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PAPER PRODUCTS CONTAINING CARBOXYLIC ACID ESTERS AND PROCESS FOR PREPARING SUCH PRODUCTS

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This application is a continuation-in-part of application Serial No. 52,344, filed August 29, 1960, and application Serial No. 62,301, filed October 12, 1960, and now both abandoned.

This invention relates to paper articles and their production. More particularly, this invention is concerned with the production of soft paper articles such as facial tissue or other types of tissue which is soft to the touch.

In preparing paper articles which are suitable for such uses as toweling or tissue, several methods of arriving at a product having satisfactory softness have been employed. In one of said methods, the pulp used in preparing the articles is beaten to such a slight degree that the paper formed therefrom has the requisite softness. However, such articles have the disadvantage of being exceptionally weak and disintegrate readily to the annoyance of the user. In a second method, the pulp used in preparing the articles is beaten to such a degree that the paper formed therefrom will have a relatively satisfactory strength and will not disintegrate in use. Here, however, the articles per se are not sufficiently soft to the touch to meet public favor. In order to render such products commercially acceptable from the standpoint of softness, it is necessary to treat them with an agent which will produce the desired softness without introducing other objectionable features. Other methods include the mechanical working of a finished sheet to impart softness and the selection of inherently softer fibers, such as spruce fibers, or fibers which are made softer by the pulping process.

Many chemical agents of the hygroscopic and waxy or wetting agent type have been tried for the purpose of softening paper. A very few have been successful to a limited extent, but they still do not give the optimum softness desired. Many agents have been assayed unsuccessfully, and their failures have been due to various reasons. One primary reason for failure is that they do not impart the requisite softness to paper articles. Although some of these agents accomplish this in some degree, they introduce complicating factors such as bad odor, poor aging properties, toxic effects, decreased water absorbency, etc. For example, glycerine, which is a hygroscopic agent, gives a softening effect but has the disadvantage of lowering the tensile strength and water absorbency of the product. An objectionable damp feel is also imparted to the paper. As another example, sodium oleate, which is a wetting agent, exhibits disadvantages of poor aging characteristics and insufficient softening action. Many other instances could be cited to illustrate different specific agents which have been found unsuitable, but it is believed that the preceding general remarks clearly emphasize that the suitability of a particular agent for softening paper products cannot be predicted.

It is an object of this invention to provide methods of softening paper products.

More specifically, it is an object of this invention to provide paper products for use as toweling or tissue, such products having the requisite softness and other desirable properties.

It is a further object of this invention to provide methods of softening paper with novel softening agents.

Still other objects, advantages and features of this invention will become apparent upon consideration of the following detailed description and the examples attendant thereto.

It has been found that paper products having the desired features are obtained by employing paper containing an aliphatic ester of certain aliphatic or an aromatic carboxylic acid, said ester having from about 8 to about 42 carbon atoms.

These esters of said aliphatic or aromatic acids, hereinafter referred to as the agents, may be applied directly to the paper after it has been formed, or they may be incorporated in the paper during the formation thereof. In the first of these procedures, the agent is applied by dipping the paper in a solution or emulsion of said agent. A sample of the paper to be treated is first dipped in water. Said sample is then pressed between wet, pressed blotting paper and weighed. A comparison of the weights before and after dipping will indicate the water pickup of the paper to be treated. Based on this figure, the concentration of the solution or emulsion necessary to put the desired amount of the agent on the paper is calculated. The solution or emulsion is then prepared, and the paper to be treated is dipped therein. Said paper is then pressed in the manner noted above and dried. The paper thus treated displays the desired softness.

In the second of the procedures mentioned above, the agent is incorporated in the paper furnish, the aqueous slurry of paper pulp from which the finished sheet or other product is produced. This type of operation is generally known as wet and application. A solution or emulsion of the agent is prepared. The concentration of said agent is based upon the amount of dry pulp in the pulp slurry. The solution or emulsion is stirred into said slurry, after which the latter is processed in the conventional manner to give the desired paper product.

