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PAPER SIZING WITH AZIRIDINES

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U.S. Cl. 162—158 14 Claims

ABSTRACT OF THE DISCLOSURE

Sizing of paper and paperboard products which comprises intimately dispersing, within the aqueous pulp slurry, or applying to a prepared paper web, an aqueous emulsion of a N-substituted aziridine compound which is prepared by means of the reaction between a carbonyl-substituted, alpha, beta-ethylenically unsaturated compound such as distearyl maleate and an alkylenimine such as ethyleneimine. The sizing agent can be uniformly dispersed with a cationic emulsifier, such as a cationic starch, for better retention on the fibers.

It is the object of this invention to provide improved sizing agents whose use results in the preparation of paper which is characterized by its reduced water and ink absorption as well as by its resistance to aqueous acid and alkaline solutions. A further object of this invention involves the use of sizing agents which may be employed with all types of paper fiber over the complete range of pH conditions which are normally encountered in the various processes utilized for paper manufacturing. Various other objects and advantages of this invention will become apparent to the practitioner from the following detailed description.

As used herein, the terms "paper" and "paperboard" include sheet-like masses and molded products made from fibrous cellulosic materials which may be derived from both natural and synthetic sources. Also included are sheetlike 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.

Paper and paperboard are often sized with various materials for the purpose of increasing their resistance to water as well as to other types of aqueous solutions. These materials are referred to as sizes or sizing agents and they may be introduced during the actual paper making operation wherein the process is known as internal wet-end, or engine sizing. Or, on the other hand, 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.

Various water-repellent or hydrophobic materials have been utilized as sizing agents. These include rosin, fortified rosin, mixtures of rosin with waxes, wax emulsions, ketene dimer emulsions, fluorocarbons, fatty acid complexes of chromium or aluminum chlorides, long chain thermoplastic copolymers, as well as some thermosetting condensation type resins. Although all of these materials

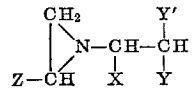
are effective under certain conditions, their use is nonetheless subject to one or more limitations.

Thus, for example, in the case of rosin, although the latter is relatively low in cost and readily available, it has poor resistance to alkaline solutions and cannot be used for the sizing of neutral or alkaline pulps. It is inoperable with the latter since it must be ordinarily used in combination with alum, or an acidic aluminum ion donor, which is present for the purpose of precipitating and setting the metal rosinate, i.e. the rosin soap, onto the fibers. The use of alum for this purpose is, however, precluded under neutral or alkaline stock conditions. This is a definite disadvantage since the paper produced from neutral or alkaline pulp has been found to have higher strength, greater stability and superior aging characteristics in comparison with the paper prepared from acidic pulp. Also, the internal use of alkaline pigments such as calcium carbonate is precluded. This same limitation also applies to the use of most wax emulsions which cannot be used on the alkaline side since they are usually combined with small quantities of alum for the purpose of breaking the emulsions. On the other hand, it may be noted that certain sizing agents will not tolerate highly acidic conditions. Furthermore, certain sizing agents cannot be adequately retained in the sheet during sheet formation and, consequently, are limited only to external or surface applications.

In addition to the above described pH limitations, the water resistance or water holdout which is attainable with many of the heretofore employed sizing agents is often inadequate for many applications which may require paper or paperboard displaying an exceptionally high degree of water resistance. On the other hand, some sizing agents provide complete water repellency as opposed to the desired water resistance. Moreover, many of these sizing agents have been found to be incompatible with the pigments, fillers, or other ingredients which are often added to paper. A further disadvantage of some sizing agents is that a considerable degree of heat curing is required in order to develop full effectiveness. Thus, in using these materials, full effectiveness and full sizing value may not be obtained immediately after formation and drying of the paper web. Also, high concentrations of some sizing agents impart undesirable low friction characteristics to paper.

