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Storage stable paper size composition containing ethoxylated castor oil.

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Description

This invention relates to a paper size comprising a self-emulsifiable mixture of 85 to 99 parts by weight of a cyclic dicarboxylic acid anhydride having hydrophobic substitution and as emulsifier 1 to 15 parts by weight of an alkoxyated castor oil containing at least 5 moles alkylene oxide per mole castor oil, an improved method for sizing paper and paperboard produced therewith.

Paper and paperboard are often sized with various hydrophobic materials including, for example, rosin, wax emulsions, mixtures of rosin waxes, ketene dimers, isocyanate derivatives, fatty acid complexes, fluorocarbons, certain styrene-maleic anhydride copolymers, as well as the substituted cyclic dicarboxylic acid anhydrides more particularly described hereinafter. These sizes may be introduced during the actual paper making operation wherein the process is known as internal or engine sizing, or they may be applied to the surface of the finished web or sheet in which case the process is known as external or surface sizing.

In order to obtain good sizing with any of these sizing compounds, it is desirable that they be uniformly dispersed throughout the fiber slurry in a small particle size. It was general practice therefore, to add the sizes in the form of an aqueous emulsion prepared with the aid of emulsifying agents including, for example, cationic or ordinary starches, carboxymethyl cellulose, natural gums, gelatin, cationic polymers or polyvinyl alcohol, all of which act as protective colloids. The use of such emulsifying agents with or without added surfactants did, however, suffer from several inherent deficiencies in commercial practice. A primary deficiency concerned the necessity of utilizing relatively complex, expensive and heavy equipment capable of exerting high homogenizing shear and/or pressures, together with rigid procedures regarding emulsifying proportions and temperatures, etc., for producing a satisfactory stable emulsion of the particular size. Additionally, the use of many surfactants in conjunction with protective colloids was found to create operational problems in the paper making process such as severe foaming of the stock and/or loss in sizing.

With particular reference to the procedures of the prior art which utilized substituted cyclic dicarboxylic acid anhydrides as sizing agents, it was necessary in commercial practice to pre-emulsify with cationic starch and/or other hydrocolloids using relatively rigid procedures with elevated temperatures to cook the starch or hydrocolloids and high shearing and/or high pressure homogenizing equipment. Unless these complicated procedures were carefully followed, difficulties such as deposition in the paper system, quality control problems and generally unsatisfactory performance were often encountered.

Many of these problems were overcome in U.S. Reissue Patent No. 29 960 which disclosed the use of a size mixture of these cyclic dicarboxylic acid anhydrides and specific polyoxyalkylene alkyl or alkyl-aryl ethers or their corresponding mono- or di-esters, which mixture was easily emulsifiable with water in the absence of high shearing forces and under normal pressure by merely stirring, passing through a mixing valve or common aspirator or by the usual agitation present in a stock preparation system. While satisfactory sizing properties for commercial uses were achieved with this method, the shelf stability of the mixture was poor and it was necessary to use the size mixture immediately after preparation thereof. The two components were therefore supplied separately to the paper manufacturer who continued the separate storage of the components until their use was required.

The issue involved in the US-A 4 529 447 is that a shelf stable paper sizing composition can be provided utilizing alkenyl succinic anhydride (ASA) together with an emulsifier component comprising at least one emulsifier selected from the group consisting of blocked polyoxyalkylenes or sulfur containing anionic surfactants. It is shown that the compositions containing ASA in conjunction with specific blocked polyoxyalkylene compounds provide satisfactory results. According to some examples only unblocked polyoxyalkylene compounds are utilized which provide unsatisfactory emulsification and sizing. Further examples show that sizing compositions can be obtained using the ASA compounds together with unblocked polyoxyalkylene compounds, but only in the presence of further emulsifiers. One example for comparative purposes illustrates that the unblocked compound does not give adequate sizing if the additional sulfur containing surfactant is not employed.

It would be desirable to be able to prepare a size in the form of a shelf stable mixture which could be stored in warehouses for periods of six months to a year, which would be self-emulsifiable and would exhibit excellent sizing properties with a limited number of emulsifiers and without the need of carrying out blocking reactions.

This object is solved by a paper size comprising a self-emulsifiable mixture of 85 to 99 parts by weight of a cyclic dicarboxylic acid anhydride having hydrophobic substitution and as emulsifier 1 to 15 parts by weight of an alkoxyated castor oil containing at least 5 moles alkylene oxide per mole castor oil which is characterized in that the alkoxyated castor oil is an unblocked ethoxyated or propoxyated castor oil and that further emulsifiers are excluded.

The method for sizing paper products according to the invention comprises the steps of

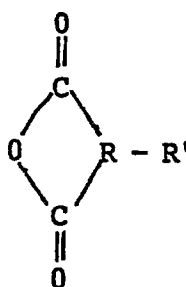
- a) providing a paper stock system;
- b) forming, in the absence of high shearing forces and under normal pressures, a sizing emulsion comprising from 85 to 99 parts by weight of a substituted cyclic dicarboxylic acid anhydride containing hydrophobic substitution; from 1 to 15 parts by weight of an alkoxyated castor oil containing at least 5 moles alkylene oxide per mole castor oil, and water;

c) forming a web from the paper stock system;

d) Dispersing said emulsion within the paper stock either before or after formation of said web but prior to passing said web through the drying stage of the paper making operation in an amount sufficient to provide a concentration of the substituted cyclic dicarboxylic acid anhydride from 0.01 to 2.0% based on dry fiber weight, characterized in that the alkoxylated castor oil is an unblocked ethoxylated or propoxylated castor oil and that further emulsifiers are excluded.