The agents contemplated by this invention may be applied to or incorporated in any paper product where softness or lack of harshness to the touch is desirable or necessary. Exemplary products include sanitary tissues, facial tissues, toilet tissues, toweling and the like. Such products are usually prepared from lightly sized to unsized pulps, such as bleached or unbleached sulfite, sulfate, soda or groundwood pulps or mixtures of these pulps. This invention is also specifically concerned with the softening of paper products which are to be employed in contact with human skin and where softness to the touch, non-toxicity, non-irritation and satisfactory strength are essential properties. The agents of the invention are preferably applied to or incorporated in paper which has the requisite strength but is lacking in the desired softness.

The amount of agent used on or in the paper product may be varied considerably depending primarily upon the particular agent employed, the intended use of the product, and the type of paper which is to be treated. In most instances, the agent will be used in small amounts, some softening being attained in paper products containing as little as about 0.05% by weight of said agent based on the dry weight of the paper. Ordinarily, no further advantages will result from the application of more than about 3% by weight of the selected agent. However, in order to avoid the possibility of altering other properties of the paper product while insuring that a substantial softening effect will occur, it is preferred to apply from about 0.5% to about 1.0% by weight of the agent based upon the dry weight of the paper product.

The agents employed in this invention are the aliphatic esters of aliphatic and aromatic mono- or polycarboxylic acids, said esters having from about 8 to about 42 carbon atoms. Preparation of such esters is most often accomplished by the reaction of the acid with an alcohol, although it should be noted that any other esterification

procedure may be used if desired. More particularly, said agents are esters of (1) aliphatic dicarboxylic acids of from 2 to 10 carbon atoms and (2) benzoic, biphenylcarboxylic and the isomeric benzene di-, tri- and tetracarboxylic acids.

Illustrative of the saturated and unsaturated aliphatic dicarboxylic acids which can be used to prepare the agents of this invention are oxalic, malonic, succinic, adipic, azelaic, sebacic, maleic, itaconic, citraconic, muconic, acetylenedicarboxylic and the like. Illustrative of the aromatic acids which can be so used are benzoic, biphenylcarboxylic, phthalic, isophthalic, terephthalic, trimellitic, trimesic, hemimellitic, pyromellitic and the like.

The esterifying group for each carboxyl group of the acids illustrated above is an aliphatic radical, preferably of from about 4 to about 20 carbon atoms. These aliphatic radicals are exemplified by such as butyl, isobutyl, amyl, 1,1-dimethylpropyl, hexyl, 1-methylpentyl, heptyl, octyl, 2-ethylhexyl, nonyl, 3,3,5-trimethylhexyl, decyl, dodecyl, tetradecyl, octadecyl, butenyl, hexenyl, octenyl, oleyl, benzyl, phenylethyl, cyclopentyl, cyclohexyl, methylcyclohexyl, cyclohexylmethyl and the like.

In readying an agent for application to a paper product or for incorporation in a paper furnish, a cationic or anionic emulsion of said agent is prepared. The concentration of the agent in the emulsion may be determined in the manner previously defined. In the selection of an emulsifier, those of the cationic type are preferred. These include primary, secondary and tertiary amine salts, quaternary ammonium compounds, other nitrogenous bases, and phosphonium and sulfonium bases. It should be noted that particularly effective results are achieved when the cationic emulsifier selected is a quaternary ammonium compound. An extensive list of the various emulsifiers mentioned, along with a discussion of the several types, may be found in "Emulsions: Theory and Practice" by P. Becher, Reinhold Publishing Company (1957). Of particular interest are Chapter 16 and pages 337–367, the latter giving both the trade and chemical names of the emulsifiers. It should be pointed out that, although quaternary ammonium compounds are known as softeners in their own right, the amounts employed as emulsifying agents are far below the level required to produce any softening agent.

In order to evaluate the softening effect of the agents of this invention, tests of the treated paper products were made with a Clark Softness Tester in accordance with TAPPI Tentative Standard, T 451–M–45. This tester consists of a support (usually a pair of rollers) for one end of a strip of paper having parallel edges. This support can be rotated about an axis parallel to the long axis of said rollers and perpendicular to the long axis of the paper strip. The overhanging length of the paper is adjusted by turning the rolls until, when the support is slowly rotated back and forth through 90°, the strip just falls over at each of the end points of rotation. The overhanging or critical length is then measured, and the softness of the paper is calculated from the formula $10^6 \log (t+1)/L^3W$. In said formula, L is the critical length, and t and W are the basic thickness and weight, respectively.

