenyl hydrocarbyl groups; and primary, secondary and branched chain alkyl- and alkenyl-substituted phenolic hydrocarbyl groups; said hydrocarbyl groups having a hydrocarbyl chain length of from about 8 to about 20, preferably from about 10 to about 18 carbon atoms.

More preferably the hydrocarbyl chain length for liquid compositions is from about 16 to about 18 carbon atoms and for solid compositions from about 10 to about 14 carbon atoms. In the general formula for the ethoxylated nonionic surfactants herein, Y is typically -O-, -C(O)O-, -C(O)N(R)-, or -C(O)N(R)R-, in which R₂, and R, when present, have the meanings given herein before, and/or R can be hydrogen, and z is at least about 8, preferably at least about 10-11. Performance and, usually, stability of the softener composition decrease when fewer ethoxylate groups are present.

The nonionic surfactants herein are characterized by an HLB (hydrophilic-lipophilic balance) of from about 7 to about 20, preferably from about 8 to about 15. Of course, by defining R₂ and the number of ethoxylate groups, the HLB of the surfactant is, in general, determined. However, it is to be noted that the nonionic ethoxylated surfactants useful herein, for concentrated liquid compositions, contain relatively long chain R₂ groups and are relatively highly ethoxylated. While shorter alkyl chain surfactants having short ethoxylated groups may possess the requisite HLB, they are not as effective herein.

Examples of nonionic surfactants follow. The nonionic surfactants of this invention are not limited to these examples. In the examples, the integer defines the number of ethoxyl (EO) groups in the molecule.

Linear Alkoxyated Alcohols

a. Linear, Primary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, and pentadeca-ethoxylates of n-hexadecanol, and n-octadecanol having an HLB within the range recited herein are useful wetting agents in the context of this invention. Exemplary ethoxylated primary alcohols useful herein as the viscosity/dispersibility modifiers of the compositions are n-C18EO(10); and n-C10EO(11). The ethoxylates of mixed natural or synthetic alcohols in the "oleyl" chain length range are also useful herein. Specific examples of such materials include oleyl alcohol-EO(11), oleyl alcohol-EO(18), and oleyl alcohol-EO(25).

b. Linear, Secondary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, pentadeca-, octadeca-, and nonadeca-ethoxylates of 3-hexadecanol, 2-octadecanol, 4-eicosanol, and 5-eicosanol having an HLB within the range recited herein can be used as wetting agents in the present invention. Exemplary ethoxylated secondary alcohols can be used as wetting agents in the present invention are: 2-C16EO(11); 2-C20EO(11); and 2-C16EO(14).

Linear Alkyl Phenoxyated Alcohols

As in the case of the alcohol alkoxylates, the hexa- through octadeca-ethoxylates of alkylated phenols, particularly monohydric alkylphenols, having an HLB within the range recited herein are useful as the viscosity/dispersibility modifiers of the instant compositions. The hexa- through octadeca-ethoxylates of p-tridecylphenol, m-pentadecylphenol, and the like, are useful herein. Exemplary ethoxylated alkylphenols useful as the wetting agents of the mixtures herein are: p-tridecylphenol EO(11) and p-pentadecylphenol EO(18).

As used herein and as generally recognized in the art, a phenylene group in the nonionic formula is the equivalent of an alkylene group containing from 2 to 4 carbon atoms. For present purposes, nonionics containing a phenylene group are considered to contain an equivalent number of carbon atoms calculated as the sum of the carbon atoms in the alkyl group plus about 3.3 carbon atoms for each phenylene group.

Olefinic Alkoxylates

The alkenyl alcohols, both primary and secondary, and alkenyl phenols corresponding to those disclosed immediately herein above can be ethoxylated to an HLB within the range recited herein can be used as wetting agents in the present invention

Branched Chain Alkoxylates

Branched chain primary and secondary alcohols which are available from the well-known "OXO" process can be ethoxylated and can be used as wetting agents in the present invention.

The above ethoxylated nonionic surfactants are useful in the present compositions alone or in combination, and the term "nonionic surfactant" encompasses mixed nonionic surface active agents.

The level of surfactant, if used, is preferably from about 0.01% to about 2.0% by weight, based on the dry fiber weight of the tissue paper. The surfactants preferably have alkyl chains with eight or more carbon atoms. Exemplary anionic surfactants are linear alkyl sulfonates, and alkylbenzene sulfonates. Exemplary nonionic surfactants are alkylglycosides including alkylglycoside esters such as Crodesta SL-40 which is available from Croda, Inc. (New York, NY); alkylglycoside ethers as described in U.S. Patent No. 4,011,389, issued to W. K. Langdon, et al. on March 8, 1977; and alkylpolyethoxylated esters such as Pegosperse 200 ML available from Glyco Chemicals, Inc. (Greenwich, CT) and IGEPAL RC-520 available from Rhone Poulenc Corporation (Cranbury, N.J.).

