

**PAPER CONTAINING POLYAMIDE RESINS AND  
PROCESS OF PRODUCING SAME**

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The present invention relates to a novel paper product and to the process of producing the same. More particularly it relates to the use of certain polyamide resin suspensoids as beater additives in the fabrication of paper. The invention involves the use of colloiddally dispersed cationic aqueous suspensions of film-forming polyamide resin polymers. These dispersions are applied as wet-end additives and preferably are used without the addition of alum, size, or other commonly employed additives. The resultant products display improved wet strength, dry strength, and waterproofing properties.

Many beater additives or sizes or similar constituents for paper are known to the art. Most of these are added for only one specific purpose, such, for example, as waterproofing or wet strength development, or dry strength development, or filling for better ink receptivity, and the like. In practically every case these additives must be used in conjunction with a precipitating agent which serves, first of all, to precipitate the additive from the dispersion in which they are usually added and thereafter serves to "fix" the precipitated material to the fibers.

The pulps which are used for the fabrication of paper are generally anionic in electrical charge because of the presence of carboxyl groups associated with the cellulose. If the sizes or other additives are also anionic—and this is very frequently the case—little retention to the fibers is observed unless a precipitating or electrical charge-reversing agent such as aluminum sulfate is also employed.

It is known, of course, that beater additives or sizes can sometimes be made cationic to increase the retention by virtue of the attraction between the positive charge of the additive and the negative charge of the pulp. However, in order to prepare cationic dispersions for beater additives it has heretofore been necessary to employ an expensive cationic dispersing agent such as a quaternary ammonium salt, said cationic dispersing agent being wholly hydrophilic in character. These extrinsically dispersed materials will adhere to the pulp fibers and retention in the beater is improved. Unfortunately, however, because of the hydrophilic nature of the dispersing agent, a wetting action is exerted with orientation at the water interface when the finished sheet is wetted. Thus penetration of the water into the sheet is fostered, and the water-proofness of the sheet is markedly lessened. Improvements in this regard are the cationic urea-formaldehyde or melamine-formaldehyde or phenol-formaldehyde resins. These do indeed improve the wet strength of the paper, but they are generally not waterproofing agents unless used in very large proportions. Furthermore they also must be "fixed" in the sheet by some co-additive, usually an acid salt which not only changes the character of the electrical charge of the mixture for paper retention but acts also as an acid catalyst to polymerize the formaldehyde complex to a water-insoluble fiber-to-resin bond in the presence of heat. In addition to the necessity for the use of large quantities of these additives, two other disadvantages are immediately ap-

parent. First of all, formaldehyde fumes are emitted, and these are a source of discomfort and actual toxicity. Accordingly, the use of formaldehyde-containing resins is to be avoided if possible. Secondly, even if these resin dispersions were made cationic in order to obtain the best retention on the fibers, this retention seldom exceeds one percent based on the dry weight of the pulp.

The disadvantages heretofore described are overcome in the present invention because the materials employed are sufficiently cationic so as to be markedly attracted to the anionic pulp fibers, and accordingly no co-precipitant is needed. As a matter of fact, the use of a co-precipitant is ordinarily undesirable. Furthermore, the material has been made cationic by the use of intrinsic emulsifiers—that is, the emulsifying entities are in themselves part of the resin. Thus the extrinsic, hydrophilic, cationic emulsifiers previously used are eliminated. Since the emulsifiers are part of the resin, the orientation at a water interface, as demonstrated by an ordinary cationic emulsifier, is practically eliminated since the emulsifying portion is bound to the resin and is not free to orient at will. Because of this the desirable effects of a cationic additive are achieved without in any way impairing the water-proofness of the final paper. Moreover, the products described in this invention need not be used in excessively high proportion unless certain specific results inherent in the use of large quantities of the material are desired. In addition, the materials employed are innocuous, and there is no need for noxious materials such as formaldehyde. Finally, the materials described in this invention provide an exceptionally high degree of wet strength, a high degree of dry bonding strength and a high degree of waterproofness. Furthermore, the degree of retention exhibited by the materials contemplated within the present invention on the pulp fibers is excellent.