The mixture according to the invention is storage stable for extended periods of time, i.e., for at least six months of natural aging, and exhibits excellent sizing properties when emulsified prior to addition to the paper making stock or when added directly to the system and emulsified in-situ.

The sizing compounds contemplated for use herein are the cyclic dicarboxylic acid anhydrides containing hydrophobic substitution. Those substituted cyclic dicarboxylic acid anhydrides most commonly employed as paper sizes are represented by the following formula:

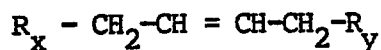


wherein R represents a dimethylene or trimethylene radical and wherein R' is a hydrophobic group containing more than 4 carbon atoms which may be selected from the class consisting of alkyl, alkenyl, aralkyl or aralkenyl groups. Sizing compounds in which R' contains more than twelve carbon atoms are preferred.

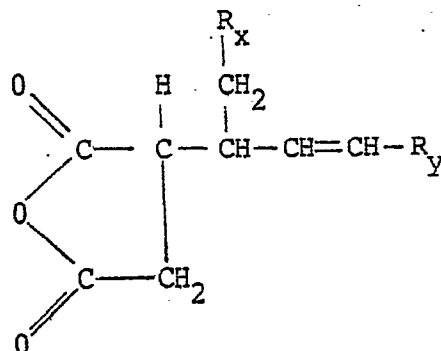
Representative of those cyclic dicarboxylic acid anhydrides which are broadly included within the above formula are sizing agents exemplified in US-A patent 3 102 064; 3 821 069, and 3 968 005 as well as by Japanese patent No. 959 923 and Sho 59 144 697.

Thus, the substituted cyclic dicarboxylic acid anhydrides may be the substituted succinic and glutaric acid anhydrides of the above described formula including, for example, iso-octadecenyl succinic acid anhydride, n- or iso-hexadecenyl succinic acid anhydride, dodecenyl succinic acid anhydride, dodecyl succinic acid anhydride, decenyl succinic acid anhydride, octenyl succinic acid anhydride, triisobutenyl succinic acid anhydride, etc.

The sizing agents may also be those of the above described formula which are prepared employing an internal olefin corresponding to the following general structure:



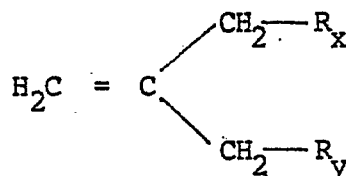
wherein R_x is an alkyl radical containing at least four carbon atoms and R_y is an alkyl radical containing at least four carbon atoms, and which correspond to the more specific formula:



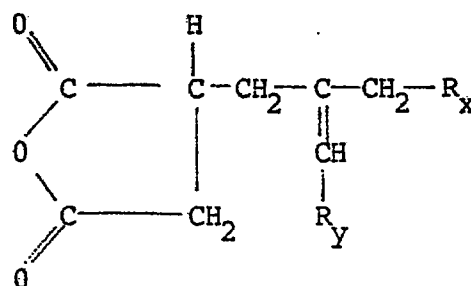
wherein R_x is an alkyl radical containing at least 4 carbon atoms and R_y is an alkyl radical containing at

least 4 carbon atoms and R_x and R_y are interchangeable. Specific examples of the latter sizing compounds include (1-octyl-2-decyl) succinic acid anhydride and (1-hexyl-2-octenyl) succinic acid anhydride.

The sizing agents may also be prepared employing a vinylidene olefin corresponding to the following general structure



wherein R_x and R_y are alkyl radicals containing at least 4 carbon atoms in each radical. These compounds correspond to the specific formula:



wherein R_x is an alkyl radical containing at least 4 carbon atoms and R_y is an alkyl radical containing at least 4 carbon atoms and R_x and R_y are interchangeable and are represented by 2-n-hexyl-1-octene, 2-n-octyl-1-dodecene, 2-n-octyl-1-decene, 2-n-dodecyl-1-octene, 2-n-octyl-1-octene, 2-n-octyl-1-nonene, 2-n-hexyl-decene and 2-n-heptyl-1-octene.

The sizing agents may also include those as described above prepared employing an olefin having an alkyl branch on one of the unsaturated carbon atoms or on the carbon atoms contiguous to the unsaturated carbon atoms. Representative of the latter agents are n-octene-1; n-dodecene-1; n-octadecene-9; n-hexene-1; 7,8-dimethyl tetradecene-6; 2,2,4,6,6,8,8-heptamethylnone-4; 2,2,4,6,6,8,8-heptamethylnone-3; 2,4,9,11-tetramethyl-5-ethyldodecene-5; 6,7-dimethyldodecene-6; 5-ethyl-6-methyln-decene-5; 5,6-diethyldodecene-5; 8-methyltridecene-6; 5-ethyldodecene-6; and 6,7-dimethyldodecene-4.

The unblocked ethoxylated castor oils used herein are those containing at least about 5 moles ethylene oxide per mole castor oil. Preferred are those containing 25 to 200 moles ethylene oxide. The castor oil base may be hydrogenated or non-hydrogenated. The alkoxylation of such castor oils with ethylene oxide is well known in the art and the oils useful herein are not limited by their method of preparation. Generally the alkoxylation is carried out at 120–180°C and 0–4 atmospheres using alkaline catalysts. Unblocked ethoxylated castor oils containing up to about 200 moles ethylene oxide are available commercially. It is contemplated that the alkoxylation may also be performed using similar levels of propylene oxide however these adducts are not as readily available and are more expensive.

