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Description

The present invention relates to a method for reducing the amount of free aldehyde, especially the amount of free formaldehyde, at the production of paper. More particularly the invention relates to a method for reducing this by addition of sulphite during the process before the final drying, to the stock or the process water, at the production of paper, paperboard or board. The invention also relates to a product suitable for use at the production of paper in order to reduce the amount of free aldehyde.

It is well-known that formaldehyde is an irritant and causes allergy and it is thus with regard to occupational and environmental hygiene desirable to reduce the amount of free formaldehyde as far as possible in the different processes where it is released. Most of the work in this area has been done in the particle board industry where the problems have been very severe. A great number of substances, predominantly urea and derivatives of urea, have been used as formaldehyde absorbing agents and been added to the formaldehyde based binders used in the process and/or to the cellulose material at the production.

So-called wet strength resins based on formaldehyde are used widely at the production of paper, and especially at the production of kraft sack paper and similar products. Most of these resins are urea-formaldehyde resins or melamine-formaldehyde resins and they can be unmodified or modified with for example amines. In the same manner as the resins which are used as binders for particle board, the wet strength resins for paper have been developed and modified to contain as low amount as possible of formaldehyde. The reduction of the amount of formaldehyde in a resin which can be made with regard to the storage stability of the resin, with regard to dilution etc, is, however, not sufficient for avoiding problems with free formaldehyde at the paper production process, but further measures must be taken.

Earlier it has been thought that the largest amount of free formaldehyde originates from the actual wet strength resin in the paper and that it is released essentially at the curing of the resin, which predominantly takes place in the drying section of the paper machine. However, it has now been found that substantial amounts of formaldehyde in the air at a paper machine originates from the process water, as such, or from the stock.

Compared with the conditions at for example production of particle board, the conditions at the production of paper are considerably different due to the large amounts of process water which are utilized. The concentration of the stock, the aqueous suspension of fibres, varies from a dry content of about one percent in the first beating and slushing steps down to 0.5 to about 0.1 per cent in the steps when paper chemicals are added. The water which is separated from the stock at the paper production, the white water, is usually recirculated to the process. It has been found that substantial amounts of formaldehyde in the air comes from the process water and it is assumed that the free formaldehyde comes partly from the free formaldehyde in commercial wet strength resins and partly from hydrolysis of the resins in the stock, varying with the temperature of this, its pH etc.

Attempts have thus been made to make a subsequent addition of urea to wet strength resins to bind the formaldehyde at an early stage. Urea is a cheap and efficient formaldehyde scavenger. However, such an addition does not solve the problems at the paper production in the long run as the reaction product formed from formaldehyde and urea, dimethylolurea, is not retained in the paper but circulates in the process with the white water and after some time hydrolysis sets in and formaldehyde is liberated.

When the above described problems with formaldehyde release by hydrolysis of resin or of the reaction product between formaldehyde and absorbing agent, such as urea, once have been realized the demands which must be made on an efficient formaldehyde absorbing agent at the production of paper is that the reaction product between formaldehyde and formaldehyde absorbing agent must not have any tendency to hydrolysis worth mentioning, that it shall have a high thermal stability and not be decomposed at the process conditions at paper production, where the temperature generally varies between 50 and 100°C, and that it preferably should also be retained in the paper. Neither must the formaldehyde absorbing agent which is used have a negative influence on the effect of the paper chemicals, but the effect of the wet strength resin as such must be permitted to be developed fully and likewise the effect of the sizing agents which are used.

According to the present invention it has been found that sulphite can be used as absorbing agent for aldehydes, particularly formaldehyde, at the production of paper and hereby bind aldehydes in a reaction product which is not readily hydrolyzed and which has a very high thermal stability and it has been found that the sulphite can be used in such a manner that retention to the paper is obtained. Further, the sulphite can be used at the production of paper in such a manner that negative influence on the effect of the paper chemicals is avoided.

The present invention thus relates to a method for reducing the amount of free aldehyde at the production of paper whereby sulphite in combination with a cationic retention agent is added to the stock or the process water as defined in the claims.

