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A New Generation of Fluorescent Whitening Agents for Paper Coatings

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1. Introduction

Whiteness is relative. Because of this, paper manufacturers are constantly seeking to increase the whiteness of their papers, so that each new paper compares favorably with previous products. Wood-free, uncoated papers in particular have become whiter and whiter. Now the same tendency can be observed in coated papers, too. Up to now, paper manufacturers have been able to choose between three classical types of fluorescent whitening agent (FWAs) in order to obtain a higher degree of whiteness:

disulfo FWAs
tetrasulfo FWAs
hexasulfo FWAs

All three types have their own characteristic properties and their own limitations (Fig. 1).

Disulfo FWAs have excellent affinity, but are highly sensitive to cationic substances and aluminum ions. Tetrasulfo FWAs have adequate affinity and good compatibility with starch and cationic substances, including aluminum ions. Hexasulfo FWAs, on the other hand, have poor affinity. This information regarding the affinity only really applies, however, when the FWAs are added internally and is not so relevant to coating application. When applied as coatings, FWAs need appropriate carrier substances such as co-binders (polyvinyl alcohol, carboxymethylcellulose (CMC)or starch) to enable them to develop their full effect. Nevertheless, it is important to know about the affinity when broke is recycled, as the FWAs used in the coating are then mobilized and go onto the fibers to a greater or lesser extent, depending on their affinity.

Even in optimized coating recipes, disulfo and tetrasulfo FWAs have now frequently reached the greening limit, or graying limit as it is also known. When this limit is reached, the

Characteristics of FWA

Disulfotype	Highly substantive	Sensitive to alum Sensitive to cationics Low compatibility to starch
Tetrasulfotype	Substantive	Good stability to cationics Good stability to alum Good compatibility to starch
Hexasulfotype	Low substantive	High stability to cationics High greening limit

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Fig. 1. Characteristic properties of fluorescent whitening agent.

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whiteness cannot be increased any further, not even by adding more FWA. At best, it decreases slightly. The shade of the finished paper shifts towards green. Nor is it possible to increase the addition of carriers such as polyvinyl alcohol or CMC because of the effect of these substances on the rheological properties of the coating slurry. Up to now, the only solution was either to make concessions with regard to the level of whiteness or to use hexasulfo FWAs. However, because of their low affinity and high anionic charge, these increase the anionic load of the circulating water when the broke is recycled.

The result is a drop in productivity due to the effect on the retention and sheet formation. In some cases, it may even be necessary to limit the amount of broke used so that the anionic load does not reach extreme levels. This naturally also affects productivity.

This adverse relationship between the use of broke and productivity has come up repeatedly in talks with customers.

2. New Tetrasulfo FWAs for Coatings

The improvements that manufacturers of the various types of graphic paper would like to see in FWAs can be summed up as follows:

1. Higher whiteness
2. Less influence on the anionic load
3. Lower co-binder requirements
4. No urea

With the introduction of the two new tetrasulfo FWAs in the BLANKOPHOR range BLANKOPHOR NC liq. and BLANKOPHOR NCC liq. it is now possible to meet all the frequently highly specific demands of coating slurry recipes. In some cases BLANKOPHOR NC liq. is adequate, in other cases the more comprehensive product BLANKOPHOR NCC liq. has to be used to cover all the requirements.

All new products of this type have to be urea-free. The affinity of the new tetrasulfo FWAs is comparable to that of the standard tetrasulfo products in use today. The performance properties, however, are on a level with those of hexasulfo FWAs.

3. Examples of Application

The following examples are designed to illustrate the potential of the new tetrasulfo FWAs and show how they can help paper manufacturers achieve a higher level of whiteness and increased flexibility in production without reducing productivity.