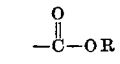
We have now discovered that the use of certain reagents as sizes for paper and paperboard has been found to result in the preparation of paper and paperboard products which display an unusually high degree of water resistance along with resistance to acidic and alkaline solutions. Of prime importance is the fact that the successful use of these new sizing agents is not restricted to any particular pH range which thus allows for their utilization in the treatment of neutral and alkaline pulp as well as acidic pulp. Still another advantage of these sizing agents is that they may be used in conjunction with other sizing agents so as to obtain additive sizing effects. A still further advantage of these sizing agents is that they do not detract from the strength of the paper and when used with certain adjuncts will, in fact, increase the strength of the finished sheets. An additional advantage of our novel sizing agents is that only mild drying and curing conditions are required in order to develop full sizing value.

The novel sizing agents of our invention correspond to the formula



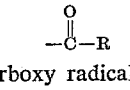
wherein:

X is a radical selected from the group consisting of hydrogen, and substituted carboxy radicals corresponding to the formula

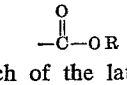


wherein R is an alkyl group containing from 8 to 22 carbon atoms;

Y is a radical selected from the group consisting of cyano radicals, substituted keto, i.e. carbonyl, radicals corresponding to the formula

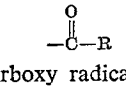


and substituted carboxy radicals corresponding to the formula

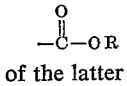


wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms;

Y' is a radical selected from the group consisting of hydrogen radicals, cyano radicals, substituted keto, i.e. carbonyl, radicals corresponding to the formula



and substituted carboxy radicals corresponding to the formula



wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms; and,

Z is a radical selected from the group consisting of hydrogen radicals and alkyl radicals containing from 1 to 2 carbon atoms.

The processes for preparing the above specified N-substituted aziridine compounds are well known to those skilled in the art. In general, these procedures comprise the reaction of an alkylenimine with a carbonyl-substituted, alpha, beta-ethylenically unsaturated compound such as an alkyl acrylate ester, a dialkyl maleate ester, or a vinyl ketone. Included among the applicable alkylenimines which may be employed in the latter reaction are ethylenimine, propylenimine and butylenimine. Suitable carbonyl-containing ethylenically unsaturated compounds are alkyl esters of acrylic acid and dialkyl esters of maleic acid wherein the alkyl groups of the latter two types of esters contain from 8 to 22 carbon atoms, as well as vinyl ketones. Specific examples of the latter reagents are: lauryl, stearyl and dodecyl acrylates; dilauryl, dipalmityl and distearyl maleates as well as mixtures of the latter maleates; and stearyl vinyl ketone. More detailed information with regard to these reaction procedures may be found in the article by Rosenthal et al. appearing in the Journal of Organic Chemistry 30, 3689 (1965).

The actual use of our novel sizing agents in the manufacture of paper is subject to a number of variations in technique any of which may be further modified in light of the specific requirements of the practitioner. It is important to emphasize, however, that with all of these procedures, it is most essential to achieve a uniform dispersal of the sizing agent throughout the fiber slurry. Uniform dispersal may be obtained by adding the sizing agent in a fully dispersed form such as an emulsion; or, by the co-addition of chemical dispersing agents to the size or fiber slurry.

Another important factor which may, if desired, be considered in the utilization of the sizing agents of our invention involves their use in conjunction with a material which is either cationic in nature or is, on the other hand, capable of ionizing or dissociating in such a manner as to produce one or more cations or other positively charged moieties. These cationic agents, as they will be hereinafter referred to, have been found useful as a means for aiding in the retention of our sizing agents as well as for bringing the latter into close proximity to the pulp fibers. Among the materials which may be employed as cationic agents, one may list: long chain fatty amines; polyamines, polyacrylamide; polyethylenimine and its derivatives; copolymers of ethylenimine with various monomers such as diethyl aminoethyl methacrylate; chromic sulfate; sodium aluminate; animal glue; cationic thermosetting resins such as the reaction products of dibasic carboxylic acids, polyalkylene polyamines and epihalohydrins; and, polyamide polymers and copolymers. Of particular interest for use as cationic agents are various cationic starch derivatives including primary, secondary, tertiary or quarternary amine starch derivatives and other cationic nitrogen substituted starch derivatives, as well as cationic sulfonium and phosphonium starch derivatives. Illustrative of such cationic starches are the products whose preparation is described in U.S. Pats. 2,813,093; 2,989,520 and 3,077,469. 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 granular form or they may be converted to pregelatinized, cold water soluble products.

