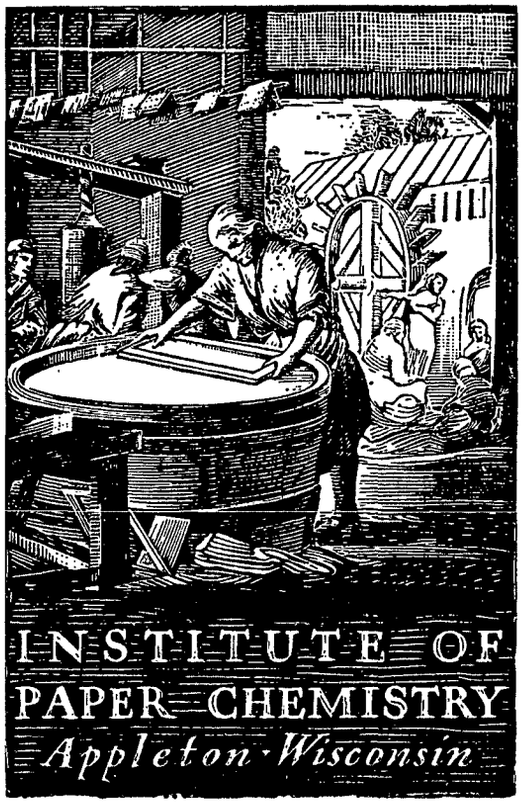

ANTHRAQUINONE/ALKALI PULPING

A LITERATURE REVIEW

Project 3370

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

July 5, 1978

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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ANTHRAQUINONE/ALKALI PULPING

A LITERATURE REVIEW

INTRODUCTION

Anthraquinone has been found to be a very effective additive for alkaline pulping processes. The subject has received a great deal of attention, and a number of publications have appeared recently. The Institute has started a project in the area, with the emphasis on mechanism, rather than optimization. The first objective was to review the literature, and this report represents a summary. Although no references were intentionally left out, it is likely that in such an intensely studied area, some publications were accidently overlooked. Also, much of the work done has not been published, for proprietary reasons.

BACKGROUND

In 1972, Bach and Fiehn (1) published their finding that water-soluble salts of anthraquinonesulfonates are effective in stabilizing hydrocellulose to alkaline degradation. Their experimental method involved measuring the weight loss after a 2 hr reflux in 2N sodium hydroxide. The amount of additive used in screening a number of compounds was 50%, based on hydrocellulose. The anthraquinonesulfonates and hydroxylamine were the only compounds of the 25 tested which showed a significant effect under these conditions. Interestingly, anthraquinone (AQ) itself was among those compounds tested, and it showed only a marginal effect under the conditions used.

In the above work (1), sodium 2-anthraquinonesulfonate (AMS) was then used as an additive for kraft and soda pulping of pine. A significant increase in yield, and reduced rejects and kappa numbers were obtained in kraft pulping upon addition of 1.0% AMS, while strength properties were only slightly affected. The soda process, which does not work well on softwoods, was accelerated by AMS. The addition of 0.1% or less gave substantially lower yields, kappa numbers, and rejects. These pulping results were the basis of a patent (2).

A few publications appeared on the use of AMS in pulping, but the enthusiasm was modest due to the high cost of AMS, lack of an adequate recovery method, and the small effect in kraft pulping. Sjostrom and Ahlstrom obtained German (3) and French (4) patents on a modification in which AMS was used in oxygen pulping. Addition of 1% gave a measurable effect. Worster and McCandless (5) patented the use of AQ salts as a pretreatment before alkaline pulping. Kenig patented a similar pretreatment before oxygen pulping (6). In all of this work, the emphasis was on the water-soluble salts of anthraquinone because of