In accordance with the method of this invention, the size mixture is formed by mixing 85 to 99 parts by weight of the aforementioned substituted cyclic dicarboxylic acid anhydride with 1 to 15 parts, preferably less than 10 parts, of the unblocked ethoxylated castor oil. The use of the latter component in excess of about 15 parts becomes uneconomical in terms of cost and may be detrimental in terms of the papermaking operation. The use of the lower levels of the ethoxylated castor oil may require greater degrees of emulsification as with a turbine.

It is to be recognized that mixtures of various combinations of substituted cyclic dicarboxylic acid anhydrides and/or castor oils of varying levels of ethoxylation may be employed in preparing a particular size mixture, as long as they fall within the scope of this invention.

The mixture of the appropriate amount of the substituted cyclic dicarboxylic acid and the ethoxylated castor oil may be prepared and held in this form for an extended period of time. Testing results obtained under accelerated aging conditions indicate, to date, the mixture is still stable and effective as a sizing agent after six months at 50°C. When use of the mixture is required, it may be readily emulsified either by pre-emulsifying with water before addition to the paper stock or it may be emulsified in-situ at any point in the manufacturing operation where adequate agitation is present.

If pre-emulsification of the size mixture is desired, it may be readily accomplished by adding the sizing components to water in sufficient quantity so as to yield an emulsion containing the substituted cyclic dicarboxylic acid anhydride in a concentration of from about 0.1 to 20% by weight. The aqueous mixture is thereafter sufficiently emulsified merely by stirring with moderate speed agitation or by passing it through a mixing valve, aspirator or orifice so that the average particle size of the resultant emulsion will be less than about 3 μm . It is to be noted in preparing the emulsion that it is also possible to add the components of the size mixture to the water separately, and that the emulsion may be prepared using continuous or batch methods.

Emulsification of the mixture readily occurs at ambient temperatures. Thus, the emulsification will occur directly in cold water and heating of the water prior to addition of the sizing mixture is unnecessary.

As to actual use, no further dilution of the emulsion is generally necessary. The thus-prepared emulsion is simply added to the wet end of the paper making machine or to the stock preparation system so as to provide a concentration of the substituted cyclic dicarboxylic acid anhydride of from about 0.01 to about 2.0% based on dry fiber weight. Within the mentioned range, the precise amount of size which is to be used will depend for the most part upon the type of pulp which is being treated, the specific operating conditions, as well as the particular end use for which the paper product is destined. For example, paper which will require good water resistance or ink holdout will necessitate the use of a higher concentration of size than paper which will be used in applications where these properties are not critical.

Alternatively, the size emulsion may be sprayed onto the surface of the formed web at any point prior to the drying step in the concentrations as prepared so as to provide the required size concentration.

The ingredients of the size mixture may also be premixed without water and added to the paper making stock system causing the substituted cyclic dicarboxylic acid anhydride to emulsify in situ in the stock preparation system without the need for prior emulsification in water. As in the case in which the size is emulsified prior to use, the amount of size employed will vary depending on conditions, however, it will generally be within the range of about 0.01 to 2.0% substituted cyclic dicarboxylic acid anhydride based on dry fiber weight.

As is conventional in synthetic sizing operations, the size mixtures are used in conjunction with a material which is either cationic or is capable of ionizing or dissociating in such a manner as to produce one or more cations or other positively charged moieties. Among the materials which may be employed as cationic agents are long chain fatty amines, amine-containing synthetic polymers (primary, secondary, tertiary or quaternary amine), substituted polyacrylamide, animal glue, cationic thermosetting resins and polyamide-epichlorohydrin polymers. Of particular use are various cationic starch derivatives including primary, secondary, tertiary or quaternary amine starch derivatives and other cationic nitrogen substituted starch derivatives as well as cationic sulfonium and phosphonium starch derivatives. Such derivatives may be prepared from all types of starches including corn, tapioca, potato, waxy maize, wheat and rice. Moreover, they may be in their original granule form or they may be converted to pregelatinized, cold water soluble products. Amphoteric natural and synthetic polymers containing both anionic and cationic groups may also be used effectively to deposit and retain the sizing agent on the fiber.

Any of the above noted cationic retention agents may be added to the stock, i.e. the pulp slurry, either prior to, along with or after the addition of the size mixture or size emulsion in conventional amounts of at least about 0.01%, preferably 0.025 to 3.0%, based on dry fiber weight. While amounts in excess of about 3% may be used, the benefits of using increased amounts of retention aid for sizing purposes are usually not economically justified.

The size mixtures are not limited to any particular pH range and may be used in the treatment of neutral and alkaline pulp, as well as acidic pulp. The size mixtures may thus be used in combination with alum, which is very commonly used in making paper, as well as other acid materials. Conversely, they may also be used with calcium carbonate or other alkaline materials in the stock.

Subsequent to the addition of the size emulsion and retention aid, the web is formed and dried on the paper making machine in the usual manner. In actual paper machine operations, full sizing is generally achieved immediately off the paper machine. Because of limited drying in laboratory procedures however, further improvements in the water resistance of the paper prepared with the size mixtures of this invention may be obtained by curing the resulting webs, sheets, or molded products. This post-curing process generally involves heating the paper at temperatures in the range of from 80° to 150°C for a period of from 1 to 60 minutes.