In the test data which follows, the agents of this invention were directly applied to paper products by dipping such products in a solution or emulsion of the agent. The products tested were either 42-lb. handsheet or Whatman No. 1 filter paper, and these products were first tested for water pickup, as described above, to determine the concentration of the solution or emulsion necessary to apply the desired amount of agent to the paper. Tests on the untreated products were made, and the percentage figures given for the softness of the treated products are based on the softness of the untreated product being 100%. A treated product having a percentage above 100% shows that said product is softer than the control.

Softening Agent	Percent Applied Based on Dry Weight of Paper	Softness, Percent of Control
Dibutyl maleate	1.0	128
Di(2-ethylhexyl) maleate	1.0	135
Do	0.75	135
Do	0.5	121
Do	0.25	117
Di(2-ethylhexyl) succinate	1.0	136
Didecyl succinate	1.0	145
Di(tridecyl) succinate	1.0	138
Do	0.75	128
Do	0.5	114
Do	0.25	110
Dicyclohexyl succinate	1.0	124
Diisobutyl adipate	1.0	135
Bis(3,3,5-trimethylhexyl) adipate	1.0	136
Do	0.75	125
Do	0.5	119
Do	0.25	114
Di(2-ethylhexyl) adipate	1.0	142
Diisodecyl adipate	1.0	142
Dicyclohexyl adipate	1.0	125
Dibutyl azelate	1.0	130
Di(2-ethylhexyl) azelate	1.0	135
Do	0.75	127
Do	0.5	119
Do	0.25	112
Diisooctyl azelate	1.0	142
Diisodecyl azelate	1.0	121
Di(2-ethylhexyl) sebacate	1.0	130
Do	0.75	121
Do	0.5	114
Do	0.25	110
Di(1-methylcyclohexylmethyl) sebacate	1.0	118
Dibutyl isosebacate	1.0	135
Di(2-ethylhexyl) isosebacate	1.0	139
Dibutyl phthalate	1.0	111
Di-2-ethylhexyl phthalate	1.0	128
Dioleyl phthalate	1.0	154
Butyl benzyl phthalate	1.0	116
Benzyl benzoate	1.0	116
Octadecyl benzoate (liquid)	1.0	132
Didecyl terephthalate (solid)	1.0	129
Di-2-ethylhexyl terephthalate	1.0	132
2-ethylhexyl biphenylcarboxylate	1.0	137
Didecyl isophthalate	1.0	161
Di-2-ethylhexyl isophthalate	1.0	132
Tris-decyl trimellitate	1.0	146
Butyl, dibenzyl trimellitate	1.0	131
Tetra-2-ethylhexyl pyromellitate	1.0	154

The softening effect of the agents of this invention was also evaluated in paper products which had such agents incorporated in the paper furnish. In this wet end application, a solution or emulsion of an agent was added to a 2% pulp slurry, and the mixture thoroughly stirred on a sizing table. The concentration of the solution or emulsion was based upon the amount of dry pulp in the slurry and the amount of agent desired in the final paper product. Handsheets were prepared from said slurry and tested with the Clark Softness Tester.

Softening Agent	Percent Applied Based on Dry Weight of Paper	Softness, Percent of Control
Bis(3,3,5-trimethylhexyl) adipate	1.0	130
Do	0.75	128
Do	0.5	115
Do	0.25	103
Diisodecyl adipate	1.0	115
Do	0.75	107

Thus it will be seen that this invention contemplates the preparation of soft paper articles by either treating a paper product, or incorporating in a paper furnish, a softening amount of an aliphatic ester of the aliphatic and aromatic acids described above. Various changes and modifications may be made in the agents, paper products and processes described herein, as will be apparent to those skilled in the art to which this invention pertains, without departing from the spirit and scope of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A cellulosic fiber paper product containing an ester of an acid selected from the group consisting of aliphatic dicarboxylic acids of from 2 to 10 carbon atoms, benzoic

acid, biphenylcarboxylic acid, and benzene di-, tri- and tetracarboxylic acids, the esterifying group for each carboxyl group of the acid being an aliphatic group, said ester having at least about 8 carbon atoms and being present in an amount sufficient to soften said paper product.