It is therefore an object of the present invention to provide novel paper products containing as beater additives polyamide suspensoids which provide continuous films.

It is another object of the present invention to provide a novel process of producing such paper products.

The cationically dispersed polyamide suspensoids capable of forming continuous films which may be employed in the present invention are those described in the pending application of Harold Wittcoff and Wesley A. Jordan entitled Polyamide Suspensoids Forming Continuous Films, Serial Number 227,535, filed May 21, 1951, now abandoned. These suspensoids are prepared by the dispersion in an acidic aqueous medium of a polyamide derived from polymeric fat acids and polyamines having at least 3 atoms intervening between the amine groups principally involved in the amidification reaction, the polyamide having an amine number of at least 5. The polymeric fat acids employed may be those resulting from the polymerization of drying or semi-drying oils, or the free acids or simple aliphatic alcohol esters thereof. Suitable drying or semi-drying oils include soybean, linseed, tung, perilla, oiticica, cottonseed, corn, tall, sunflower, safflower, dehydrated castor oil, and the like. In the polymerization process for the preparation of the polymeric fat acids, the fatty acids with sufficient double bond functionality combine, for the most part, probably by a Diels-Alder mechanism to provide a mixture of dibasic and higher polymeric acids. The acids with insufficient functionality to react remain as monomers and may be removed by distillation. The residue after distillation consists of the desired polymeric acids, and this mixture is used for the preparation of the polyamide resin. In place of this method of polymerization, any other method of polymerization may be employed, whether the resultant polymer possesses residual unsaturation or not. The term "polymeric fat acid" as used herein is intended to include

the polymerized mixture of acids obtained, which mixture usually contains a predominant proportion of dimeric acids, a smaller quantity of trimeric and higher polymeric acids, and some residual monomer.

The polyamines which may be employed for the preparation of the polyamides are those in which the amine groups which are principally involved in the amidification reaction are separated by at least three atoms. These three atoms may be carbon atoms or hetero atoms. Typical of the polyamines which may be used are diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diamine butane, 1,3-diamino butane, hexamethylene diamine, diacetone diamine, 3-(N-isopropylamino) propylamine, 3,3'-iminobispropylamine, and the like. It will be observed that in the case of the first three named polyamines, there are amine groups which are separated by only two carbon atoms. However, the amidification reaction involves the primary amine groups principally, and the product obtained is suitable for the purposes of the present invention. It is also apparent that some of the polyamines contain only a single primary amine group and in addition a secondary amine group. Under these circumstances the secondary amine group also becomes involved in the amidification reaction to a large extent whereas in the case of diethylene triamine, for example, the two primary amine groups are amidified to the virtual exclusion of the secondary amine group. From the above discussion it is apparent that a wide variety of polyamines may be employed as long as the amine groups primarily involved in the amidification reaction are separated by at least 3 atoms.