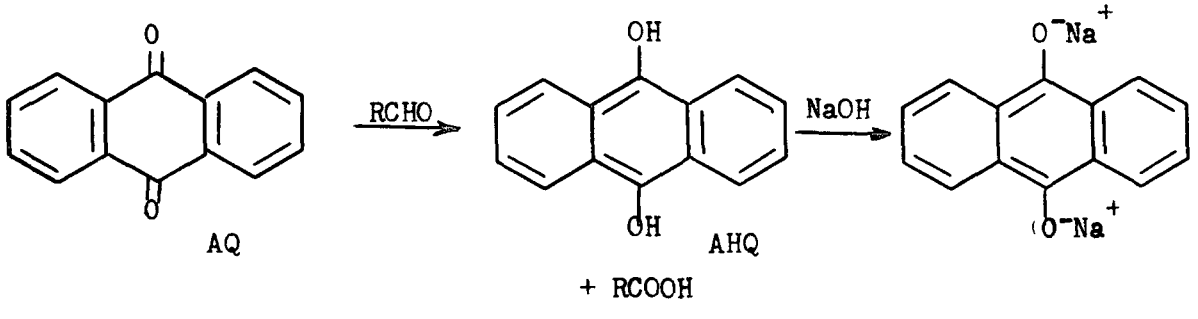
the negative results of Bach and Fiehn (1) on anthraquinone itself in their rather specialized system.

In the work on AMS, most of the discussions on chemistry centered on the carbohydrate fraction of the wood. Heikala and Sjostrom (7) showed reduced carbohydrate degradation, which they attributed to oxidation of the aldehydic end-groups, leading to stabilization against the peeling reaction. Little attention was given to the lignin chemistry. The small amounts of AMS required were rationalized in terms of the small number of end-groups.

ANTHRAQUINONE

The event which did the most to spark the enthusiam for quinone additives was the disclosure by Holton (8) in 1976 that AQ itself is an effective additive in alkaline pulping. In fact, he claimed that a modified soda process employing AQ surpasses an unmodified kraft process in rate and yield in pulping hardwoods and softwoods. The addition of AQ to the kraft process resulted primarily in an increase in yield. He suggested that the stability of the quinone additive was probably more important than the solubility. This work was subsequently published as a paper (9).

AQ is insoluble in water, and only slightly soluble in most organic solvents. This insolubility is misleading in the context of alkaline pulping, and probably delayed the discovery of the effectiveness of AQ. In the presence of reducing sugars and alkali, AQ is rapidly reduced to the hydroquinone (AHQ), as shown in Equation (1). The hydroquinone is acidic, and forms a water-soluble disodium salt in alkali. These reactions occur readily at room temperature if soluble carbohydrates are used, and can be seen by the deep red color of the disodium salt.



AQ AHQ

+ RCOOH (1)

In this way, a substantial amount of AQ can be kept in solution in the reduced form. This soluble material is readily available if a catalytic cycle is involved.

The subsequent patents by Holton (10-13) described the results from a large number of different additives related to AQ. Of these, AQ was among the best. Electron-donating, alkyl substituents made AQ slightly more effective, but this is more of interest from a mechanistic viewpoint, since the advantage probably does not justify the additional cost.

The enthusiam for the patented process was almost immediate. Very little capital equipment is required for the actual use of the additive, although the resulting changes in recovery and the additional pulp which might be produced could require substantial changes such as increased lime kiln and bleach plant capacity. Furthermore, virtually every lab which tried was able to reproduce the claims of the patent. Eventually, a number of publications began to appear in the literature.

A group at the Australian Paper Manufacturers Ltd. discovered independently the effect of anthraquinone on soda pulping. Their published work (14) on eucalyptus and pine showed that the addition of 0.1% AQ to soda cooks gave higher yields and lower kappa numbers, these values being similar to kraft. Strength values were similar to kraft for laboratory pulps. Pulps prepared in a mill trial gave lower strengths than the laboratory pulps, but "approached that of commercial kraft pulp." They also verified the effects of AQ in kraft pulping, using 0.15% AQ.

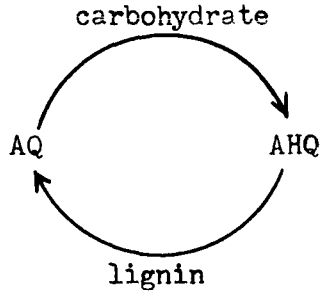
The title and emphasis in his first paper (9) suggested that Holton was advocating soda/AQ as a replacement for kraft, even though extensive data were given for the use of AQ in both soda and kraft. However, this was followed by a paper by Holton and Chapman (15) in which they gave the results of a mill trial using AQ in kraft. Here they consider the immediate applications of soda/AQ to be limited to existing soda mills, and to a few kraft mills which are under

sufficient environmental pressure to convert. In this work, 0.05% AQ was used for kraft pulping southern pine chips to produce linerboard grade pulp. The mill trials utilized black liquor recycling. Under these conditions, H-factors could be reduced 25-35%, and alkali could be reduced by 5% as well. This gave pulp of quality equivalent to standard kraft pulp at the same kappa number. Laboratory simulation indicated that half the effect was due to AQ addition (makeup), and half to black liquor recycle. Several cooks were required for the AQ level to reach a steady state in the recycled black liquor.