Any of the above cationic agents may be added to the stock, i.e. the pulp slurry, either prior to, along with or after the addition of the sizing agent. However, in order to achieve maximum distribution, it is preferable that the cationic agent be added either subsequent to or in direct combination with the sizing agent. The actual addition to the stock of either the cationic agent or the sizing agent may take place at any point in the paper making process prior to the ultimate conversion of the wet pulp into a dry web or sheet. Thus, for example, our sizing agents may be added to the pulp while the latter is in the headbox, beater, hydropulper or stock chest.

In order to obtain good sizing, it is desirable that our sizing agents be uniformly dispersed throughout the fiber slurry in as small a particle size as it is possible to obtain. One method for providing such uniform dispersions is to emulsify the sizing agent prior to its addition to the stock utilizing either mechanical means, such as high speed agitators, mechanical homogenizers, or ultrasonic homogenizers, or by the addition of a suitable emulsifying agent. The latter emulsification may, if desired, be accomplished by employing the cationic agent as the emulsifier and this procedure is particularly successful where cationic starch derivatives are utilized. Among the applicable non-cationic emulsifiers which may be used as emulsifying agents for our sizing agents, one may list such hydrocolloids as conventional starches, non-cationic starch derivatives, dextrines, carboxymethyl cellulose, hydroxyethyl cellulose, gum arabic, gelatin and polyvinyl alcohol as well as various surfactants. When such non-cationic emulsifiers are used, a cationic agent may be separately added to the pulp slurry. In preparing these emulsions with the use of an emulsifier, the latter is first dispersed in water and the sizing agent is then introduced along with vigorous agitation.

Further improvements in the water resistance of the paper prepared with the novel sizing agents of this invention may be obtained by curing the resulting webs, sheets or molded products. This curing process involves heating the paper at temperatures in the range of from 80 to 150° C. for a period of from 1 to 60 minutes. However, it should again be noted that post curing is not essential to the successful operation of our sizing processes.

The sizing agents of this invention may, of course, be successfully utilized for the sizing of paper prepared from all types of both cellulosic and combinations of cellulosic with non-cellulosic fibers. The cellulosic fibers which may be used include bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical, chemi-groundwood, ground wood, and any combination of these fibers. These designations refer to wood pulp fibers which have been prepared by means of a variety of processes which are known in the pulp and paper industry. In addition, synthetic fibers of the viscose rayon or regenerated cellulose type as well as of the chemically synthesized type can also be used.

All types of pigments and fillers may be added to the paper which is to be sized with our novel sizing agents. Such materials include clay, talc, titanium dioxide, calcium carbonate, and diatomaceous earths. Other sizing agents can also be used in conjunction with our sizing agents.

With respect to proportions, our sizing agents may be employed in amounts ranging from about 0.05 to about 5.0% of the dry weight of the pulp in the finished sheet or web. Within this range, the precise amount which is used will, of course, depend for the most part upon the type of pulp which is being utilized, the specific operating conditions, as well as the particular end use for which the paper is destined. Thus, for example, paper which will require good water resistance or ink holdout will necessitate the use of a higher concentration of sizing agent than paper which will be used in applications where only a small amount of sizing is needed. These same factors also apply in relation to the amount of cationic agent which may be used in conjunction with our sizing agents. Thus, the practitioner will be able to use these materials in any concentration which is found to be applicable to his specific operating conditions. However, under ordinary circumstances a range of from about 0.5 part to 2.0 parts, by weight, of cationic agent per 1.0 part of sizing agent is usually adequate. Thus, the cationic agent may be present in a quantity which is at least 0.025% of the dry weight of pulp in the paper.