In the preparation of the polyamide the polymeric fat acids are reacted with any of the polyamines referred to above either singly or in admixture. The final polyamide obtained must have some free amine groups, the relative number of which is referred to as the amine number. As used herein "amine number" means the milligrams of KOH equivalent to the free amine groups in one gram of the product. Preferably this amine number should be at least 5 and preferably is at least 10. Amine numbers may be as high as 100 or more. This amine number may be the result of the employment of the polyamine in excess or as a result of only partial reaction of the polyamine which is employed. Thus in the case of diethylene triamine, triethylene tetramine and tetraethylene pentamine, it is usually preferred to employ the polyamide in a quantity such that the primary amine groups are approximately equivalent to the carboxyl groups in the polymeric fat acids including the carboxyls in the polybasic acids as well as the carboxyl groups in any monomer which may be present. When these proportions are employed, the reaction between the carboxyl groups and the polyamines involves almost entirely the primary amine groups, and the secondary amine groups remain as free amine groups in the polymer. Where less polyamine is employed than that which is equivalent in primary amine groups to the carboxyl groups, some of the secondary amine groups may react with the carboxyl groups and there is the possibility of obtaining cross-linked polymers which would have a tendency to gel. Accordingly it is preferred not to involve the secondary amine groups in the amide-forming reaction where such polyamines as diethylene triamine, triethylene tetramine, and tetraethylene pentamine are employed. Too large an excess of amine groups should be avoided inasmuch as this tends to reduce the size of the polymer to the point where the product might not possess the desired physical characteristics. In general, amine numbers between 5 and 100 are satisfactory, and those skilled in the art can readily determine the particular proportions of amine and polymeric fat acids to be employed for the production of a polymer having the desired characteristics.

Polyamides of this type generally have molecular weights varying from 1,000 to 10,000, and are resistant to the corrosive action of water, alkali, oils, greases, and

organic solvents. The melting points vary depending upon the reactants and the reaction conditions. These melting points may vary from about 25° C. to 95° C. They vary in degrees of hardness, depending upon the melting point, but in general, all are tacky resins. Some resins of this type have been disclosed in Cowan et al. Patent No. 2,450,940, and such resins are useful in the present invention.

In preparing a suspensoid from these polyamides, the polyamide is simply melted and then poured into water containing a small amount of acid while the mixture is being agitated. The mixture is heated and stirred and as a result dispersion of the polyamide readily occurs. A wide variety of acids may be employed in the aqueous phase. Suitable acids include formic, acetic, propionic, butyric, monochloroacetic, hydrochloric, phosphoric, boric, fumaric, lactic, maleic, oxalic, tartaric, glycolic, benzoic, succinic, terephthalic, furoic, and gallic acids. Only a small quantity of acid is necessary to effect the dispersion. The quantity of acid is only a small portion of that which would be required to neutralize free amine groups in the polymer where the polymer has an amine number of 20 or more. In the case of polymers having amine numbers below 20 a substantial portion of the amine groups should be neutralized. Polymers having amine numbers below 10 would require substantially complete neutralization of the amine groups. For example, with diethylene triamine resins sufficient acid is employed to neutralize amine groups equivalent to an amine number of about 7 to 15. The optimum quantity of acid for any particular polyamide varies with the resin and can readily be determined by trial. When larger quantities of acid are employed, colloidal solutions or gels may be formed, especially where the amine number is above 20. These are useful in some applications, but in general, are less desirable than the suspensoids which are preferred. This phenomenon, however, may be made use of in controlling the viscosity of the suspensoid, particularly in the case of polyamides of high amine number.

The solids concentrations in these suspensoids can be varied widely. Preferred compositions frequently have solids concentrations in the range of 35-60%. Higher and lower concentrations are, of course, possible and extreme dilutions are feasible. The particle size in these suspensoids is of the order of 1 micron.

During the preparation of these suspensoids, it is possible to incorporate other ordinarily non-dispersible reagents into the reaction mixture. These include waxes such as paraffin wax, rosin, rosin esters, and a great variety of other resinous materials such as phenol-formaldehyde resins, acrylic polymers, vinyl polymers of many kinds, urea-formaldehyde, melamine polymers, and the like. The incorporation of additives of this nature in small quantities, especially material such as paraffin wax or antioxidants, has been found to be advantageous from certain points of view as will be detailed below in the examples.

The process for the preparation of paper containing such suspensoids is extremely simple. Thus it is merely necessary to add the suspensoid to the pulp, after which the pulp is well agitated and the paper is manufactured in the conventional way. The pulps which may be used include bleached sulfite pulps, reclaimed paper, kraft pulps, ground wood pulp, neutral sulfite pulps, soda pulps, and in fact any type of wood pulp, straw, rags, or other pulp material of cellulosic origin.