Addition of sulphite herein refers to addition of sulphites, bisulphites (hydrogen sulphites) and disulphites which in an aqueous solution give sulphite-, hydrogensulphite-and/or disulphite- ions which can react with aldehydes and refers to additions of such sulphites in combination with alum or other at paper production conventionally used cationic retention agents, such as for example cationic starch, polyethyleneimines, polyacrylamides and polyamidoamines. By combination of sulphite and alum or other cationic retention agent is should of course be understood that the quantity of cationic

retention agent required for the formaldehyde scavenging by sulphite in an efficient papermaking process may form part of the at a papermaking process usually added quantity or be added additionally to this, depending on the systems and the charges in the systems. The sulphite is preferably alkali metal or ammoniumsulphite and most preferably sodium sulphite or sodium bisulphite is used. According to a particularly preferred embodiment a combination of alum and sulphite or bisulphite is added. Solid sulphites can be added as such but it is preferred to add aqueous solutions of the sulphites.

The reaction between formaldehyde and sulphite or bisulphite is in itself well-known and has been used for analysis of formaldehyde. It is also previously known to modify urea-formaldehyde wet strength resins with bisulphite. This type of anionic urea-formaldehyde resins has, however, only limited use today. From the US patent 4409375 it is also known to use bisulphite as formaldehyde scavenging addition for particle board glue and further to use solutions of bisulphite as scavenger for airborne formaldehyde. From the European patent application 96797 it is further known to use sulphites as formaldehyde scavengers at the actual production of particle board.

The addition according to the present invention for absorbing free aldehydes at paper production is made to the stock, ie the very dilute fibre suspension, or the process water. The most substantial amounts of free aldehyde, and especially free formaldehyde, arise in the white water, as explained earlier, and thus addition of sulphite to this or to the stock will scavenge a considerable part of aldehyde and improve the environment at paper production. For a reduction of the amount of free aldehyde throughout the papermaking process the addition according to the invention can be combined with an addition to an optional surface size solution or coating slip. Sulphite can further also be added to the process water, the washing water, which is used in the drying section in order to scavenge optionally remaining amounts of aldehyde here. Unreacted sulphite remaining in the paper can also absorb formaldehyde which is later liberated from the resin.

The addition according to the present invention for absorbing free aldehydes can be made directly to the process water, the white water, to bind, in the white water, aldehydes which originates from the cellulose and are naturally present in the cellulose. The wood substance contains different types of aldehydes, mainly such with a diterpene nucleus, which are released at the pulp cooking and which can give rise to odour and taste problems in the finished paper. Direct addition to the white water can also be made to bind formaldehyde which comes from a previous run using formaldehyde based wet strength resins. However, the method of the invention is particularly applicable for utilization at the production of wet strength paper wherein formaldehyde based wet strength resins are used and such resins can be modified or unmodified, cationic or anionic, urea-formaldehyde resins and melamine-formaldehyde resins or mixtures of such, and the addition is then preferably made to the process water. The addition can arbitrarily be made before or after the addition of resin, or at the same time as this.

According to the invention sulphite or bisulphite is added to the stock or the process water in combination with a cationic retention agent. The formaldehyde scavenging agent and the cationic retention agent can hereby be added simultaneously or close in time to each other so that a complex is formed which can be retained in the paper. The cellulose is in itself slightly negatively charged and as the sulphites are strongly anionic, retention problems would arise at a direct addition of for example sodium bisulphite. It is further desirable to disturb the original charge of the stock as little as possible with regard to dosage and retention of the actual paper chemicals. At addition to the stock and at direct addition to the process water which will be recirculated to the stock, the formaldehyde absorbing agents according to the present invention are used in combination with at paper production per se known and used cationic retention agents such as alum, cationic starch, polyethyleneimines, polyacrylamides and polyamidoamines. Alum is the cheapest and most common retention agent and is also advantageous with regard to its charge. It is thus particularly preferred to use a combination of alum and sulphite and particularly such which give complexes with a charge that will disturb the z-potential of the system as little as possible. The complexes react with free aldehyde and the formed reaction product is retained in the paper.