The size mixtures of the present invention may be successfully utilized for the sizing of paper and paperboard prepared from all types of both cellulosic and combinations of cellulosic with non-cellulosic fiber. Also included are sheet-like masses and molded products prepared from combinations of cellulosic and non-cellulosic materials derived from synthetics such as polyamide, polyester and polyacrylic resin fibers as well as from mineral fibers such as asbestos and glass. The hardwood or softwood cellulosic fibers which may be used include bleached and unbleached sulfate (Kraft) bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite semi-chemical, groundwood, chemi-groundwood, and any combination of these fibers. In addition, synthetic cellulosic fibers of the viscose rayon or regenerated cellulose type can also be used, as well as recycled waste papers from various sources.

All types of pigments and fillers may be added in the usual manner to the paper product which is to be sized. Such materials include clay, talc, titanium dioxide, calcium carbonate, calcium sulfate and diatom-

ceous earths. Stock additives, such as defoamers, pitch dispersants, slimicides, etc. as well as other sizing compounds, can also be used with the size mixtures described herein.

As noted above, the size mixtures described herein exhibit extended shelf life, and, when emulsified and used in the paper stock system, yield paper products having superior sizing properties, even after these extended storage periods.

In the following examples, all parts given are by weight and all temperatures in degrees Celsius unless otherwise specified.

EXAMPLE I

This example illustrates the use of a size mixture representative of the size mixtures of this invention utilized in the form of an aqueous emulsion. This emulsion is compared, in terms of particle size and water resistance of the resulting sized paper, with a conventional emulsion made with a mixture of substituted cyclic dicarboxylic acid anhydride and a polyoxyalkylene alkyl-aryl ether.

A size mixture was prepared by combining 7 parts of unblocked ethoxylated castor oil containing 40 moles ethylene oxide per mole castor oil and 93 parts of alkenyl substituted succinic acid anhydride wherein the alkenyl groups contained 15 to 20 carbon atoms (hereinafter referred to as ASA). The mixture was aged for varying lengths of time at 50°C. When emulsification was desired, the emulsion was formed by agitating 2 parts of the mixture with 98 parts of a cooked aqueous dispersion of cationic corn starch (containing sufficient starch to provide 0.05% based on dry fiber weight) using a propeller-type agitator at moderate speed (500 rpm) for 10 seconds (Emulsion No. 1). A control was prepared in accordance with U.S. Reissue Patent 29 960 using 93 parts of the same ASA and 7 parts of polyoxyalkylene alkyl-aryl ether wherein the alkyl group contained 9 carbon atoms, the aryl radical was phenol, and the polyoxyalkylene moiety was formed with 9.5 moles of ethylene oxide.

Calculated amounts of the emulsions prepared as described above were added to aqueous slurries of bleached sulfate pulp having a Williams freeness of 400, a consistency of 0.5% and a pH of about 7.6, so as to yield a concentration of ASA on dry fiber weight of 0.25%. Then 0.5% alum based on dry fiber weight, was added to the pulp slurry before addition of the sizing emulsions. Sheets were formed in accordance with TAPPI standards, dried on a rotary print drier (surface temperature approx. 90°C.) then cured for 1 hour at 105°C and conditioned overnight at 22°C. and 50% R.H. before testing. The basis weight of these sheets was 55 lbs. (24.75 kg)/ream (24 X 36 inch, 61 x 91 cm. — 500 sheets).

The Hercules Size Performance Test (HST) was employed to compare the ink resistance of the sheets prepared. The test comprises applying an amount of acid ink (pH 2.3) to the upper paper surface. With the use of a photoelectric cell, the underside of the paper is monitored for reflectance. The time it takes for the ink to cause a decrease in reflectance from 100% to 80% is the paper's HST time. The HST of the paper is a measure of the sizing performance of a given size. The longer the HST time, the better the size is.

The average particle size (APS) was measured by optical microscopic observation using a calibrated graduated eye piece under 400–600x magnification.

Table I presents the average particle size (APS in μm) and internal sizing data (HST in seconds) for the above-described emulsions.

TABLE I

Emulsion	Accelerated Aging							
	Fresh		1 Month		2.5 Months		3.5 Months	
	HST	APS	HST	APS	HST	APS	HST	APS
Control	247	<1 μm	0	20 μm	0	30 μm	0	30 μm
1	300	<1 μm	253	<1 μm	265	<1 μm	253	2 μm

Both the emulsion quality (shown by particle size) and sizing performance (shown by the HST results) indicate that there is no loss in performance with the use of the size employing the ethoxylated castor oil, whereas after only one month accelerated aging, the control made a poor emulsion with no sizing.

EXAMPLE II

This example shows the effect of varying the level of the ethoxylated castor oil in size mixtures prepared as in Example I from 4% to 7%. All four levels showed excellent performance both freshly made and after 2.5 months aging. After 3.5 months aging there was a slight drop in performance using this accelerated aging procedure at 50°C.