In the same issue of Tappi, Gratzl and coworkers at North Carolina State University compared AQ and AMS as additives for kraft and soda cooking of water oak (16). Their work suggests that the two additives behave similarly, but that AQ is much more effective. The beneficial effects on pulping were similar to those obtained by others. In addition, they explored a sequence involving soda-AMS pulping to a high kappa number (ca. 50), followed by an oxygen-alkali treatment to bring the kappa number down to about 10. The resulting pulps could be bleached to 85 brightness in only three stages, suggesting that the oxygen/alkali treatment could be substituted for the first chlorination and extraction stages of typical five-stage bleaching. Some of the conclusions in this paper relating to AQ are based on experiments done with AMS, and they should be verified with AQ before being fully accepted.

MECHANISM OF ANTHRAQUINONE PULPING

Although the mechanism is not well understood, most workers consider AQ to be functioning as a redox catalyst. Based on earlier work with AMS (7), it was reasonable to assume that carbohydrate end-groups are oxidized by AQ. Lignin can then complete the catalytic cycle by oxidizing AHQ back to AQ, being reduced in the process. This is shown schematically below.



Löwendahl and Samuelson demonstrated quite conclusively the carbohydrate portion of the above cycle in both kraft (17) and soda (18) pulping. Their technique involved hydrolyzing the pulps and separating the monocarboxylic acids by anion exchange chromatography. With AQ, the amount of aldonic acids, corresponding to end-group oxidation, increased. At the same time, a lower yield of "alkaline-stopping" acids was obtained with AQ. This reduced yield is due to less peeling, and is consistent with higher yields of carbohydrates when pulping with AQ.

A group from the Pulp and Paper Research Institute of Canada recently showed the importance of redox potential on rates of nonsulfur pulping (19). Although their work emphasized a series of amines which were added in large amounts (typically 40% on wood), they claimed their results could be generalized to AQ pulping. They developed a method of monitoring the electrical potential of a cook, relative to the saturated calomel electrode. The potentials started out

slightly positive, and then became progressively more negative (reducing) as the pulping progressed. They found a definite correlation between the rate of delignification and the redox potential of the spent liquor for the series of amines. Interestingly, the soda-amine pulps were found to have exceptionally high tear strengths.

The same group, in extending their work to anthraquinone pulping, found that the addition of AQ to a soda cook resulted in a more negative redox potential for the liquor (20). This is consistent with faster pulping in the amine series. Their proposed mechanism involved a catalytic cycle which included both carbohydrates and lignin, as shown above. They suggested that a reduced form of AQ prevented an undesirable side reaction (e.g., condensation) of the lignin, and thus, the solubilizing reactions of delignification are enhanced. Their work shows why Bach and Fiehn (1) did not find an effect with AQ. The previous work (1) used hydrocellulose, and did not have lignin to complete a catalytic cycle. Under these special conditions, the more soluble AMS was much more effective at stabilizing carbohydrates.

In contrast, at the same meeting, Gratzl described model compound results in which AMS was acting as an oxidizing agent on the lignin model (21). It could be argued that the system was set up to enhance oxidation, since only the quinone form of AMS was present initially and to get the observed results, stoichiometric amounts must have been added. No carbohydrate was present to complete a catalytic cycle. The differences between the two groups demonstrates the importance to having both carbohydrate and "lignin" present when studying the effects of AQ and AMS.

HEALTH ASPECTS OF ANTHRAQUINONE

This section is based largely on the results of a literature search made available to us by Bruce Burba, of Mobay Chemical Corporation. In general, only the abstracts were read by this reviewer. Substituted anthraquinones, particularly the amino derivatives, are more hazardous than the parent compound, and will not be included in this discussion. As is generally the case with biological studies, conflicting reports appear in the literature, and it is best not to base a conclusion on a single study. It should also be noted that much of the commercial anthraquinone is derived from coal tar, which contains a number of carcinogenic compounds, such as benzpyrene. Therefore, test results using such material might actually be due to these impurities. Different results might be obtained from a purified sample, or from anthraquinone prepared synthetically from pure compounds.

