REGENERATION OF CAUSTIC SODA-SODIUM SULFIDE COOKING LIQUOR

Robert R. Fuller, Tuscaloosa, Ala., and Vernon Woodside, Niagara Falls, N. Y., assignors to Mathieson Chemical Corporation, a corporation of Virginia.

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1 This invention relates to the preparation of aqueous solutions of caustic soda and sodium sulfides such, for instance, as used in the cooking or digesting of cellulose fibers, or the like, in the preparation of pulp for the manufacture of paper. The invention provides an improved method whereby such solutions or cooking liquors may be more readily and economically prepared. It will be understood that the invention is of general application to the preparation of such solutions and is not dependent upon the intended use of the solution.

Seed flax straw, for instance, has been used extensively in the manufacture of paper for special purposes requiring a high degree of purification and defiberization. For this purpose such bast fibers have been pulped by cooking in a caustic soda-sodium sulfide liquor. The usual process for preparing this liquor involves the dissolving in water of prescribed amounts of caustic soda and sodium sulfide.

Though this customary practice has been found generally effective, it is subject to the economic disadvantage of high cost of chemicals employed. In such operations large amounts of caustic soda and sodium sulfide are used. The sodium sulfide, particularly, is a relatively expensive chemical and materially adds to the cost of the operation. The caustic soda, though usually less expensive than sodium sulfide, is still an item of considerable expense.

It has heretofore been proposed to prepare digestion liquors for use in the preparation of paper pulp by separately adding caustic soda and elemental sulfur directly to the digester containing the cellulose material and water. The substitution of sodium carbonate and lime for the caustic soda in such operations has likewise been suggested.

In our co-pending application Serial No. 491,056 (now abandoned), filed June 16, 1943, of which the present application is in part a continuation, we have specifically described a highly advantageous application of the present invention to the pulping of wood by a process somewhat resembling the "kraft" process.

In paper manufacture, by the "kraft" process, for instance, wood chips are cooked in an aqueous solution containing as essential ingredients, sodium hydroxide and sodium sulfide. Such solutions also usually contain minor proportions of sodium polysulfide. Following the cooking or digesting period the spent liquor is conventionally regenerated by eliminating water to form the so-called "black liquor," carbonizing the organic matter therein, and smelting the salt mixture thus formed, dissolving the smell in water, and causticizing the resultant liquor. The liquor comprising the dissolved smell is commonly called "green liquor," and the causticized green liquor is commonly called "white liquor."

Make-up soda and sulfur to replace that consumed or lost in the cooking operation are conventionally added to the black liquor or to the carbonizing and smelting operation as sodium sulfate, which is reduced to sodium sulfide by reaction with the organic material. It has also been proposed to add make-up soda and sulfur separately either as sodium carbonate and elemental sulfur to the green liquor prior to the causticizing operation, or as sodium carbonate to the green liquor and as elemental sulfur to the white liquor. Sodium carbonate added to the green liquor is converted to sodium hydroxide in the causticizing operation.

At an elevated temperature, elemental sulfur will react with caustic soda to form sodium-sulfur compounds consisting of sodium monosulfide and considerable proportions of polysulfides. However, we have found that this reaction proceeds relatively slowly and that, under ordinary conditions, the passing of the added elemental sulfur into solution is so time-consuming as to detract materially from the economic advantage of its use over the use of sodium sulfide as such.

In accordance with our present invention, the cooking liquor is prepared by dissolving in water alone or in green liquor an intimate admixture of elemental sulfur and soda ash and causticizing the solution, as by the further addition of lime in sufficient quantities to convert the soda ash to caustic soda.

We have discovered that the dissolving of the elemental sulfur is very substantially accelerated if it be added in intimate admixture with sodium carbonate. The admixture may with advantage be prepared by intimately mixing mechanically the soda ash and sulfur in appropriate proportions. However, we have obtained particularly beneficial results by adding the soda ash and sulfur as an intimate admixture agglomerated by fusion as described in United States Letters Patent No. 2,223,631 to Robert B. MacMullin. There is described in said patent a fused admixture consisting essentially of sodium carbonate and sulfur in proportions by weight of about 10 parts sodash and 3 parts sulfur intimately admixed and agglomerated by fusion of the sulfur in a non-oxidizing atmosphere and in which the two constituents are chemically uncombined, these pro-
portions being substantially those in which the constituents combine to produce sodium sulfide. This agglomerated admixture has been referred to in said patent as “synthetic saltcake” and, for convenience, is so designated herein.

Though the synthetic saltcake described in said patent, in which the soda ash and sulfur are present in molecularly combining weights to produce Na₂S₃, has been found particularly desirable for use in accordance with our present invention, it will be understood that the proportions of soda ash and sulfur may be varied considerably to meet the requirements of particular operations.