TABLE II

Ethoxylated Castor Oil	Fresh		1 Month		2.5 Months		3.5 Months	
	HST	APS	HST	APS	HST	APS	HST	APS
4%	356	>1 μm	243	<2 μm	311	>2 μm	200	4 μm
5%	413	<1 μm	274	<1 μm	271	1 μm	210	4 μm
6%	316	<1 μm	240	<1 μm	279	<1 μm	223	3 μm
7%	300	<1 μm	253	<1 μm	265	<1 μm	253	2 μm

EXAMPLE III

Mixtures of ASA and ethoxylated castor oil were prepared as in Example I with unblocked ethoxylated castor oil of varying levels of ethylene oxide (E.O.) substitution. These mixtures were evaluated (fresh) for emulsification and sizing performance. Five moles of ethylene oxide provided minimally acceptable performance. With 25, 40, and 80 moles of ethylene oxide excellent results were obtained. The maximum commercially available level of 200 moles of ethylene oxide provided acceptable sizing; however the emulsion was of poorer quality.

TABLE III

Moles of E.O.	Avg. Particle Size	Hercules Size Test
5	>10 μm	203
25	1 μm	280
40	<1 μm	273
80	<1 μm	249
200	>2 μm	269
Control (of Ex. I)	<1 μm	270

EXAMPLE IV

This example shows a comparison of direct (un-emulsified) addition and pre-emulsified addition to the stock with both freshly made and three month (accelerated) aged sizing mixtures. The pre-emulsified product was prepared using the procedure of Emulsion 1 in Example I. With direct addition of the ASA/unblocked ethoxylated castor oil mixtures the emulsification occurs in-situ due to the shear inherent to the system. In this case, the mixture of Example I was added directly to a slurry of bleached sulfate pulp at 1.5% consistency in a laboratory beater (supplied by Allis Chalmers) and beaten very lightly for a few minutes. The pulp was then diluted to 0.5% consistency, and 0.4% on dry fiber weight of the cationic starch described in Example I was added separately to the slurry to act as a retention aid during sheet formation. Sheers were then formed, conditioned and tested in the HST test as described in Example I.

TABLE IV

Emulsion	Pre-Emulsified Addition		Direct Pulp Addition	
	HST	APS	HST	APS
Freshly made control	178	<1 μm	158	<1 μm
Three month aged control	0	30 μm	0	20 μm
Freshly made mixture	199	<1 μm	171	<1 μm
Three month aged mixture	224	<1 μm	178	<1 μm

The results show that the ethoxylated castor oil/ASA mixtures provided better sizing and equivalent particle size compared to the control as described in Example I by both pre-emulsion and direct addition and that three months accelerated aging had no adverse effect on the performance of the mixtures.

EXAMPLE V

In this example the ethoxylated castor oil was evaluated as an emulsifier for four different cyclical dicarboxylic acid anhydrides prepared as in Example I using 7 parts of the unblocked ethoxylated castor oil and 93 parts of the anhydride. The results show that good performance could be achieved with all four anhydride structures.

TABLE V

Emulsions	Fresh		One Month	
	HST	APS	HST	APS
Alkenyl succinic acid anhydride	267	1 μ m	256	1 μ m
Iso-octadecenyl succinic acid anhydride	143	>1 μ m	167	<2 μ m
Hexapropylene succinic acid anhydride	231	2 μ m	229	2 μ m
1-octyl, 2-decenyl succinic acid anhydride	295	<1 μ m	288	1 μ m

EXAMPLE VI

In this example the mixture of ethoxylated castor oil, prepared as in Example I, was compared to four other classes of emulsifiers described in U.S. Reissue Pat. 29 960. Even though these emulsifiers showed improved stability over the polyoxyalkylene alkyl aryl ether emulsifiers, used as a control in Example I, the degree of stability does not approach the level of that achieved by use of the ethoxylated castor oils as described herein.

TABLE VI

Emulsions	Freshly made		One month aged	
	HST	APS	HST	APS
1	239	<1 μ m	*	20 μ m
2	254	1 μ m	*	20 μ m
3	181	>3 μ m	*	20 μ m
4	198	>2 μ m	*	20 μ m
5	236	<1 μ m	243	<1 μ m

1. Polyoxyalkene alkyl-aryl ether (as in the control of Example I).

2. Polyoxyalkene alkyl ether wherein the alkyl group contains 12 carbon atoms and the polyoxyalkene moiety was formed with 6 moles of ethylene oxide.

3. Polyoxyethylene monooleate ester wherein the molecular weight of the polyoxyethylene moiety was 400.

4. Polyoxyethylene dilaureate ester wherein the molecular weight of the polyoxyethylene moiety was 600.

5. Unblocked ethoxylated castor oil.

* Emulsions too poor to evaluate.

These results show that upon aging only the unblocked ethoxylated castor oil retains 100% of its original performance. When freshly made the unblocked ethoxylated castor oil exhibited at least equivalent performance to all of the other emulsifiers.

EXAMPLE VII

In this example the level of ethoxylated castor oil varied from 1–20%, as shown in the table to ascertain the effect of high levels in the sizing mixture. The mixtures and emulsions were prepared in accordance with Example I but varying the relative amounts of the ethoxylated castor oil and ASA.

TABLE VII

Emulsion	HST	APS
Control	300	<1 μm
1% ethoxylated C.O.	345	>2 μm
5% ethoxylated C.O.	307	<1 μm
10% ethoxylated C.O.	166	<1 μm
15% ethoxylated C.O.	127	<1 μm
20% ethoxylated C.O.	133	<1 μm

This data shows that levels as low as 1% work effectively, and that 10% or more, while acceptable, causes reduced sizing results.