3.1 Overcoming the greening limit of hexasulfo FWAs

Hexasulfo FWAs are used wherever high whiteness is required and standard tetrasulfo FWAs are unsuitable because of their low graying limit. Fig. 2 shows an example of the production of fine paper with a single coating. It can be seen from the graph that at an addi-

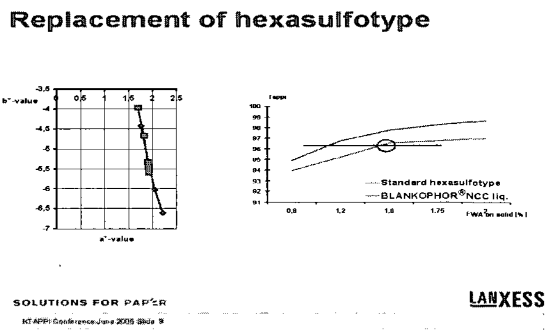

Fig. 2. a*b* diagram and whiteness build-up (Tappi) of BLANKOPHOR NCC liq. as compared with a hexasulfo FWA.

tion of 1.75 % hexasulfo FWA there is already a tendency towards greening. The same quantity of the new, special FWA gives higher whiteness, while the original whiteness target can be achieved with an addition of only 1.2 %. Considerable savings are therefore possible in the amount of FWA used.

In the a*b* diagram, both the standard hexasulfo FWA and the new product display a similar performance in the red/blue direction. At higher additions, however, the hexasulfo FWA reaches its greening limit and does not build up any more in the violet direction.

In order to quantify the anionic load deriving from FWAs in the broke, a model calculation was carried out to determine the quantity of FWA released. The calculation was based on a 60 g/m paper coated on both sides with 15 g/m. If 1.75 % hexasulfo FWA is added to the coating, 0.58 % FWA is released when the broke is recycled and goes onto the fibers according to the affinity. By contrast, only 1.2 % of the new FWA is required to obtain the same degree of whiteness of the coating, and so only 0.4 % FWA is released on recycling the broke.

Fig. 3 shows the cationic demand that can be attributed entirely to the FWAs. It can be seen that, at an addition of 25 % broke, the anionic load of the water is significantly lower if the hexasulfo FWA is replaced by the new tetrasulfo product.

This reduction in the anionic trash load can be explained by the fact that, when switching from hexasulfo FWAs to the new, special FWAs, about 30 % less product is required per se to obtain the desired degree of whiteness. Furthermore, the anionic load of tetrasulfo FWAs is one third lower than thatof hexasulfo products. And the considerably higher affinity of the tetrasulfo FWAs compared with the hexasulfo type means that less FWA remains dissolved in the white water. It also means that the whiteness of the base paper obtained with BLANKOPHOR NCC liq. is comparable to that obtained with hexasulfo FWAs (Fig. 4), even though 30 % less product is used.

So there is less dissolved FWA in the white water and this FWA content has a lower anionic trash load. The advantages of this are felt throughout the entire paper manufacturing system resulting in savings in the amount of retention agent required, better sheet formation and fewer breaks. All this leads to an appreciable increase in productivity, as was confirmed not just during mill trials, but in everyday paper production as well.

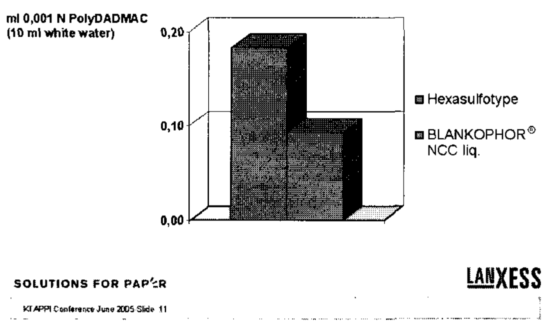

Fig. 3. Cationic demand of FWAs from the brok.