2. A cellulosic fiber paper product as defined in claim 1 wherein said ester contains from about 8 to about 42 carbon atoms.

3. A cellulosic fiber paper product as defined in claim 1 wherein said ester is present in amounts of from about 0.05% to about 3% by weight based upon the dry paper product.

4. A cellulosic fiber paper product as defined in claim 1 wherein said ester is present in amounts of from about 0.5% to about 1.0% by weight based upon the dry paper product.

5. A cellulosic fiber paper product containing an ester of a benzene carboxylic acid having from 1 to 4 carboxyl groups, the esterifying group for each carboxyl group of the acid being an aliphatic group of at least 4 carbon atoms, said ester being present in amounts of from about 0.05% to about 3% by weight based upon the dry paper product.

6. A cellulosic fiber paper product containing an ester of an aliphatic dicarboxylic acid of from 2 to 10 carbon atoms, the esterifying group for each carboxyl group of the acid being an aliphatic group of at least 4 carbon atoms, said ester being present in amounts of from about 0.05% to about 3% by weight based upon the dry paper product.

7. A process of softening a cellulosic fiber paper product which comprises applying to said product an ester of an acid selected from the group consisting of aliphatic dicarboxylic acids of from 2 to 10 carbon atoms, benzoic acid, biphenylcarboxylic acid, and benzene di-, tri- and tetracarboxylic acids, the esterifying group for each carboxyl group of the acid being an aliphatic group, said ester having at least about 8 carbon atoms and being applied to said product in an amount sufficient to soften said product.

8. A process as defined in claim 7 wherein said ester is applied in amounts of from about 0.05% to about 3% by weight based upon the dry paper product.

9. A process as defined in claim 7 wherein said ester is applied to said paper product in the form of an emulsion.

10. A process as defined in claim 9 wherein said ester is applied to said paper product in a cationic emulsion.

11. A process of softening a cellulosic fiber paper product which comprises applying to said product an ester of a benzene carboxylic acid having from 1 to 4 carboxyl groups, the esterifying group for each carboxyl group of the acid being an aliphatic group of at least 4 carbon atoms, said ester being applied to said product in an amount sufficient to soften said product.

12. A process of softening a cellulosic fiber paper product which comprises applying to said product an ester of an aliphatic dicarboxylic acid of from 2 to 10 carbon atoms, the esterifying group for each carboxyl group of the acid being an aliphatic group of at least 4 carbon atoms, said ester being applied to said product in an amount sufficient to soften said product.

13. A process of producing a soft cellulosic fiber paper product which comprises adding an ester of an acid selected from the group consisting of aliphatic dicarboxylic acids of from 2 to 10 carbon atoms, benzoic acid, biphenylcarboxylic acid, and benzene di-, tri- and tetracarboxylic acids, the esterifying group for each carboxyl group of the acid being an aliphatic group, said ester having at least about 8 carbon atoms, to an aqueous slurry of paper pulp and forming said paper pulp into a paper product, said ester being present in an amount sufficient to soften the product prepared from said paper pulp.

14. A process as defined in claim 13 wherein said ester is added to said slurry in an amount equal to from about 0.05% to about 3% by weight based upon the amount of dry pulp in said slurry.

15. A process of producing a soft cellulosic fiber paper product which comprises adding an ester of an aliphatic dicarboxylic acid of from 2 to 10 carbon atoms, the esterifying group for each carboxyl group of the acid being an aliphatic group of at least 4 carbon atoms, to an aqueous slurry of paper pulp and forming said paper pulp into a paper product, said ester being present in an amount sufficient to soften the product prepared from said paper pulp.

16. A process of producing a soft cellulosic fiber paper product which comprises adding an ester of a benzene carboxylic acid having from 1 to 4 carboxylic groups, the esterifying group for each carboxyl group of the acid being an aliphatic group of at least 4 carbon atoms, to an aqueous slurry of paper pulp and forming said paper pulp into a paper product, said ester being present in an amount sufficient to soften the product prepared from said paper pulp.

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