It should also be noted that our novel sizing agents, whether in aqueous emulsion or organic solvent solution form, may be externally applied to paper by means of any conventional surface sizing procedures, such as the tub, calender-stack and size-press sizing techniques, etc. Needless to say, these surface sizing systems may also contain any of the cationic and non-cationic agents previously mentioned as well as any other conventional paper additives.

In any event, the use of our novel reagents has been found to provide for the preparation of paper and paperboard products displaying a degree of water resistance which is comparable, and in many cases superior, to the results obtained with other heretofore employed sizing agents. Morewover, our sizing agents impart a resistance to acid and alkali which is often unattainable with other sizing agents.

The following examples will further illustrate the embodiment of this invention. In these examples all parts given are by weight unless otherwise noted.

EXAMPLE I

This example illustrates the use of a typical sizing agent of this invention in the form of an aqueous emulsion wherein a cationic agent was used as the sole emulsifier. It further illustrates the improved properties exhibited by paper that has been sized with our novel agents.

An aqueous emulsion of the sizing agent comprising the reaction product of ethylenimine and distearyl maleate was prepared by first cooking 7.5 parts of the beta-diethyl amino ethyl chloride hydrochloride ether of corn starch, whose preparation is described in Example I of U.S. Pat. 2,813,093, in 85 parts of water which was heated in a

boiling water bath. After being cooked for 20 minutes, the dispersion of the cationic starch derivative was cooled to room temperature and then transferred to a high speed agitator whereupon 7.5 parts of the above identified sizing agent were slowly added to the agitated dispersion. Agitation was continued for 5 minutes and the resulting emulsion was then diluted by the addition of another 900 parts of water. A final 10-fold dilution was effected and the emulsion was then added to an aqueous slurry of bleached softwood kraft pulp. Sheets were formed and dried in accordance with TAPPI standards, the latter sheets containing 1% of both the sizing agent and the cationic agent, based on the weight of the dry pulp. By means of the same procedure, an additional number of comparable sheets were prepared which each contained different amounts of the sizing agent.

The water resistance of the resulting sheets was then determined by means of the "Uranine Dye" test and the "Ink Penetration" test. The Uranine Dye Test involves placing a small amount of uranine dye powder on the upper surface of a swatch of the test paper which is then set afloat on distilled water. As the water is absorbed into the paper, the dye is moistened and thus becomes sensitive to ultra-violet light. The time, in seconds, required for this ultra-violet sensitivity to occur is thus in direct relation to the water resistance of the paper since a more water resistant paper will, of course, retard the moistening of the dye which had been placed upon its upper surface.

The Ink Penetration Test involves floating a swatch of the treated paper on a reservoir of ink. The time required for the ink to penetrate the paper so that it becomes visible over a 50% area of the upper surface of the paper swatch is noted as the "ink penetration" time. Needless to say, a longer ink penetration time is indicative of increased water resistance on the part of the paper sample.

The following table presents the results which were obtained upon submitting the various paper sheets to the latter test procedures.

Percent sizing agent, by weight of dry pulp	Percent cationic agent, by weight of dry pulp	Uranine dye test (sec.)	Ink penetration test (sec.)
0.25	0.25	76	2,000+
0.50	0.50	91	2,000+
0.75	0.75	101	2,000+
1.00	1.00	108	2,000+
3.00	3.00	186	2,000+
0.00 (control)	0.00	0	0

The results summarized above clearly indicate the excellent water resistance exhibited by paper sheets which have been treated with the novel sizing agents of this invention.

EXAMPLE II

This example illustrates the use of additional sizing agents of this invention in the form of aqueous emulsions wherein a cationic agent was used as the sole emulsifier. It further illustrates the improved properties exhibited by paper sheets which have been sized with these novel sizing agents.

Aqueous emulsions of the sizing agents utilized in this example were prepared according to the emulsification procedure set forth in Example I; the cationic agent in each instance being the beta-diethyl amino ethyl chloride hydrochloride ether of corn starch. Paper sheets, which were internally sized with the respective emulsions, were thereafter prepared and dried in accordance with TAPPI standards. The water resistance of the resulting sheets was then determined by means of the Uranine Dye Test set forth in Example I.