In the preparation of the synthetic saltcake, the soda ash and sulfur, preferably of relatively small, uniform particle size, are advantageously admixed at room temperature, prior to agglomerating by fusion, and then heated in a non-oxidizing atmosphere, with continued agitation, to a temperature above the melting point of the sulfide (120° C.), but below that at which substantial reaction between the constituents will result. Preferably the agitation is discontinued during cooling so as to prevent the formation of large lumps.

The proportions of soda ash and sulfur used will depend upon the proportion of caustic soda and sodium sulfide required in the cooking liquor and whether the entire caustic soda constituent of the cooking liquor is to be supplied by the soda ash-sulfur admixture. It will be observed that the proportions previously noted are such as to result in the formation of Na₂S₃ without provision for additional caustic soda requirement of the cooking liquor. Additional soda ash may be separately added or added in admixture with the sulfur to supply the entire caustic soda requirement. A further alternative is to add any further requirement of caustic soda as such.

We have found also that the dissolving of the elemental sulfur is still further expedited by the presence of a small amount of pre-formed sodium sulfide. As a convenient source of the sodium sulfide used for this purpose, a portion of the cooking liquor from a previous operation may be used with advantage. In starting-up the operation, when no previously used cooking liquor is available, sodium sulfide from an outside source may be used and, if desired, sodium sulfide from an extraneous source may be used throughout to accelerate the dissolving of the sulfur. However, a small amount of the previously used cooking liquor has been found to be entirely satisfactory for this purpose and is available without extra cost.

The amount of sodium sulfide added to accelerate the dissolving of the sulfur is not particularly critical. Amounts substantially less than 1%, generally a small fraction of 1%, say 0.1% to as low as 0.05% or even less, has been found to be effective.

We cannot explain with certainty the chemical or physical reactions resulting in the dissolving of the elemental sulfur, just how and why these reactions are affected by the conditions contemplated by our invention. The invention is not so dependent upon any theory as to the reasons for the improved results obtained and, the utility of the invention is not affected by the absence of such explanation.

We have observed, however, that when sulfur in the form of flowers of sulfur is separately added to the liquor, a large portion thereof, at least, floats on the surface of the liquor with considerable persistence but that, when the sulfur is added in intimate admixture with the soda ash, particularly when a fused admixture of the soda ash and sulfur, as previously described, is used, the sulfur passes readily into solution. It appears likely that, by reason of the close proximity of the sulfur to the soda ash during the dissolving of the latter, the dissolution of the former with the formation of more or less monosulfide and sodium polysulfides is accelerated. We cannot account for the further acceleration of this action by the presence of preformed Na₂S₃.

In the preparation of the sulfide cooking liquor, in accordance with our present invention, an intimate admixture of the soda ash and sulfur in appropriate proportions may be used, in amounts depending upon the particular concentration of the liquor required. As previously noted, it is not necessary that the full equivalent of the NaOH requirement of the liquor be added with the sulfur. However, the minimum amount of soda ash thus added should be substantially equivalent to that required for the conversion of the sulfur to Na₂S₃. After the addition of the soda ash-sulfur admixture or prior to or concurrently therewith, there is added lime, or other source of limestone, in an amount sufficient to convert the soda ash to caustic soda. The solution is preferably agitated and heated during the addition of these various ingredients. Thereafter the solution is advantageously further heated to a temperature approaching the boiling temperature for 90 to 90 minutes or at least until the sulfur is substantially completely dissolved.

Where additional sodium carbonate is added, it should be added prior to the causticization step. However, where NaOH is added as such, the addition may be made either before or after the causticization. The causticization of the solution results in the formation of calcium carbonate which may be removed from the solution by precipitation or, in many instances, may be allowed to remain in the liquor.

Cooking liquors conventionally used in digestion operations such as referred to herein ordinarily contain caustic soda and sodium sulfide in amounts equivalent to about 10 to 12 pounds of caustic soda and 3 to 6 pounds of sodium sulfide per 100 pounds of dry fiber treated.

The proportions of caustic soda and sodium sulfides in the cooking liquor may vary, considerably, depending upon the particular cellulose material being digested and other operating conditions employed, including temperature and duration of the cooking and also the desired characteristics of the product.

In carrying out the process embodying the improvements of our present invention, one should first determine the proportions and concentrations of caustic soda and sodium sulfides to be employed under the selected conditions of operation. The proportions and concentrations may be determined in accordance with conventional practice as is well understood in the industry. Having determined what proportions and concentrations of caustic soda and sodium sulfides are to be employed, the amounts and, relative proportions of sodium carbonate and elemental sulfur to be used may be determined in the customary manner, as by analysis, of the resultant liquor by conventional methods.