The dosage of the formaldehyde scavenger will of course be dependent on the amount of formaldehyde, or other aldehyde, which will be present in the system, the stock and the process water. An efficient amount with regard to this and the desired degree of reduction is used. The amount of the added alum or other cationic retention agent in combination with the sulphite for the formaldehyde absorption should be such that the total charge of the complex formed is zero or slightly positive. Synthetic polymers can be used with sulphite when they are used as such in the stock. The added amount of these polymers for the sulphite will then together with the sulphite have a net charge of slightly positive sites in the polymer. The total Z-potential in the system should be 0+-5 meV for best retention. There should be no problems for the man skilled in the art to find out the dosage required in each case. With regard to the production of wet strength paper using formaldehyde based wet strength resins, which generally are added in amounts of from about 0.5 to about 2.5 per cent by weight, calculated as dry and based on dry fibre weight, suitable amounts of sulphite are within the range of 4 to 12 per cent by weight, based on added wet strength resin, calculated as dry, and preferably the amount is within the range of 5 to 10 per cent by weight. Of course the degree of recirculation in the actually used paper machine must be considered at dosage. A suitable amount of cationic retention agent to be used in combination with the sulphite amounts given is within the range of 1 to 3 times the weight of sulphite for alum, and preferably 1.3 to 1.7 times the weight. For other cationic retention agents suitably 10 to 20 times the

weight of sulphite is used, depending on the charge and nature of the cationic retention agent.

Paper production herein refers to the production of paper, paperboard and board from conventional stocks, ie fibre suspensions with dry contents of from about 0.1 to about 0.5 per cent by weight. The process water in paper production contains very small amounts of fibre, e.g. of the order 500 to 2000 ppm.

The present invention also relates to a product, which can be used in the above described steps at the production of paper, for absorption of free aldehydes, especially free formaldehyde. The product is an aqueous solution of a combination of a cationic retention agent and sulphite as defined in the claims. The cationic retention agent is such an agent commonly used at paper production, for example alum, cationic starch, polyethyleneimines, polyacrylamides and polyamidoamines. It is particularly preferred that the cationic retention agent in the product is alum. The dry content of the solution may vary within wide limits and the upper limit is mainly dependent on storage- and transport times as too high dry contents may result in precipitations at longer storage- and transport times. From a practical point of view the dry content of the solutions should thus suitably be kept within the range 20 to 40 per cent by weight. The ratio of sulphite to cationic retention agent in the aqueous solution is suitably such that the charge of the formed complex is zero or slightly positive. For cationic retention agents such as starches and synthetic polymers this means that suitable combinations comprise about 10 to 20 times as much cationic retention agent as sulphite. Alum, ie papermaker's alum, with the general composition $Al_2(SO_4)_3 \times 18H_20$, exists in a large number of configurations with varying charges. The exact ratio between sulphite and alum in a solution has to be determined with regard to the alum and with regard to the z-potential of the stock in question. Usually the mole ratio of sulphite to alum is within the range 2:1 to 7:1 , suitably within the range 3:1 to 6 : 1 and preferably within the range 4:1 to 5:1 . As alum is widely used at the production of paper optionally required adjustments with regard to the z-potential of the stock can easily be made at the addition of a product according to the invention, by supplementary addition of alum or, alternatively, by reducing the normally added amount of alum.

The invention is further illustrated in the following examples, which, however, are not intended to limit the same. Parts and per cent relate to parts by weight and per cent by weight, respectively, unless otherwise stated.

Example 1

By studies on a large-scale kraft sack paper machine with a production of 20 tons per hour it was verified that formaldehyde in the drying section to the main part originates from formaldehyde dissolved in the white water. At the production of paper about 2.2 per cent by weight of urea-formaldehyde resin, calculated as dry and based on dry fibre weight, was added. When the machine had run for a couple of days and equilibrium had been attained the supply of wet strength resin was shut off and the amount of formaldehyde in the white water and in the drying section was measured. Directly after the shut down the amount of formaldehyde in the white water was 340 ppm and in the drying section it was 5.9 ppm. After 4 hours the amounts were 105 ppm and 2.2 ppm respectively, and after 24 hours the amounts were 11 and 0.25 ppm respectively.