The contents of the various sizing systems as well as the degree of water resistance exhibited by the paper

sheets prepared therewith are presented in the following table:

Sizing agent	Percent sizing agent, by weight of dry pulp	Percent cationic agent, by weight of dry pulp	Uranine dye test (sec.)
Control			0
The reaction product of ethylenimine and stearyl acrylate	0.50	0.50	58
Do	1.00	1.00	91
The reaction product of ethylenimine and di-n-octyl maleate	0.50	0.50	62
Do	1.00	1.00	98
The reaction product of propylenimine and an equimolar mixture of disteary and dipalmityl maleates	0.50	0.50	90
Do	1.00	1.00	104
The reaction product of butylenimine and didoeicosyl maleate	0.50	0.50	105
Do	1.00	1.00	110
The reaction product of ethylenimine and stearyl beta-cyano acrylate	0.25	0.25	43
Do	0.50	0.50	105
Do	1.00	1.00	108
The reaction product of ethylenimine and di-n-dodecyl maleate	0.50	0.50	70
Do	1.00	1.00	100
The reaction product of ethylenimine and di-n-tetradecyl maleate	0.50	0.50	80
Do	1.00	1.00	104
The reaction product of ethylenimine and hexadecyl acrylate	0.50	0.50	60
Do	1.00	1.00	95
The reaction product of ethylenimine and stearyl vinyl ketone	0.50	0.50	50
Do	1.00	1.00	90

The above noted results further emphasize the excellent water resistance imparted to paper sheets by the use of our novel sizing agents.

EXAMPLE III

This example illustrates the use of our novel sizing agents in the form of aqueous emulsions prepared with a non-cationic emulsifier as well as the performance of the paper sheets that have been sized with these emulsion products.

Thus, the identical emulsification procedure set forth in Example I, hereinabove, was utilized to prepare the stock emulsion described in this example with the exception that slightly anionic, unmodified corn starch was utilized as the emulsifying agent for the ethylenimine-distearyl maleate sizing agent in place of the cationic starch ether. The resulting emulsion was then utilized either alone, in combination with alum, or in combination with the cationic beta-diethyl amino ethyl chloride hydrochloride ether of corn starch, for the internal sizing of paper sheets which were prepared in accordance with TAPPI standards. The alum and cationic starch ether were independently added at the same point in the paper making operation at which the sizing emulsion was introduced. The water resistance of the resulting paper sheets was then determined by means of the Uranine Dye Test set forth in Example I, hereinabove.

The results of the latter determinations are presented in the following table:

Percent sizing agent, by weight of dry pulp	Cationic additive	Percent cationic additive by weight dry pulp	Uranine dye test (sec.)
0.25	None		65
0.50	do		88
0.25	Alum	1.0	90
0.50	do	1.0	100
0.10	Cationic starch ether	0.5	38
0.25	do	0.5	81
0.50	do	0.5	104

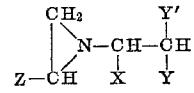
The results summarized clearly indicate the excellent water resistance imparted to paper by the use of our novel sizing agents regardless of the form in which they may be utilized or the particular additives which may also be present in the system.

Furthermore, the sizing emulsion containing the ethylenimine-distearyl maleate product and the corn starch emulsifier was also utilized in a surface sizing operation. Thus, the latter system was externally applied by means of a conventional size-press sizing technique to a paper sheet which had been prepared from bleached softwood kraft pulp in accordance with TAPPI standards. Upon being dried, the resulting paper sheet which had been surface sized with 0.9% of the sizing agent, as based on the dry weight of the pulp, exhibited excellent water resistance.

Summarizing, it is thus seen that this invention provides a novel process for the sizing of paper and paperboard products. Variations may be made in procedures, proportions and materials without departing from the scope of this invention which is defined by the following claims.

