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71 Applicant: **PRODECO S.p.A.**
Piazza Boldrini
I-20097 San Donato Milanese (Milano)(IT)

72 Inventor: **Spina, Nicola**
Via Triulziana 27
I-20097 San Donato Milanese Milano(IT)

72 Inventor: **Isolati, Antonio**
Corso Mazzini, 187
I-47100 Forlì(IT)

74 Representative: **Bühling, Gerhard, Dipl.-Chem. et al,**
Patentanwaltsbüro Tiedtke-Bühling-Kinne
Gruppe-Pellmann-Grams-Struif-Dragotti Bavariaring 4
D-8000 München 2(DE)

54 Paper sizing process.

57 In the sizing of paper filled with calcium carbonate, the precipitation of the resin sizing agent is carried out by means of aluminium polyhydroxychloride or aluminium polychloride.

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The present invention relates to a paper sizing process and more specifically to a process for the sizing of paper filled with calcium carbonate.

In the traditional sizing of paper, the fiber aqueous suspension is supplemented with a resin sizing agent, normally based on colophony, which is precipitated by means of a precipitating agent.

The precipitating agent of most popular and common use is the aluminium sulphate which is added to the aqueous suspension of fibers in form of a water solution.

It is also known that, depending on the final use of the paper, the fiber suspension is added with an inert filler, suitable for giving particular properties to the paper.

Since the precipitation with aluminium sulphate takes place at an acidic pH, particularly at a pH of between 4.5 and 6, there are no problems in the cases in which the acidic environment has no effect on the filler or the latter does not interfere with the behaviour of the precipitating agent. A typical example of such a situation is the kaolin, which however must be particularly pure, since impurities like calcium carbonate react with the aluminium sulphate, forming calcium sulphate whereby part of the precipitating agent is withdrawn from the desired action and causing carbon dioxide to be liberated, which remains trapped within the fiber suspension and in the resulting paper with the evident problems and drawbacks.

These problems and drawbacks are raised at the maximum degree when the filler is really calcium carbonate. In fact if aluminium sulphate had to be used as precipitating agent, a reaction between aluminium sulphate and calcium carbonate would first of all take place until the complete exhaustion of the calcium carbonate and disappearance of the filler; only at that time, by adding further aluminium sulphate, it would be possible to carry out the precipitation of the sizing agent.

Besides the already mentioned problems and drawbacks, there would also occur, the production of relevant amounts of salts, particularly calcium sulphate, which furthermore involve pollution problems and thus the depuration of the process effluents.

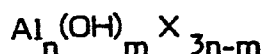
On the other side, with the colophony based sizing agents used up to date, it was not possible to use aluminium sulphate at a neutral or alkaline pH, since the precipitation did not take place, presumably owing to the lack of neutralization of the electrical charges in fig. 3 in the suspension.

Lastly, it should not be forgotten that in the case of paper filled with calcium carbonate

the problem exists of the recycling to the paper manufacturing process of the so-called coated brokes which are too highly filled with calcium carbonate.

For these reasons before the present invention for the sizing of paper in the presence of calcium carbonate as the filler recourse was made to synthetic sizing agents (e.g. Aquabel manufactured and sold by Hercules Inc.) which did not raise the afore mentioned technical problems, but involved an exceedingly higher cost due to the use of these sizing agents.

The improvement of the paper sizing by avoiding the use of aluminium sulphate is also proposed in the Canadian Patent No. 759.363, wherein for this purpose the use of a basic alumium salt is foreseen having the following general formula:



wherein X is a monovalent anion, for instance chlorine, wherein n is 1 to 20, particularly 4 to 10, m is less then 3n and the ratio Al/X is of between 1.5 and 6, particularly of between 2 and 4.

In the specification and in the examples however, the filler used is not practically mentioned.

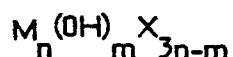
As regards the operating pH, the specification indicated a general range of 5 to 8, and a preferred interval of 5.5 to 7.0.

However in the examples the pH, when stated, has a maximun value of 6.8 (example 3).

It is thus evident that in this process the problem of the filler and particularly of the use of calcium carbonate is not taken into consideration.

In turn the published French Patent Application No. 2418297 does definitely face the problem of reducing the contents of suspended matters in the effluent water resulting from paper sizing operations, by improving the properties of the thus obtained paper.

To this end there is taught the use, as the precipitating agent, of a basic salt having the formula:



wherein M can be aluminium, X chloride, $3n-m > 0$ and the basicity namely the ratio $m/3n$ % is of between 30% and 75%.

There is particularly preferred the presence in the stated salt of a polyvalent anion, for example the anion of a mineral acid such as sulphuric acid.

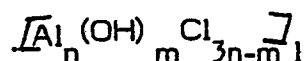
As a consequence it is evident that in this process no account is taken of the type of

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filler, although in the preamble the possible fillers are indicated, namely kaolin, calcium carbonate, talc, etc. without establishing any difference amongst them.

Lastly, in order to complete the above technical picture, the fact is to be mentioned that in recent years there has been suggested and successfully experimented the use of aluminium polychloride and polyhydroxychloride as precipitating agents as a substitution for aluminium sulphate, and operating under the same conditions.

By aluminium polychloride and polyhydroxychloride polymers are meant which for instance in the case of the polyhydroxychlorides have the general formula:



wherein l is an integer varying between 5 and 15 for instance of the type produced according to the USP No. 3909439.

However, it should be pointed out that theoretically the aluminium polyhydroxychloride upon being hydrolized, should give place to a weakly acidic environment, wherein on one side, there was a justification of the function of a substitute for the aluminium sulphate and, on the other side, such a hypothesis would lead to exclude the use thereof in the case of calcium carbonate and like fillers.