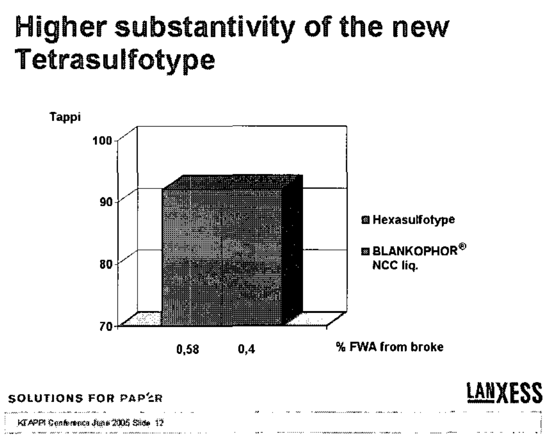

Fig. 4. Whiteness of the base paper when using hexasulfo and tetrasulfo FWA.

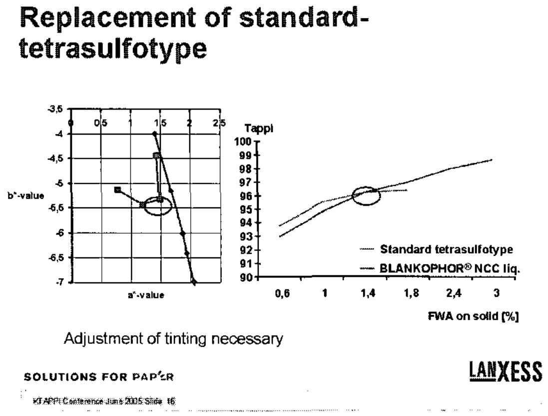

Fig. 5. a*b* diagram and whiteness build-up (Tappi) of BLANKOPHOR NCC liq. as compared with a standard tetrasulfo FWA.

3.2 Greening limit of standard tetrasulfo FWAs in wood-free paper

The next example shows how the greening limit of a standard tetrasulfo FWA can be overcome on a wood-free, double-coated fine paper.

As can be seen from Fig. 5, the graying limit of the standard tetrasulfoFWA is reached at an addition of 1.4 %. At this point, BLANKOPHORNCC liq. does not show any tendency to greening; in other words, a further increase in the level of whiteness is still possible. This difference in the tendency of the two products to greening can be seen particularly clearly in the a*b* diagram. As the new FWA is also slightly redder than the standard tetrasulfo FWA, slight correction of the tinting is necessary. For the given shade, less violet is needed, but slightly more blue. This change in the tinting leads to higher brilliance, which in turn means improved brightness and a higher L-value.

3.3 Replacement of standard tetrasulfo FWAs in wood-containing LWC paper

The fiber material here consists of TMP and fresh pulp. The paper mill works with standard tetrasulfo FWAs at the greening limit, as can be seen from the whiteness build-up and the a*b* diagram in Fig. 6.

An addition of 1.6 % product on coating solids represents the upper limit. The greening tendency of the standard tetrasulfo FWA at this addition level can be seen clearly in the a*b* diagram.

The two formulations based on the new FWA type show no tendency to greening in the a*b* diagram. This means that further increases in the degree of whiteness are possible. Fig. 6 also shows, however, that considerably larger quantities of BLANKOPHOR NC liq. are required to obtain the given degree of whiteness than of BLANKOPHOR NCC liq.

In this example, the paper manufacturer can choose between three strategies if using BLANKOPHOR NCC liq.:

1. He can achieve a higher final degree of whiteness by adding correspondingly more FWA.

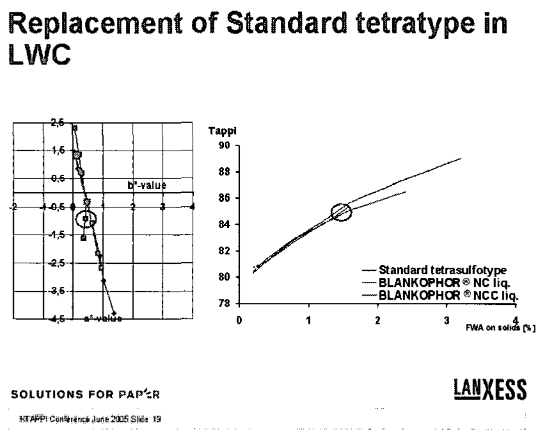

Fig. 6. a*b* diagram and whiteness build-up (Tappi) of the new tetrasulfo FWAs as compared with a standard tetrasulfo FWA.