We claim:

1. A method of sizing paper which comprises the step of intimately dispersing within the wet pulp, prior to the ultimate conversion of said pulp into a dry web, a sizing agent corresponding to the formula



wherein

X is a radical selected from the group consisting of hydrogen and substituted carboxyl radicals corresponding to the formula

wherein R is an alkyl group containing from 8 to 22 carbon atoms;

Y is a radical selected from the group consisting of cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms;

Y' is a radical selected from the group consisting of hydrogen radicals, cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbons atoms; and,

Z is a radical selected from the group consisting of hydrogen radicals and alkyl radicals containing from 1 to 2 carbon atoms;

the amount of said sizing agent being from about 0.05 to 5.0% of the dry weight of the pulp.

2. The method of claim 1, wherein said sizing agent is in the form of an aqeuous emulsion.

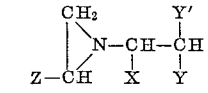
3. The method of claim 1, in which there is dispersed within the wet pulp, prior to the ultimate conversion of

said pulp into a dry web, a cationic starch along with the sizing agent, the amount of said cationic starch being from 0.5 to 2.0 parts, by weight, per part of said sizing agent.

4. The method of claim **3**, wherein said sizing agent is in the form of an aqueous emulsion in which the cationic starch is the primary emulsifier.

5. The method of claim **3**, wherein said sizing agent is in the form of an aqueous emulsion in which a non-cationic starch is the primary emulsifier.

6. A paper product having intimately dispersed therein a sizing agent corresponding to the formula



wherein

X is a radical selected from the group consisting of hydrogen and substituted carboxy radicals corresponding to the formula

wherein R is an alkyl group containing from 8 to 22 carbon atoms;

Y is a radical selected from the group consisting of cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms;

Y′ is a radical selected from the group consisting of hydrogen radicals, cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

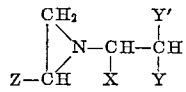
wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms; and,

Z is a radical selected from the group consisting of hydrogen radicals and alkyl radicals containing from 1 to 2 carbon atoms;

the amount of said sizing agent being from about 0.05% to 5.0% of the weight of the dry pulp in said paper.

7. The paper product of claim **6** in which there is also intimately dispersed from 0.5 to 2.0 parts by weight of a cationic starch per part of said sizing agent.

8. A method of sizing a previously prepared paper web which comprises applying to at least one surface of said paper web, a sizing agent corresponding to the formula



wherein

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wherein R is an alkyl group containing from 8 to 22 carbon atoms;

Y is a radical selected from the group consisting of cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms;

Y′ is a radical selected from the group consisting of hydrogen radicals, cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms; and,

Z is a radical selected from the group consisting of hydrogen radicals and alkyl radicals containing from 1 to 2 carbon atoms;

and thereafter drying the thus treated paper web; the amount of said sizing agent being from 0.05% to 5.0% of the dry weight of the pulp in said paper web.

9. The method of claim **8**, wherein said sizing agent is in the form of an aqueous emulsion.

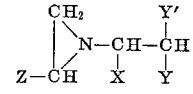
10. The method of claim **8**, wherein said sizing agent is in the form of an organic solvent solution.

11. The method of claim **8**, in which there is applied to at least one surface of said paper web a cationic starch along with the sizing agent; the amount of said cationic starch being from 0.5 to 2.0 parts by weight, per part of said sizing agent.

12. The method of claim **11**, wherein said sizing agent and said cationic agent are combined in the form of an aqueous emulsion.

13. The method of claim **11**, wherein said sizing agent and said cationic agent are combined in the form of an organic solvent solution.

14. A paper product to which has been applied on at least one surface thereof a sizing agent corresponding to the formula



wherein

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wherein R is an alkyl group containing from 8 to 22 carbon atoms;

Y is a radical selected from the group consisting of cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms;

Y' is a radical selected from the group consisting of hydrogen radicals, cyano radicals, substituted keto radicals corresponding to the formula

and substituted carboxy radicals corresponding to the formula

wherein R, in each of the latter two radicals, is an alkyl group containing from 8 to 22 carbon atoms; and,

Z is a radical selected from the group consisting of

hydrogen radicals and alkyl radicals containing from 1 to 2 carbon atoms;

the amount of said sizing agent being from about 0.5% to 5.0% by weight of the dry pulp in said paper.

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