We have found, however, that, in the digestion operation, a substantial proportion of the polysulfide formed by the reaction of the elemental sulfur with the caustic appears to react with the NaOH to form the monosulfide and, by this reaction, a portion of the caustic soda is consumed.
Therefore, the analysis of the digestion liquor prior to use is not a wholly accurate guide with respect to causticity of the cooking liquor in the digester. A more accurate guide for determining the amounts and proportions of sodium carbonate and sulfur to be added is the analysis of a sample of the liquor from the digester after a brief period of the cooking.

The concentration of the cooking liquor and proportions of constituents thereof prepared in accordance with our present invention may with advantage be those customarily used. For instance, the amount of water used in the preparation thereof may be about two to ten times the dry weight of the fiber to be treated. For each 100 pounds of fiber, 1 to 4 pounds of sulfur, 10 to 20 pounds of soda ash and 4 to 10 pounds of lime may be used, depending upon the desired causticity and fluidity of the liquor.

In our above-noted co-pending application we have described an operation in which the soda ash-sulfur mixture is added to the green liquor resulting from the dissolving of the smelt from a previous cooking operation. In that operation conditions are adjusted and controlled so as to maintain a particularly high ratio of sodium polysulfide to sodium monosulfide in the cooking liquor. The present invention is especially applicable to operations in which such conditions are maintained but its use is not so restricted.

In commercial pulping operations in which elemental sulfur is used, the sulfur is usually used in lump form rather than the more expensive and less readily handled flowers of sulfur. The solution of elemental sulfur in either form in either water alone or in green liquor is a relatively troublesome time-consuming operation. The advantages derived from our present invention will appear from the following specific illustrations of the invention as applied to the addition of the soda ash-sulfur mixture to a green liquor. For comparison, the time required to dissolve the sulfur when separately added in lump form and as flowers of sulfur to the green liquor is included.

In order more accurately to determine and standardize conditions, the green liquor used in each of these tests was prepared by dissolving sodium sulfide and sodium carbonate in water to form a solution containing 45 grams per liter of sodium sulfide and 140 grams per liter of sodium carbonate. In each test the resultant green liquor was heated on a heat plate to 80°C, before the additional ingredients were added, and was stirred by means of a constant speed stirrer at a relatively low speed in order to approximate as nearly as possible the agitation obtained in a dissolving tank in commercial operation. In each instance the proportions of soda ash and elemental sulfur were 10:3. Also, in each instance the point indicated as that when substantially complete solution was attained was that when substantially all of the solid had passed into solution and the liquor between any remaining solid particles was clear.

Where synthetic salt cake such as previously described herein was used, substantially complete solution of the solid was attained in 2 minutes. Repeated tests confirmed this result. Where soda ash and finely divided elemental sulfur in unfused intimate admixture were added, substantially complete solution was attained in 7 minutes. Where soda ash and finely divided sulfur were separately added simultaneously, only about three-fourths of the sulfur had passed into solution at the end of 11 minutes, and about 20 minutes was required for substantially complete solution of the sulfur. Similarly, where soda ash and lump sulfur were simultaneously added, about 20 to 22 minutes was required to attain substantially complete solution of the solids.

We claim:

1. In the preparation of aqueous solutions of caustic soda and sodium sulfide for use in the manufacture of paper pulp by the "kraft" process, in which the make-up sulfur and sodium are added to the "green liquor" as elemental sulfur and sodium carbonate, respectively, and the "green liquor" then causticized, the improvement which comprises adding the sulfur and sodium carbonate in intimate admixture with one another in amounts to regenerate the cooking liquor.

2. In the preparation of aqueous solutions of caustic soda and sodium sulfide for use in the manufacture of paper pulp by the "kraft" process, in which the make-up sulfur and sodium are added to the "green liquor" as elemental sulfur and sodium carbonate, respectively, and the "green liquor" then causticized, the improvement which comprises adding the sulfur and sodium carbonate in intimate admixture with one another in amounts to regenerate the cooking liquor.

3. In the preparation of aqueous solutions of caustic soda and sodium sulfide for use in the manufacture of paper pulp by the "kraft" process, in which the make-up sulfur and sodium are added to the "green liquor" as elemental sulfur and sodium carbonate, respectively, and the "green liquor" then causticized, the improvement which comprises adding the sulfur and sodium carbonate in intimate admixture with one another in amounts to regenerate the cooking liquor.

ROBERT R. FULLER.
VERNON WOODSIDE.

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The following references are of record in the file of this patent:

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<thead>
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