2. He can obtain the same degree of whiteness with less FWA. In this case, the tinting has to be adjusted, but as a result the L-value increases.

3. If more FWA is added, a whiter coating is obtained. Another possible option for the paper manufacturer is therefore to adhere to the original whiteness target and reduce the whiteness of the base paper. In this way he can also save on the bleaching of the fibers or the whiteness of the raw materials (fibers, fillers) for the base paper. However, it is then necessary to adjust the tinting of the yellower base paper if the original hue is to be obtained.

3.4 Replacement of disulfo FWAs in fine paper

In this example, the aim was to increase the whiteness of the double-coated paper. The existing level of whiteness had been produced with a disulfo FWA. As can be seen from Fig. 7, the greening limit of the system is reached at an addition of only 1.4 %. Polyvinyl alcohol is used as a carrier. By using the new, special FWA, the customer can achieve a higher degree of whiteness, although it will be necessary to adjust the tinting in order to obtain the original hue. Here, too, as when replacing standard hexasulfo FWAs, use of the special FWA may lead to an increase in the L-value.

Fig. 8 shows clearly that, without polyvinyl alcohol as a carrier, the required whiteness level of 102 cannot be attained with the disulfo FWA. With BLANKOPHOR NCC liq., on the other hand, this level can be reached without any problem, and as the shade is within the acceptable range, there is no need for correction.

The new product thus enables paper manufacturers to obtain whiter papers and at the same time to control the degree of whiteness better at high additions. Alternatively, they can optimize the coating costs by retaining the original degree of whiteness and doing without polyvinyl alcohol.

3.5 Replacement of standard tetrasulfo FWAs and reducing the viscosity of the coating slurry in LWC

In this example, the customer was aiming to increase productivity by modifying his coater. This necessitated reducing the viscosity of the coating slurry and increasing the solids content.

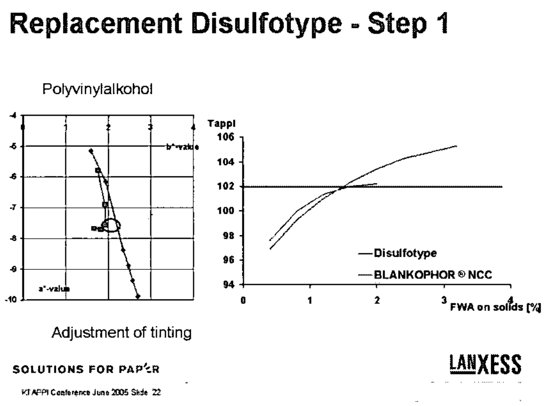

Fig. 7. a*b* diagram and whiteness build-up (Tappi) with polyvinyl alcohol.

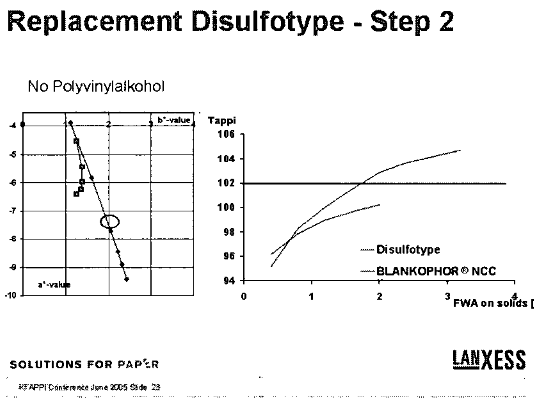

Fig. 8. a*b* diagram and whiteness build-up (Tappi) without polyvinyl alcohol.