B. Strength additives:

Other types of chemicals which may be added, include the strength additives to increase the dry and wet tensile strength of the tissue webs. The present invention may contain as an optional component an effective amount, preferably from about 0.01% to about 3.0%, more preferably from about 0.2% to about 2.0% by weight, on a dry fiber weight basis, of a water-soluble strength additive resin. These strength additive resins are preferably selected from the group consisting of dry strength resins, permanent wet strength resins, temporary wet strength resins, and mixtures thereof.

(a) Dry strength additives

The dry strength additives are preferably selected from the group consisting of carboxymethyl cellulose resins, starch based resins and mixtures thereof. Examples of preferred dry strength additives include carboxymethyl cellulose, and cationic polymers from the ACCO chemical family such as ACCO 711 and ACCO 514, with ACCO chemical family being most preferred. These materials are available commercially from the American Cyanamid Company of Wayne, New Jersey.

(b) Permanent wet strength additives

Permanent wet strength resins useful herein can be of several types. Generally, those resins which have previously found and which will hereafter find utility in the papermaking art are useful herein. Numerous examples are shown in the aforementioned paper by Westfelt, incorporated herein by reference.

In the usual case, the wet strength resins are water-soluble, cationic materials. That is to say, the resins are water-soluble at the time they are added to the papermaking furnish. It is quite possible, and even to be expected, that subsequent events such as cross-linking will render the resins insoluble in water. Further, some resins are soluble only under specific conditions, such as over a limited pH range.

Wet strength resins are generally believed to undergo a cross-linking or other curing reactions after they have been deposited on, within, or among the papermaking fibers. Cross-linking or curing does not normally occur so long as substantial amounts of water are present.

Preferably the permanent wet strength resin binder materials are selected from the group consisting of polyamide-epichlorohydrin resins, polyacrylamide resins, and mixtures thereof.

Of particular utility are the various polyamide-epichlorohydrin resins. These materials are low molecular weight polymers provided with reactive functional groups such as amino, epoxy, and azetidinium groups. The patent literature is replete with descriptions of processes for making such materials. U.S. Pat. No. 3,700,623, issued to Keim on October 24, 1972 and U.S. Pat. No. 3,772,076, issued to Keim on November 13, 1973 are examples of such patents and both are incorporated herein by reference.

Polyamide-epichlorohydrin resins sold under the trademarks Kymene 557H and Kymene 2064 by Hercules Incorporated of Wilmington, Delaware, are particularly useful in this invention. These resins are generally described in the aforementioned patents to Keim.

Base-activated polyamide-epichlorohydrin resins useful in the present invention are sold under the Santo Res trademark, such as Santo Res 31, by Monsanto Company of St. Louis, Missouri. These types of materials are generally described in U.S. Pat. Nos. 3,855,158 issued to Petrovich on December 17, 1974; 3,899,388 issued to

Petrovich on August 12, 1975; 4,129,528 issued to Petrovich on December 12, 1978; 4,147,586 issued to Petrovich on April 3, 1979; and 4,222,921 issued to Van Eenam on September 16, 1980, all incorporated herein by reference.

Other water-soluble cationic resins useful herein are the polyacrylamide resins such as those sold under the Parex trademark, such as Parex 631NC, by American Cyanamid Company of Stamford, Connecticut. These materials are generally described in U.S. Pat. Nos. 3,556,932 issued to Coscia et al . on January 19, 1971; and 3,556,933 issued to Williams et al . on January 19, 1971, all incorporated herein by reference.

Other types of water-soluble resins useful in the present invention include acrylic emulsions and anionic styrene-butadiene latexes. Numerous examples of these types of resins are provided in U.S. Patent No. 3,844,880, Meisel, Jr. et al ., issued October 29, 1974, incorporated herein by reference.

Still other water-soluble cationic resins finding utility in this invention are the urea formaldehyde and melamine formaldehyde resins. These polyfunctional, reactive polymers have molecular weights on the order of a few thousand. The more common functional groups include nitrogen containing groups such as amino groups and methylol groups attached to nitrogen.

Although less preferred, polyethylenimine type resins find utility in the present invention.