It has been now surprisingly found and it is the subject of the present invention that, by using aluminium polyhydroxychloride as the precipitating agent, it is possible on one hand to carry out the precipitation of colophony based resin size at a pH value from neutral to alkaline and, on the other hand, to carry out the sizing of paper filled with calcium carbonate or a substance like thereto.

Thus the present invention provides a process for the paper sizing, of the type in which a precipitating agent is added to an aqueous suspension of fibers containing a colophony based resin size, wherein moreover calcium carbonate or a like substance is used as the paper filler, characterized in that as the precipitating agent there is used a compound selected among aluminium polyhydroxychlorides, having the formula:



wherein $0.85 \leq x < 6$

and aluminium polychlorides having the formula



wherein $0 \leq \gamma \leq 4$, the precipitation taking place at a pH of neutral to alkaline.

As already mentioned, the process according to the invention permits unexpected and

unforeseeable results to be achieved, since it becomes possible to use traditional sizing agents instead of special highly expensive sizing agents, whereby also this sizing operation is brought within a traditional technology, satisfactorily used since long time. There is moreover permitted the recovery and recycling of the coated brokes. Examples are now given illustrating, in a non limiting manner, the results achieved by the present invention.

EXAMPLE 1

This example discloses a traditional sizing treatment, relating to the production of fine white paper, having a weight of 140 g/sq.m. wherein kaolin is used as the filler. The paper pulp comprises bleached cellulose (90%) and waste paper pulp (10%). In the following table 1 there are reported both the results and the conditions under which the experiments were carried out. In the table by A alum or aluminium sulphate is indicated and by B alimunium polyhydroxychloride of the type commercially available under the name of PRODEFLOC SAB 19 of the Prodeco Spa is indicated.

TABLE 1
SIZING TESTS

ph	% of size in emulsion	Al ₂ O ₃ % by weight		sizing rate, Cobb ₆	
		A	B	A	B
6.5	1.2	0.14	0.13	24	20
7.0	1.2	0,08	0.07	not sized	22

EXAMPLE 2

This example relates to the production of paper for exercise books having a weight of 65g/sq.m. filled with 5% of calcium carbonate and 5% of kaolin, these percentages being referred to the dry paper.

The paper pulp forming the fiber suspension had the following composition:

bleached cellulose	50%
semichemical pulp	20%
wood pulp	10%
waste paper pulp	20%

In the following table 2 there are reported the results of the sizing tests.

TABLE 2

SIZING EXPERIMENTS

ph	% of sized in emulsion	Al ₂ O ₃ % by weight		sizing rate	
		A	B	A	B
6.5	5.5	0.63	0.63	sized	sized
7.0	5.5	0.13	0.13	not sized	sized

EXAMPLE 3

This example relates to the production of 50 g/sq.m paper useful as a support for coated paper.

The pulp forming the fiber suspension had the following composition:

bleached cellulose	33%
bleached wood pulp	22%
coated brokes	45%

It is to be noted that the coated brokes have on the overage a calcium carbonate content of 20-30%.

The results of the sizing tests are reported in the following table 3.

TABLE 3

Sizing experiments

ph	% of size in emulsion	Al ₂ O ₃ % by weight		sizing rate	
		A	B	Cobb ₆	
				A	B
6.5	2	0.47	0.45	18	17
7.0	2	0.35	0.30	not sizing	18

From the preceeding tables it cearly appears that the pH at which the precipitation of the resin size is carried out is determining since upon the neutrality is reached the paper is unsized with the usual precipitating agent whereas it is satisfactorily sized by using the process of the invention.

By repeating the afore said experiments with aluminium polychlorides like results are obtained.

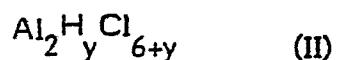
CLAIMS

1. A process for the paper sizing, of the type in which a precipitating agent is added to an aqueous suspension of fibers containing a colophony based resin size, wherein furthermore calcium carbonate or a substance like thereto is used as the filler of the paper, characterized in that as the precipitating agent there is used a compound selected among aluminium polyhydroxy chlorides having the formula



wherein $0.85 \leq x < 6$

and aluminium polychlorides having the formula



wherein $0 \leq y \leq 4$

the precipitation taking place at a pH from neutral to alkaline.

2. A process according to claim 1, characterized in that said precipitation is carried out at pH 7.



European Patent
Office

EUROPEAN SEARCH REPORT

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EP 83 10 6892

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D,X Y	CA-A- 759 363 (MORIMOTO et al.) * Claims 1,2; page 4, lines 4-28; page 5, line 18 - page 6, line 27; examples 1-3 *	1,2	D 21 D 3/00
D,X Y	FR-A-2 418 297 (PRODUITS CHIMIQUES UGINE KUHLMANN) * Claims 1,2; example 2 *	1,2	
A	FR-A-1 005 346 (M. CHENE) * Page 1; page 2, left-hand column, paragraphs 3-5; examples 4,5 *	1,2	
A	ABSTRACTS BULL. INST. PAPER CHEM., vol. 49, no. 3, September 1978, page 252, no. 2132, Appleton, Wisconsin, USA V.A. SMIRNOV: "Effect of pulp pH and type of aluminum compound on rosin sizing of paper" & SB. TR. TSENTR. NAUCH.-ISSLED. INST. BUMAGI no. 10, 16-22, 1975		TECHNICAL FIELDS SEARCHED (Int. Cl. 3) D 21 D D 21 H
A	TAPPI J. TECHN. SASS. PULP PAPER IND., vol. 65, no. 3, March 1982, pages 125-130, Atlanta, Georgia, USA T.R. ARNSON: "The chemistry of aluminum salts in papermaking"		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-10-1983	Examiner NESTBY K.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			