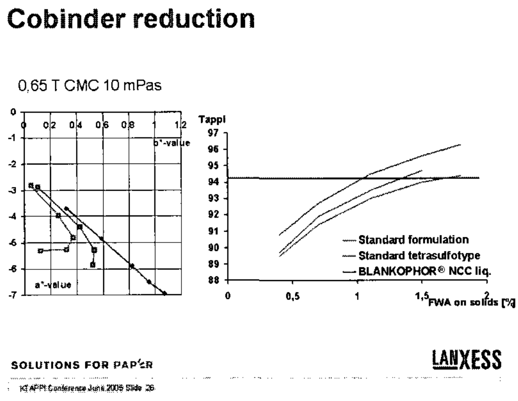

Fig. 9. a*b* diagram and whiteness build-up (Tappi) with a reduced amount of CMC (0.65parts) and lower viscosity.

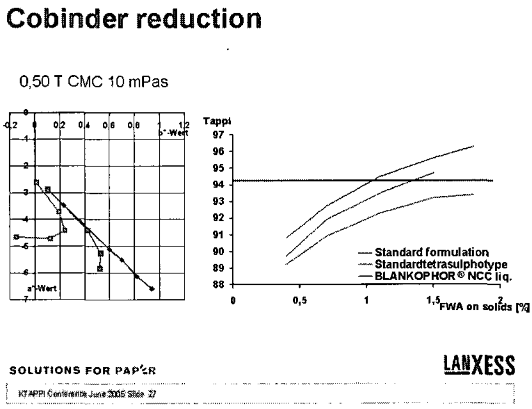

Fig. 10. a*b* diagram and whiteness build-up (Tappi) with a reduced amount of CMC (0.5 parts) and lower viscosity.

In addition to the usual constituents, the coating slurry used so far also contained 0.85 parts carboxymethylcellulose with a viscosity of 30 mPas (according to Hppler). This was therefore the obvious place to start tackling the problem of the viscosity. The customer was recommended to reduce the amount of carboxymethylcellulose added and also to reduce the inherent viscosity of the particular type of carboxymethylcellulose used to 10 mPas. Fig. 9 shows the whiteness build-up and the development of the hue when the addition of CMC is reduced to 0.65 parts.

The curve for the standard recipe represents the initial situation with a standard tetrasulfo FWA as a benchmark. The product has clearly reached the greening limit.

When using a standard tetrasulfo FWA, the degree of whiteness decreases noticeably if the viscosity of the CMC is lowered and the amount added is reduced to 0.65 parts. The a*b* diagram shows clearly that in this case greening sets in considerably earlier and the results obtained are no longer ideal. With the special FWA, on the other hand, the whiteness continues to increase even with the reduced amounts of CMC. There is thus potential for increasing the degree of whiteness further still. This potential can also be utilized to further reduce the amount of CMC to 0.5 parts. The results of these trials are illustrated in Fig. 10.

If we look at the original situation which was taken as a benchmark, we see that these results cannot be achieved under the altered conditions with the standard tetrasulfo FWA, as greening sets in considerably earlier. With the special FWA, however, the required whiteness can still be obtained without any problems and the customer can achieve his goal of increasing the productivity of his coater.

Conclusion

The new generation of FWAs represented by BLANKOPHOR NC liq. and BLANKOPHORN CC liq. makes it possible to overcome the greening limits of traditional FWAs and set new standards in whiteness. In many cases the new FWAs can simply be substituted for the previous products without having to optimize the coating slurry recipe. Replacing hexasulfo FWAs and special hexasulfo types by the new generation of FWAs also improves the productivity of the paper machine by reducing the amount of anionic trash introduced into the circulating water along with the broke. And finally, coating costs can be reduced by optimizing the additions of co-binders such as polyvinyl alcohol and carboxymethylcellulose.