More complete descriptions of the aforementioned water-soluble resins, including their manufacture, can be found in TAPPI Monograph Series No. 29, **Wet Strength In Paper and Paperboard**, Technical Association of the Pulp and Paper Industry (New York; 1965), incorporated herein by reference. As used herein, the term "permanent wet strength resin" refers to a resin which allows the paper sheet, when placed in an aqueous medium, to keep a majority of its initial wet strength for a period of time greater than at least two minutes.

(c) Temporary wet strength additives

The above-mentioned wet strength additives typically result in paper products with permanent wet strength, i.e., paper which when placed in an aqueous medium retains a substantial portion of its initial wet strength over time. However, permanent wet strength in some

types of paper products can be an unnecessary and undesirable property. Paper products such as toilet tissues, etc., are generally disposed of after brief periods of use into septic systems and the like. Clogging of these systems can result if the paper product permanently retains its hydrolysis-resistant strength properties. More recently, manufacturers have added temporary wet strength additives to paper products for which wet strength is sufficient for the intended use, but which then decays upon soaking in water. Decay of the wet strength facilitates flow of the paper product through septic systems.

Examples of suitable temporary wet strength resins include modified starch temporary wet strength agents, such as National Starch 78-0080, marketed by the National Starch and Chemical Corporation (New York, New York). This type of wet strength agent can be made by reacting dimethoxyethyl-N-methyl-chloroacetamide with cationic starch polymers. Modified starch temporary wet strength agents are also described in U.S. Pat. No. 4,675,394, Solarek, et al., issued June 23, 1987, and incorporated herein by reference. Preferred temporary wet strength resins include those described in U.S. Pat. No. 4,981,557, Bjorkquist, issued January 1, 1991, and incorporated herein by reference.

With respect to the classes and specific examples of both permanent and temporary wet strength resins listed above, it should be understood that the resins listed are exemplary in nature and are not meant to limit the scope of this invention.

Mixtures of compatible wet strength resins can also be used in the practice of this invention.

The above listings of optional chemical additives is intended to be merely exemplary in nature, and are not meant to limit the scope of the invention.

The following example illustrates the practice of the present invention but are not intended to be limiting thereof.

EXAMPLE

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. A 3% by weight aqueous slurry of

NSK (Northern Softwood Kraft (such as Grand Prairie from Weyerhaeuser Corporation of Tacoma Washington)) is made up in a conventional re-pulper. A 2% solution of the temporary wet strength resin (i.e., National starch 78-0080 marketed by National Starch and Chemical corporation of New-York, NY) is added to the NSK stock pipe at a rate of 0.75% by weight of the dry fibers. The adsorption of the temporary wet strength resin onto NSK fibers is enhanced by an in-line mixer. The NSK slurry is diluted to about 0.2% consistency at the fan pump. A 3% by weight aqueous slurry of Eucalyptus (such as Aracruz of Brazil) fibers is made up in a conventional re-pulper. The Eucalyptus slurry is diluted to about 0.2% consistency at the fan pump. The individual furnish components are sent to separate layers (i.e., Euc. to the outer layers and NSK in the center layer) in the head box and deposited onto a Fourdrinier wire to form a three-layer embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 33 machine-direction and 30 cross-machine-direction monofilaments per centimeter, respectively. The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 18% at the point of transfer, to a second papermaking belt. The second papermaking belt is an endless belt having the preferred network surface and deflection conduits. The papermaking belt is made by forming a photo-polymeric network on a foraminous woven element made of polyester and having 14 (MD) by 12 (CD) filaments per centimeter in a four shed dual layer design according to the process disclosed in U.S. No. 5,334,289 issued to Trokhan. The filaments are about .22 mm in diameter machine-direction and .28 mm in diameter cross-machine-direction. The photosensitive resin used in the process is Merigraph resin EPD1616C, a methacrylated-urethane resin marketed by Hercules, Incorporated, Wilmington, Delaware. The papermaking belt is about 1.1 mm thick.

The embryonic web is carried on the papermaking belt past the vacuum dewatering box, through blow-through predryers after which the web is transferred onto a Yankee dryer. The other process and machine conditions are listed below. The fiber consistency is about 27% after the vacuum dewatering box and, by the action of the predryers, about 65% prior to transfer onto the Yankee dryer; creping

adhesive comprising a 0.25% aqueous solution of polyvinyl alcohol is spray applied by applicators; the fiber consistency is increased to be an estimated 99% before dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees; the Yankee dryer is operated at about 350°F (177°C); the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry creped web is then passed between two calender rolls. The two calender rolls are biased together at roll weight and operated at surface speeds of 660 fpm (about 201 meters per minute). The calendered web is wound on a reel (which is also operated at a surface speed of 660 fpm) and is then ready for use.