EXAMPLE VIII

This example shows that the hydrogenated unblocked ethoxylated castor oil works as well as the non-hydrogenated unblocked ethoxylated castor oil when the sizing mixture is freshly made and after three and one-half months accelerated aging. Mixtures and emulsions were prepared and evaluated as in Example I.

TABLE VIII

Emulsions	Freshly made		3.5 month aged	
	HST	APS	HST	APS
Non-hydrogenated C.O.*	231	>1 μm	217	<2 μm
Hydrogenated C.O.*	236	<1 μm	233	>1 μm

* unblocked

In summary, the invention is seen to provide the practitioner with a size mixture useful in the manufacture of sized paper products. The size mixture is shelf stable over an extended period of time, and is easily emulsified when desired for use under a wide variety of paper making conditions to provide superior sized paper products.

Claims

1. A paper size comprising a self-emulsifiable mixture of 85 to 99 parts by weight of a cyclic dicarboxylic acid anhydride having hydrophobic substitution and as emulsifier 1 to 15 parts by weight of an alkoxy-lated castor oil containing at least 5 moles alkylene oxide per mole castor oil, characterized in that the alkoxy-lated castor oil is an unblocked ethoxylated or propoxylated castor oil and that further emulsifiers are excluded.

2. A method for sizing paper products comprising the steps of

a) providing a paper stock system;

b) forming, in the absence of high shearing forces and under normal pressures, a sizing emulsion comprising from 85 to 99 part by weight of a substituted cyclic dicarboxylic acid anhydride containing hydrophobic substitution; from 1 to 15 parts by weight of an alkoxy-lated castor oil containing at least 5 moles alkylene oxide per mole castor oil; and water;

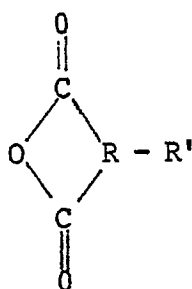
c) forming a web from the paper stock system;

d) dispersing said emulsion within the paper stock either before or after formation of said web but prior to passing said web through the drying stage of the paper making operation in an amount sufficient to provide a concentration of the substituted cyclic dicarboxylic acid anhydride from 0.01 to 2.0% based on dry fiber weight, characterized in that the alkoxy-lated castor oil is an unblocked ethoxylated or propoxylated castor oil and that further emulsifiers are excluded.

3. Claim 1 or 2 wherein the cyclic dicarboxylic acid anhydride is represented by the formula:

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wherein R represents a dimethylene or trimethylene radical and wherein R' is a hydrophobic group containing more than 4 carbon atoms which may be selected from the class consisting of alkyl, alkenyl, aralkyl, or aralkenyl groups.

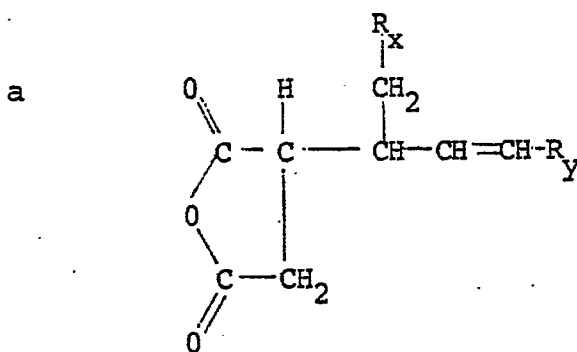
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4. Claim 3 wherein the cyclic dicarboxylic acid anhydride is selected from the group consisting of:

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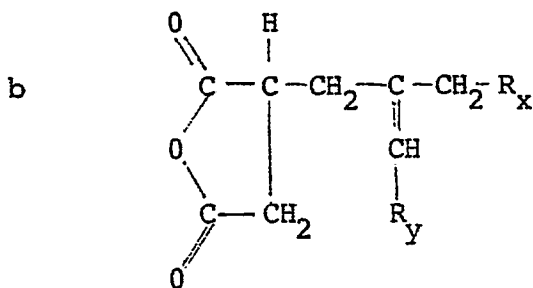


wherein Rx is an alkyl radical containing at least 4 carbon atoms and Ry is an alkyl radical containing at least 4 carbon atoms and Rx and Ry are interchangeable;

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wherein Rx is an alkyl radical containing at least 4 carbon atoms and Ry is an alkyl radical containing at least 4 carbon atoms and Rx and Ry are interchangeable.

5. Claim 1 or 2 wherein the unblocked ethoxylated castor oil contains 25 to 200 moles ethylene oxide per mole castor oil and is present in an amount less than 10 parts by weight of the mixture.

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6. Claim 2 wherein the sizing emulsion is formed in-situ within the paper stock system.

7. Claim 2 wherein the sizing emulsion is formed prior to introduction into the paper stock system.

8. Claim 7 wherein the size mixture is emulsified in an aqueous dispersion of a cationic or amphoteric retention agent in a sufficient quantity to yield an emulsion containing the substituted cyclic dicarboxylic acid anhydride in a concentration of from 0.1 to 20%, by weight of the total emulsion, prior to addition to the paper stock system.

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9. Claim 2 wherein there is dispersed with in the paper stock prior to the conversion of the paper stock into a dry web, at least 0.01% based on dry fiber weight, of a cationic retention agent.