In general the concentration of the suspensoids contemplated in the present invention may vary from 1% to 20%, as suspensoid solids based on the dry weight of the pulp fibers. In general, however, it is preferred to operate within the range of 3% to 6%. It is advantageous to heat-treat and/or calender the paper after it has been fabricated, as will be shown in the examples.

5

## Example 1

A polyamide was prepared from a polymeric fat acid having the following composition:

Percent monomer-----	10.0
Percent dimer-----	69.5
Percent trimer-----	20.5
D/T ratio-----	3.39
Acid number-----	186.5
Saponification equivalent-----	291.1

Forty pounds of this polymeric fat acid, 2.4 pounds of cottonseed fatty acids, and 7.48 pounds of a 95.6% aqueous solution of diethylene triamine were heated with stirring to 200° C. Heating was effected slowly since a tendency toward foaming was observed. After the temperature reached 200° C. it was maintained there for 3 hours with vigorous agitation, and during the last hour vacuum was employed. At the end of the reaction period the vacuum was released and the product was cooled. The reaction mixture was maintained under an inert gas blanket during all the time at which it was at an elevated temperature with the exception of the time during which the vacuum was employed. The product had the following properties:

Melting point (ball and ring)-----°C--	46.0-46.5
Color <sup>1</sup> (Gardner)-----	10-11
Viscosity <sup>1</sup> at 25° C. (Gardner-Holdt)-----	B-C
Acid number-----	5.2
Amine number-----	86

<sup>1</sup> Determinations carried out on 35% solutions in butanol-toluene (1:1).

To 32.3 pounds of the above resin heated to 160° C. there was added with vigorous stirring 32.3 pounds of hot water containing 0.26 pounds of acetic acid. After agitation for one hour, there resulted an extremely smooth dispersion, which provided a continuous tacky film. The suspensoid demonstrated the following properties:

Percent solids-----	52.1
Acid number-----	6.0, 6.1
Amine number-----	43.2, 43.8
pH-----	7.6

This suspensoid was added directly to a bleached sulfite pulp in the beater at the rate of 3% suspensoid solids based on the weight of the dry fiber. The usual rosin size and alum were omitted. The sheet was formed in a normal way and after the normal drying it was cured for from 10 to 20 minutes by heating at 240-280° F. The product obtained had a wet strength over 6 times the wet strength of an untreated sheet when both were wetted with a dilute solution of a wetting agent such as sodium lauryl sulfate. The product demonstrated a bursting and tensile strength of 1.4 times that of the untreated sheet, and a water resistance as measured by TAPPI standard T433M-44 dry indicator method of at least that attained by 3% rosin size and alum to pH 4.5 to 5.0. These results are indicated in the following table:

	Untreated Sheet	Rosin Sized Sheet	Polyamide Treated Sheet
TAPPI size, seconds-----	1	85	86
Wet tensile strength, 15 mm. paper strip wetted with dil. soln. of Na Lauryl Sulfate, grams-----	100	-----	637
Dry tensile, lb. per 15 mm. paper strip-----	5.68	-----	8.1
Bursting strength, lb. per sq. in.-----	-----	10	14

## Example 2

349.3 parts of the polymeric fat acid of Example 1 and 116.8 parts of triethylene tetramine were heated with stirring to 200° C. The heating period required about 2 hours, during which time the vapor temperature was never allowed to exceed 99° C. The reaction mixture was then

6

maintained with stirring at 200° C. for 3 hours, and during the last hour vacuum was employed. Thereafter the product was cooled. Again an inert atmosphere was employed while the product was at an elevated temperature.