Anthraquinone is not considered to be a particularly toxic chemical. It has a slight allergic effect on sensitive people. However, because it is usually handled as a very fine powder, it is difficult to prevent significant amounts from becoming suspended in the air. This can even lead to an explosion hazard. Because of this, protective clothing, including rubber gloves and a dust mask, is recommended when handling large amounts of anthraquinone powder.

An average concentration of 12.2 mg/m^3 of dust in air caused threshold level effects in rats, rabbits, and mice. A maximum permissible dose of 10 mg/m^3 for industrial working areas was recommended, although this seems to allow a rather small safety margin (22). Repeated injection of 20% of the LD_{50} dose of anthraquinone into experimental animals caused damage to the liver, kidneys, and blood. The effect of anthraquinone was smaller than that of 1,2- and 1,5-diaminoanthraquinone (23).

Anthraquinone has also been shown by several different investigators to have a beneficial effect on the liver. At a dose level of 50 mg/kg, it had a therapeutic effect in treating hepatitis of rats caused by carbon tetrachloride (24). The same laboratory found that the same dose on healthy rats caused an inhibition of liver functions, while 1 mg/kg had no effect (25). Anthraquinone was found by others to stimulate regeneration of rat livers which had been partially removed surgically. Carcinogenic hydrocarbons were found to have a similar effect (26).

Anthraquinone has been identified as a component in cigarette smoke, but no mention was made in the abstract of toxic or carcinogenic effects (27).

Anthraquinone appears on a government list of suspected carcinogens (28). The list contains the original reference (29) and the toxicity data. The lowest toxic dose was reported to be 72 g/kg orally in rats, administered over a 90-day period. The toxic effect was a neoplastic effect (production of tumors). This list of suspected carcinogens is extremely long, and has been widely criticized for including many things which probably should not have been included, and omitting many things which should have been included. The reference to anthraquinone in particular has been seriously questioned. Many of the possible impurities in AQ derived from coal tar could have given a false test. Several new tests are underway.

Interestingly, the more recent Environmental Protection Agency list (30) includes a section on 9,10-anthraquinones, which states "In general, anthraquinone *per se* is a relatively inert compound." Most of the carcinogenic and mutagenic activity described in this section of the document involves hydroxy, amino, and nitro derivatives of anthraquinone, and nothing more is said about such activity in the parent compound.

A number of studies are presently underway and these should demonstrate whether there are any toxic or carcinogenic effects associated with AQ. Also of concern is the effect of bleaching (e.g., chlorination) on AQ residues.

THE FUTURE

The future for anthraquinone will depend largely on any decisions made by the Food and Drug Administration (FDA). If it is to be used widely, it must be cleared as an indirect food additive. If its use is approved, it should be accepted almost immediately, since very little capital is required. If such approval is not obtained, its use should be very limited, since most paper products eventually find their way into food applications through recycling. The industry must be careful not to have a repeat of the PCB's problem.

One might expect the substitution of soda/AQ for kraft, thus completely eliminating sulfur from the cooking chemicals. However, a more likely course would be evolutionary, with the use of AQ to reduce the sulfidity, active alkali, and/or cooking times for kraft pulping. Most kraft mills would probably not have enough causticizing capacity to make a complete switch from kraft to soda/AQ. The number of soda mills presently operating is very small, so the impact on soda pulping will have a small effect on the overall industry.

The benefits of AQ probably justify the cost for most mill situations. However, as the details of the mechanism become more completely understood, alternative compounds may be found which accomplish the same thing at lower cost. Also, if FDA approval is not obtained, such alternative compounds may also need to be found before the benefits can be realized. Considering the large amount of research presently being expended in this area, we might well be entering the era of redox pulping.

CONCLUSIONS

Anthraquinone is an effective additive for both kraft and soda pulping. Higher yields and faster pulping rates are obtained through its use with both softwoods and hardwoods. It makes the soda process useful for pulping softwoods as well as hardwoods. The mechanism, although not well understood, probably involves a catalytic redox cycle. Oxidation of carbohydrate end-groups is almost certainly part of the cycle. Reduction of one or more functional groups in lignin or lignin-derived intermediates may well complete the cycle. However, some oxidation of lignin may also occur. Although nothing has been found to suggest that AQ will not qualify for FDA approval, its widespread use must await such a decision.

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