Based on the above studies paper sheets were formed from an unbleached sulphate stock in a laboratory sheet machine. The sheets were formed according to standard methods with addition of 0.2% of rosin and 2.0% of alum at a pH of 4.5. After 10 sheets had been formed 2.0 g of CH_2O (about 100 ppm) were added to the white water system and also 46 g of a solution of alum and sodium bisulphite (10.4 g of alum + 6.7 g of sodiumbisulphite in 50 ml of water). After production of totally 13 sheets the white water was analysed for free formaldehyde and this had then been reduced by 50%. The sizing degree was determined for all the sheets by measuring Cobb-number according to SCAN-P 12:64 and the values were between 21 and 22 g/m2 which means that the addition of sulphite did not have a detrimental effect on the sizing.

In the same manner sheets were prepared with addition of 1% wet strength resin, a cationic urea-formaldehyde resin, and for the formed sheets wet tensile index and wet strength was measured, both for a series without addition of bisulphite and for a series with addition of bisulphite in the form of a solution with alum as above. For the first series the mean value for wet tensile index was 17.4 Nm/g and for the wet strength 28.3%. For the second series the corresponding mean values were 17.5 Nm/g and 28.1% respectively, which shows that the addition according to the present invention does not have any detrimental effect on the wet strength of the paper.

For sheets produced with added alum-bisulphite solution analysis was also made to determine the amount of sulphur and hereby 30% of added sulphur was found in the sheets, as one-pass retention, which shows that good retention to the paper is obtained.

Example 2

The method for reduction of the amount of free formaldehyde was tested on a large kraft sack paper machine with a production of 18 tons of paper per hour. 1035 kg urea-formaldehyde wet strength resin, containing 35% dry weight resin and 2.6% free formaldehyde, was added per hour.

The white water system was 2450 m^3 and the mean white water cycle was estimated to 16 minutes. Bisulphite and alum were added continuously and at the same time to the white water system immediately after the wire section. The added amount of bisulphite per hour was estimated to react with half the amount of formaldehyde. 780 kg of formaldehyde was already in the white water before the test started. The total amount of alum added during the test was 6200 kg and of these 1700 kg were added in

combination with the sulphite. Totally 1425 kg bisulphite were added during the test. The maximum reduction would thus be some 40 to 50%, depending on the temperature, pH etc and would be reached within 24 hours in this paper production system.

Measurement of the reduction of formaldehyde in the drying section after 17 hours showed that the reduction was 45%.

Claims

1. A method for reducing the amount of free aldehyde at the production of paper, characterized in that a sulphite compound, which is a sulphite, a bisulphite and/or a disulphite, is added to the stock or the process water in combination with a cationic retention agent, the amount of added cationic retention agent in combination with said sulphite compound for the formaldehyde absorption being such that a complex having zero or slightly positive charge is formed.

2. A method according to claim 1, characterized in that the sulphite compound is sodium sulphite or sodium bisulphite.

3. A method according to claim 1, characterized in that the cationic retention agent is alum.

4. A method according to any of the preceding claims, characterized in that the sulphite compound and the cationic retention agent are added to the stock or the process water at production of paper wherein formaldehyde based wet strength resins are used.

5. A product suitable for use in paper production, characterized in that it is an aqueous solution comprising a combination of a sulphite compound, which is a sulphite, a bisulphite and/or a disulphite, and a cationic retention agent, the ratio of sulphite compound to cationic retention agent being such that a complex having zero or slightly positive charge is formed.

6. A product according to claim 5, characterized in that the sulphite compound is sodium sulphite or sodium bisulphite.

7. A product according to claim 5 characterized in that the cationic retention agent is alum.

8. A product according to claim 7, characterized in that the mole ratio of the sulphite compound to alum is within the range of from 2:1 to 7:1.

9. A product according to claim 8, characterized in that the mole ratio of the sulphite compound to alum is within the range of from 3:1 to 6:1.