The product had the following properties:

Melting point (ball and ring)-----°C--	27-28
Color (Gardner)-----	8-9
Viscosity at 25° C. (Gardner-Holdt)-----	A-1
Acid number-----	3.4
Amine number-----	177.0

Five hundred parts of the resin were heated to 150° C. and to the heated resin were added 930 parts of water containing 4 parts of glacial acetic acid, the water having been heated first to 90° C. After the addition vigorous stirring was employed for approximately one-half hour, and a stable suspensoid resulted. This suspensoid, likewise, produced continuous tacky films.

This cationic suspensoid was added to bleached sulfite pulp as the sole beater additive. The pulp was made into paper, which was then heat-treated at 238° F. for 12 minutes. The improved wet tensile strength and size characteristics which were obtained are indicated in the following table:

Sheet containing as Beater additive	Wet tensile Strength	
	TAPPI4 T433-M4	Size Test
	Grams	Seconds
3% resin suspensoid solids as described in Example 2-----	377	36
6% resin suspensoid solids as described in Example 2-----	403	36
Blank sheet, no additive-----	100	1

## Example 3

A comparison was made between the papers obtained by the employment of the polyamide suspensoids of the present invention and papers obtained using urea-formaldehyde resins as additives. The suspensoid employed was that described in Example 1. For comparison purposes a so-called urea-formaldehyde "stage" resin was employed. This material was a partially polymerized urea-formaldehyde resin which had not yet reached the insoluble and infusible stage. The resin was employed in the form of a cationic solution and was characteristic of urea-formaldehyde resins employed for this purpose in the paper industry. The papers produced were heat treated in the manner set forth in the preceding examples. This heat treatment is particularly important in the case of the urea-formaldehyde resins in order to "set" such resins. The superior results obtained by the employment of the polyamide suspensoid are indicated in the following table:

Description of Additive	(Sheet) Test Results	
	Wet tensile Strength	TAPPI T433-M44 Size Test
	Grams	Seconds
3% urea-formaldehyde resin only-----	237	1
3% urea-formaldehyde resin + 4% alum-----	450	1
3% of polyamide resin suspensoid described in Example 1-----	637	85
No additive-----	100	1

## Example 4

The effect of varying concentrations of suspensoid on the resultant paper are indicated by the present example in which a series of papers were formed from the same paper pulp to which increasing increments of polyamide suspensoid were added as a beater additive. The sheets were finished and heat treated as described in Example 2.

The wet strength and water resistance results of these sheets are shown in the following table:

Amount of Suspensoid Introduced as Beater Additive	Wet tensile Strength	TAPPI T433-M44 Size test
	Grams	Seconds
6% resin solids on weight pulp.....	587	135
9% resin solids on weight pulp.....	600	240
12% resin solids on weight pulp.....	800+	-----
15% resin solids on weight pulp.....	793	-----
Blank sheet, no additive.....	100	1

The effect of varying time periods of heat treatment is demonstrated in the present example in which a series of papers were prepared, all containing 3% of suspensoid solids based on the dry weight of the fiber. These suspensoids were again added as the sole beater additive and the papers were made and heat treated for varying times on an electrically heated drier with a surface temperature of 238° F. For comparison purposes one sheet was air-dried and a blank sheet containing no polyamide suspensoid was dried for 6 minutes at 238° F. The results are indicated in the following table:

Percent Polyamide Resin Suspensoid	Heating Time at 238° F.	Wet Tensile Strength	TAPPI T433-M44 Size test
	Min.	G.	Sec.
Blank sheet.....	6	113	14
3% Resin (sheet air-dried).....	3	187	16
3% Resin.....	6	257	22
Do.....	9	327	37
Do.....	12	487	48
Do.....	15	470	75
Do.....	20	490	58
Do.....	30	570	63
Do.....	30	720	63

#### Example 6

Paraffin wax was employed in conjunction with the polyamide resin suspensoid. For this purpose the resin described in Example 1 was used. The suspensoid was prepared in the following manner: To a melt of 100 parts of the polyamide resin and 5 parts of paraffin wax (melting point 135-137° F.) heated to 140° C., was added with rapid agitation a hot (90° C.) solution of 1.6 parts of acetic acid and 185 parts of water. Vigorous agitation gave a smooth dispersion which provided a continuous tacky film. The product had a solids content of 36% and a pH of 8.8