10. Paper or paperboard prepared by the method of Claim 2.

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Patentansprüche

1. Papierleim mit einem Gehalt an einer selbstemulgierbaren Mischung von 85 bis 99 Gewichtsteilen eines cyclischen Dicarbonsäureanhydrids mit hydrophober Substitution und, als Emulgator, 1 bis 15 Gewichtsteilen eines alkoxylierten Rizinusöls, das mindestens 5 Mol Alkylenoxid pro Mol Rizinusöl enthält, dadurch gekennzeichnet, daß das alkoxylierte Rizinusöl ein nicht blockiertes ethoxyliertes oder propoxyliertes Rizinusöl ist und daß weitere Emulgatoren ausgeschlossen sind.

2. Verfahren zum Verleimen von Papierprodukten, das die Maßnahmen umfaßt

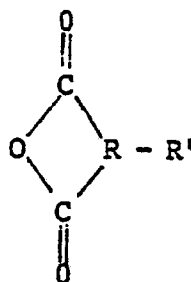
a) Bereitstellen eines Papierrohstoffsystems,

b) Ausbilden einer Leimemulsion in Abwesenheit hoher Scherkräfte und unter normalem Druck, die 85 bis 99 Gewichtsteile eines substituierten cyclischen Dicarbonsäureanhydrids mit hydrophober Substitution, 1 bis 15 Gewichtsteile eines alkoxylierten Rizinusöls, das mindestens 5 Mol Alkylenoxid pro Mol Rizinusöl enthält, und Wasser enthält,

c) Ausbilden einer Bahn aus dem Papierrohstoffsystem und

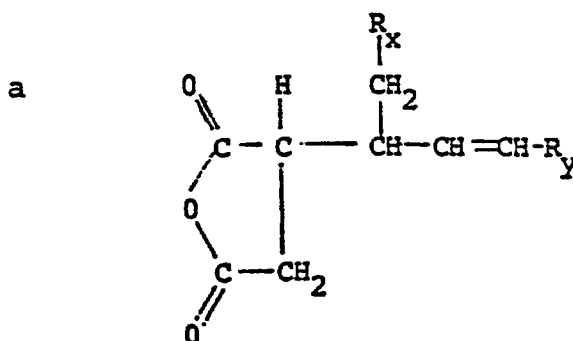
d) Dispergieren der Emulsion in dem Papierrohstoff entweder vor oder nach der Ausbildung der Bahn, jedoch bevor die Bahn durch die Trocknungsstufe des Papierfabrikationsbetriebs tritt, in einer ausreichenden Menge, um eine Konzentration des substituierten cyclischen Dicarbonsäureanhydrids von 0,01 bis 2,0%, bezogen auf das Trockenfasergewicht, einzustellen, dadurch gekennzeichnet, daß das alkoxylierte Rizinusöl ein nicht blockiertes ethoxyliertes oder propoxyliertes Rizinusöl ist und daß weitere Emulgatoren ausgeschlossen sind.

3. Anspruch 1 oder 2, wonach das cyclische Dicarbonsäureanhydrid wiedergegeben wird durch die Formel:

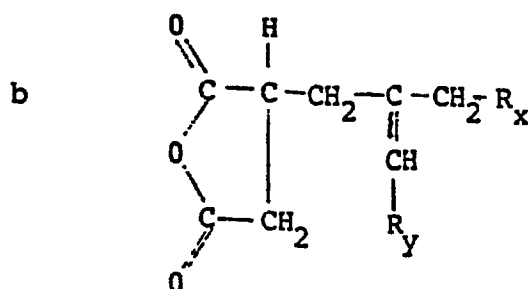


worin R ein Dimethylen- oder Trimethylen-Radikal und R' eine hydrophobe Gruppe mit mehr als 4 Kohlenstoffatomen ist, die aus der aus Alkyl-, Alkenyl-, Aralkyl-, oder Aralkenyl-Gruppen bestehenden Klasse ausgewählt worden ist.

4. Anspruch 3, wonach das cyclische Dicarbonsäureanhydrid aus der Gruppe ausgewählt worden ist, die besteht aus:



worin R_x ein Alkyl-Radikal mit mindestens 4 Kohlenstoffatomen und R_y ein Alkyl-Radikal mit mindestens 4 Kohlenstoffatomen ist und R_x und R_y austauschbar sind,



worin R_x ein Alkyl-Radikal mit mindestens 4 Kohlenstoffatomen und R_y ein Alkyl-Radikal mit mindestens 4 Kohlenstoffatomen ist und R_x und R_y austauschbar sind.

5. Anspruch 1 oder 2, worin das nicht blockierte ethoxylierte Rizinusöl 25 bis 200 Mol Ethylenoxid pro Mol Rizinusöl enthält und in einer Menge von weniger als 10 Gewichtsteilen der Mischung vorliegt.

6. Anspruch 2, wonach die Leimemulsion innerhalb des Papierrohstoffsystems insitu gebildet wird.

7. Anspruch 2, wonach die Leimemulsion vor Einführen in das Papierrohstoffsystem gebildet wird.

8. Anspruch 7, wonach die Leimmischung in einer wäßrigen Dispersion eines kationischen oder amphoteren Retentionsmittels in einer ausreichenden Menge emulgiert wird, um eine Emulsion die das substituierte cyclische Dicarbonsäureanhydrid in einer Konzentration von 0,1 bis 20 Gew.-% der gesamten Emulsion enthält, vor Zugabe zu dem Papierrohstoffsystem zu liefern.