Patentansprüche

1. Verfahren zur Verminderung der Menge an freiem Aldehyd bei der Herstellung von Papier, dadurch gekennzeichnet, daß man eine Sulfitverbindung, bei der es sich um ein Sulfit, ein Bisulfit und/oder ein Disulfit handelt, zu dem Papierstoff oder dem Verfahrenswasser im Kombination mit einem kationischen Retentionsmittel zugibt, wobei die Menge des in Kombination mit der Sulfitverbindung für die Formaldehydabsorption zugegebenen kationischen Retentionsmittels derart ist, daß ein Komplex mit der Ladung null oder mit einer schwach positiven Ladung gebildet wird.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die Sulfitverbindung Natriumsulfit oder Natriumbisulfit ist.

3. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das kationische Retentionsmittel Alaun ist.

4. Verfahren gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Sulfitverbindung und das kationische Retentionsmittel zu dem Papierstoff oder dem Verfahrenswasser bei einer Papierherstellung zugegeben werden, bei der Naßfest-Harze auf Formaldehydbasis verwendet werden.

5. Für die Verwendung bei der Papierherstellung geeignetes Produkt, dadurch gekennzeichnet, daß es eine wäßrige Lösung ist, die eine Kombination einer Sulfitverbindung, bei der es sich um ein Sulfit, ein Bisulfit und/oder ein Disulfit handelt, und eines kationischen Retentionsmittels enthält, wobei das Verhältnis der Sulfitverbindung zu dem kationischen Retentionsmittel derart ist, daß ein Komplex mit einer Ladung null oder einer schwach positiven Ladung gebildet wird.

6. Produkt gemäß Anspruch 5, dadurch gekennzeichnet, daß die Sulfitverbindung Natriumsulfit oder Natriumbisulfit ist.

7. Produkt gemäß Anspruch 5, dadurch gekennzeichnet, daß das kationische Retentionsmittel Alaun ist.

8. Produkt gemäß Anspruch 7, dadurch gekennzeichnet, daß das Molverhältnis der Sulfitverbindung zu dem Alaun im Bereich von 2:1 bis 7:1 liegt.

9. Produkt gemäß Anspruch 8, dadurch gekennzeichnet, daß das Molverhältnis der Sulfitverbindung zu dem Alaun im Bereich von 3:1 bis 6:1 liegt.

Revendications

1. Procédé pour réduire la quantité d'aldéhyde libre dans la fabrication du papier, caractérisé en ce qu'un composé sulfitique, qui est un sulfite, un bisulfite et/ou un disulfite, est ajouté à la pâte à papier ou à l'eau de traitement, en combinaison avec un agent cationique de rétention, la proportion ajoutée d'agent cationique de rétention en combinaison avec ledit composé sulfitique pour l'absorption du formaldéhyde, étant telle qu'un complexe ayant une charge nulle ou légèrement positive soit formé.

2. Procédé selon la revendication 1, caractérisé en ce que le composé sulfitique est le sulfite de sodium ou le bisulfite de sodium.

3. Procédé selon la revendication 1, caractérisé en ce que l'agent cationique de rétention est l'alun.

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le composé sulfitique et l'agent cationique de rétention sont ajoutés à la pâte à papier ou à l'eau de traitement lors de la fabrication du papier dans laquelle on utilise des résines renforçatrices de la résistance à l'état humide, à base de formaldéhyde.

5. Produit approprié pour l'utilisation dans la fabrication du papier, caractérisé en ce que c'est une solution aqueuse comprenant une combinaison d'un

composé sulfitique, qui est un sulfite, un bisulfite et/ou un disulfite, et d'un agent cationique de rétention, le rapport du composé sulfitique à l'agent cationique de rétention étant tel qu'un complexe ayant une charge nulle ou légèrement positive soit formé.

6. Produit selon la revendication 5, caractérisé en ce que le composé sulfitique est le sulfite de sodium ou le bisulfite de sodium.

7. Produit selon la revendication 5, caractérisé en ce que l'agent cationique de rétention est l'alun.

8. Produit selon la revendication 7, caractérisé en ce que le rapport molaire du composé sulfitique à l'alun est dans la gamme de 2:1 à 7:1.

9. Produit selon la revendication 8, caractérisé en ce que le rapport molaire du composé sulfitique à l'alun est dans la gamme de 3:1 à 6:1.