A series of paper sheets were made from this mixed suspensoid of polyamide and wax and compared with sheets made from the polyamide suspensoid in Example 1. These sheets were heat treated as previously described at the temperatures and for the time periods indicated. It will be seen from the following table that the paraffin-containing suspensoid provides a more water resistant sheet at moderate curing temperatures than does the resin alone even at higher curing temperatures. In addition, the wet strength of such sheets is improved by the presence of a paraffin.

Beater Additive	Temperature and Time of drying	Wet Tensile Strength, g.	TAPPI T433-M44 Size Test, sec.
3% resin with wax.....	238° F., 12 min.....	667	98
6% resin with wax.....	238° F., 12 min.....	+900	98
3% resin with wax.....	238° F., 6 min.....	440	40
3% resin.....	250° F., 12 min.....	517	49
Do.....	250° F., 20 min.....	480	51
Do.....	260° F., 12 min.....	570	49
Do.....	260° F., 20 min.....	567	79
3% resin with wax.....	250° F., 12 min.....	613	52
Do.....	250° F., 20 min.....	678	62
Do.....	260° F., 12 min.....	597	51
Do.....	260° F., 20 min.....	760	48

Other waxes such as microcrystalline wax, montan wax, carnauba wax, and the like, can also be used. Paraffin

wax, however, is preferable because of its low price and availability. The ratio of waxes to resin solids may also be varied above and below the five percent level demonstrated here, but for the most part, the preferred results are obtained with 5%. Other co-additives may also be used in the suspensoid such as latex emulsions, stabilizers, and certain gums.

We claim as our invention:

1. A cellulosic paper product comprising fibers having dispersed among the fibers thereof a polyamide having the polyacyl group of polymeric fat acids, and the polyamino group of an aliphatic polyamine, the amino groups primarily involved in the polyamide formation being separated by at least 3 atoms, the polyamide having a molecular weight within the approximate range of 1,000 to 10,000, said polyamide having an amine number of at least 5.

2. A cellulosic paper product comprising fibers having dispersed among the fibers thereof a polyamide having the polyacyl group of polymeric fat acids, and the polyamino group of an aliphatic polyamine, the amino groups primarily involved in the polyamide formation being separated by at least 3 atoms, the polyamide having a molecular weight within the approximate range of 1,000 to 10,000, said polyamide having an amine number of from 10 to 100.

3. Product according to claim 1 in which the polyamine used in preparing the polyamide is diethylene triamine.

4. Product according to claim 1 in which the polyamine used to prepare the polyamide is triethylene tetramine.

5. Process of producing cellulosic paper products which comprises adding to paper pulp as a better additive a suspensoid in an aqueous medium of a polyamide having the polyacyl group of polymeric fat acids, and the polyamino group of an aliphatic polyamine, the amino groups primarily involved in the polyamide formation being separated by at least 3 atoms, the polyamide having a molecular weight within the approximate range of 1,000 to 10,000, said polyamide having an amine number of at least 5 and being dispersed in an aqueous medium by means of sufficient acid to produce a stable suspensoid, said suspensoid being capable of forming continuous tacky films, and converting said pulp into a paper product.

6. Process according to claim 5 in which the polyamine employed for the preparation of the polyamide is diethylene triamine.

7. Process according to claim 5 in which the polyamine employed for the preparation of the polyamide is triethylene tetramine.

8. Process according to claim 5 in which the polyamide is employed in the quantity of from 3% to 6% calculated as suspensoid solids and based on the dry weight of the fiber in the pulp.

9. Process according to claim 5 in which the paper product after formation is cured at temperatures within the range of 230° F. to 280° F. for a time period within the approximate range of 3 to 20 minutes.

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