An aqueous solution containing a plasticizer-emulsion mixture is continuously applied onto the paper-contacting surface of the papermaking belt via an emulsion distribution roll before the papermaking belt comes in contact with the embryonic web. The aqueous emulsion applied by the distribution roll onto the deflection member contains five ingredients: water, Regal Oil (a high-speed turbine oil marketed by the Texaco Oil Company), ADOGEN TA 100 (a distearyldimethyl ammonium chloride surfactant marketed by the Witco Corporation, cetyl alcohol (a C16 linear fatty alcohol marketed by The Procter & Gamble Company) and glycerol. The relative proportions of the five ingredients are as follows: 6.1% by weight Regal Oil, 0.3% by weight Adogen, 0.2% by weight cetyl alcohol, 31.1% by weight of glycerol, and the remainder water. To form the emulsion oil phase, the emulsion is first mixed with the surfactants listed above, and finally with water and glycerol. The volumetric flow rate of the aqueous emulsion applied to the papermaking belt is about 0.50 gal/hr.-cross-direction ft. (about 6.21 liters/hr-meter). The wet web has a fiber consistency of about 25%, total web weight basis, when it comes in contact with the aqueous emulsion.

The web is converted into a one ply tissue paper product. The tissue paper has about 18 #/3M Sq Ft basis weight, contains about 1% of the glycerol, about 1% of the Regal oil and about 0.2% of the temporary wet strength resin. Importantly, the resulting tissue paper is soft, absorbent and is suitable for use as facial and/or toilet tissues.

CLAIMS

1. Tissue paper characterized in that it comprises:
 - a) wet-laid cellulosic fibers;
 - b) from 0.01% to 5% of a water soluble polyhydroxy compound, based on the dry fiber weight of said tissue paper, wherein said polyhydroxy compound is preferably selected from glycerol, polyglycerols having a weight average molecular weight from 150 to 800, polyoxyethylene glycol and polyoxypropylene glycol or polyoxyethylene / polyoxypropylene glycol copolymers having a weight average molecular weight from 200 to 1000, and mixtures thereof; and
 - c) from 0.01% to 5% of an oil selected from petroleum-based oils, polysiloxane-based oils, and mixtures thereof, based on the dry fiber weight of said tissue paper, wherein said petroleum-based oil is preferably a petroleum-based turbine oil comprised primarily of saturated hydrocarbons;wherein said tissue paper has a basis weight of from 10 to 65 g/m² and a density of less than 0.60 g/cc.
2. The tissue paper of Claim 1 wherein said polyhydroxy compound is a polyoxyethylene glycol having a weight average molecular weight from 200 to 1000, more preferably a weight average molecular weight from 200 to 600.
3. The tissue paper of Claim 1 wherein said polyhydroxy compound is a mixture of glycerol and polyoxyethylene glycol having a weight average molecular weight from 200 to 1000.
4. The tissue paper of Claim 1 wherein said polyhydroxy compound is a mixture of polyglycerols having a weight average molecular weight from 150 to 800 and polyoxyethylene glycol having a weight average molecular weight from 200 to 1000.

5. The tissue paper of any of Claims 1 - 4 wherein said polysiloxane-based oil has an intrinsic viscosity ranging from 100 centipoises to 1000 centipoises.
6. The tissue paper of any of Claims 1 - 5 further comprising an effective amount of a strength additive selected from permanent wet strength resins, temporary wet strength resins, dry strength resins, and mixtures thereof.
7. The tissue paper of Claim 6 wherein said strength additive is a permanent wet strength resin, wherein said permanent wet strength resin is preferably selected from polyamide-epichlorohydrin resins, polyacrylamide resins, and mixtures thereof, most preferably a polyamide-epichlorohydrin resin.
8. The tissue paper of Claim 6 wherein said strength additive is a temporary wet strength resin, wherein said temporary wet strength resin is preferably a starch-based temporary wet strength resin.
9. The tissue paper of Claim 6 wherein said strength additive is a dry strength resin, wherein said dry strength resin is preferably selected from carboxymethyl cellulose resins, starch based resins, and mixtures thereof, most preferably a carboxymethyl cellulose resin.
10. The tissue paper of any of Claims 1 - 9 wherein said polyhydroxy compound and said oil having been applied to at least one surface of a wet tissue paper web.

1/1