9. Anspruch 2, wonach innerhalb des Papierrohstoffs vor der Überführung des Papierrohstoffs in eine trockene Bahn mindestens 0,01%, bezogen auf das Trockenfasergewicht, eines kationischen Retentionsmittels dispergiert werden.

10. Papier oder Pappe, hergestellt nach dem Verfahren des Anspruchs 2.

Revendications

1. Colle pour papier comprenant un mélange auto-émulsionnable de 85 à 99 parties en poids d'un anhydride d'acide dicarboxylique cyclique à substitution hydrophobe et, comme émulsionnant, de 1 à 15 parties en poids d'une huile de ricin alkoxylée contenant au moins 5 moles d'oxyde d'alkylène par mole d'huile de ricin, caractérisée en ce que l'huile de ricin alkoxylée est une huile de ricin éthoxylée ou propoxylée non bloquée et que des émulsionnants supplémentaires sont exclus.

2. Procédé de collage de papiers, comprenant les étapes consistant:

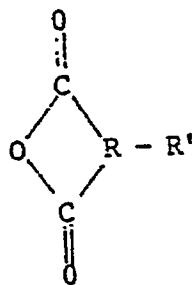
a) à préparer une composition de pâte à papier;

b) à former, en l'absence de fortes forces de cisaillement et sous des pressions usuelles, une émulsion de collage comprenant 85 à 99 parties en poids d'un anhydride d'acide dicarboxylique cyclique substitué, à substitution hydrophobe, 1 à 15 parties en poids d'une huile de ricin alkoxylée contenant au moins 5 moles d'oxyde d'alkylène par mole d'huile de ricin, et de l'eau;

c) à former une bande à partir de la composition de pâte à papier;

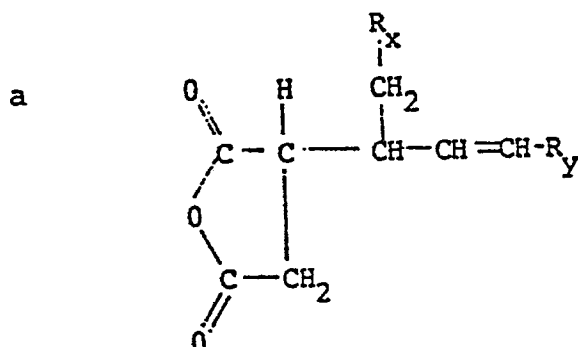
d) à disperser ladite émulsion dans la pâte à papier avant ou bien après formation de ladite bande, mais avant le passage de ladite bande au stade de séchage de l'opération de production de papiers, en une quantité suffisante pour parvenir à une concentration de l'anhydride d'acide dicarboxylique cyclique substitué de 0,01 à 2,0%, sur la base du poids des fibres sèches, caractérisé en ce que l'huile de ricin alkoxylée est une huile de ricin éthoxylée ou propoxylée non bloquée et que des émulsionnants supplémentaires sont exclus.

3. Revendication 1 ou 2, dans laquelle l'anhydride d'acide dicarboxylique cyclique est représenté par la formule:

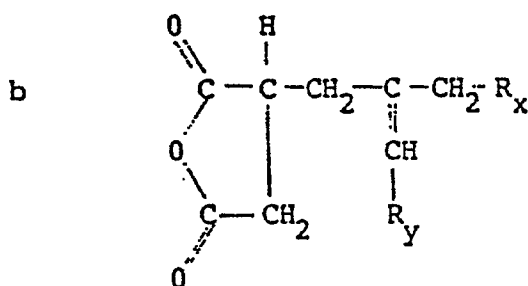


dans laquelle R représente un radical diméthylène ou triméthylène et R' représente un groupe hydrophobe contenant plus de 4 atomes de carbone qui peut être choisi entre des groupes alkyle, alcényle, aralkyle ou aralcényle.

4. Revendication 3, dans laquelle l'anhydride d'acide dicarboxylique cyclique est choisi dans le groupe comprenant des composés de formule:



dans laquelle R_x représente un radical alkyle contenant au moins 4 atomes de carbone et R_y représente un radical alkyle contenant au moins 4 atomes de carbone, R_x et R_y étant interchangeable;



dans laquelle R_x représente un radical alkyle contenant au moins 4 atomes de carbone et R_y représente un radical alkyle contenant au moins 4 atomes de carbone, R_x et R_y étant interchangeable.

5. Revendication 1 ou 2, dans laquelle l'huile de ricin éthoxylée non bloquée contient 25 à 200 moles d'oxyde d'éthylène par mole d'huile de ricin et est présente en une quantité inférieure à 10 parties en poids de mélange.

6. Revendication 2, dans laquelle l'émulsion de collage est formée in-situ dans la composition de pâte à papier.

7. Revendication 2, dans laquelle l'émulsion de collage est formée avant l'introduction dans la composition de pâte à papier.

8. Revendication 7, dans laquelle le mélange de collage est émulsionné dans une dispersion aqueuse d'un agent de rétention cationique ou amphotère, en une quantité suffisante pour donner une émulsion contenant l'anhydride d'acide dicarboxylique cyclique substitué en une concentration de 0,1 à 20% en poids de l'émulsion totale, avant l'addition à la composition de pâte à papier.

9. Revendication 2, dans laquelle au moins 0,01%, sur la base du poids des fibres sèches, d'un agent cationique de rétention est dispersé dans la pâte à papier avant la transformation de la pâte à papier en une bande sèche.

10. Papier ou carton préparé par le procédé suivant la revendication 2.