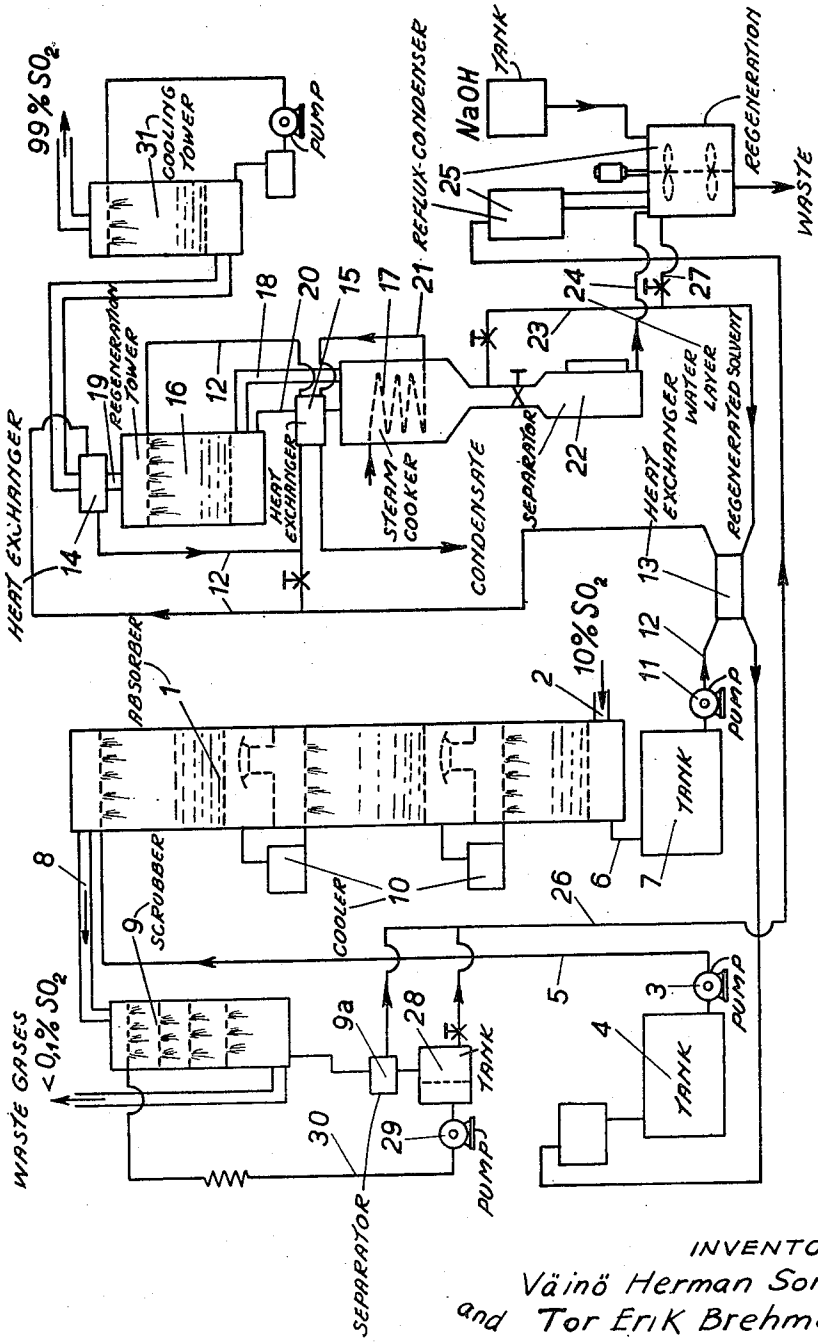
March 13, 1951 V. H. SOMER ET AL 2,545,389

METHOD FOR INCREASING THE SULFUR DIOXIDE CONTENT OF THE COOKING ACID USED IN THE MANUFACTURE OF SULFITE PULP

Filed Oct. 26, 1946



INVENTORS.
Väinö Herman Somer
and Tor Erik Brehmer
BY
Albert M. Parker
ATTORNEY.

Patented Mar. 13, 1951 2,545,389

UNITED STATES PATENT OFFICE

2,545,389

METHOD FOR INCREASING THE SULFUR DIOXIDE CONTENT OF THE COOKING ACID USED IN THE MANUFACTURE OF SULFITE PULP

Väinö Herman Somer, Lauritsala, and Tor Erik Brehmer, Jarvenpaa, Finland, assignors, by direct and mesne assignments, of one-half to said Somer and one-half to Aktiebolaget Kaukas Fabrik, Lauritsala, Finland

Application October 26, 1946, Serial No. 706,008
In Finland January 30, 1946

3 Claims. (Cl. 23—129)

1

The present tendency in the manufacture of chemical pulp by the sulfite method is to use as strong a cooking acid as possible, i. e., an acid with a high content of sulfur dioxide. This is because a strong acid impregnates the chips better than a weak one, and the time required for the cook can thus be shortened appreciably. The pulp thus obtained is better and, before all, more even in quality, which is of great importance particularly in view of the growing demand for high grade pulp of the artificial fiber industry. A contributory cause for the increased necessity for a stronger cooling acid lies in the fact that the pulp mills are nowadays for various reasons seldom in a position to use dry and seasoned logs and have mostly to content themselves with such that are green or recently floated. As a result the water content of the chips may rise as high as 55–57%, whereas seasoned logs generally contain but approximately 20–25% of water.

It is more difficult nowadays to secure a stronger cooking acid due to the fact that the Finnish sulfite pulp mills are at present obliged to produce their sulfur dioxide by roasting pyrites. The gas obtained in this way usually contains only 9–12% by volume of sulfur dioxide, and often even less than that, whereas it is possible to obtain gas mixtures containing 17–18% by volme of sulfur dioxide by burning elementary sulfur.

Outside of the usual gasification in which the gaseous products are cooled and conducted into the tower acid for increasing the sulfur dioxide content of the cooking acid, several other methods have been developed based on the utilization of the gasification products. However, these methods are neither sufficiently flexible nor fast enough, the apparatus needed is often expensive, and only a limited variation of the cooking acid sulfur dioxide content is possible. Naturally, the use of liquid sulfur dioxide to add to the tower acid would give unlimited possibilities for varying the cooking acid strength, but such a method could hardly be economically carried out in view of the expense in production and transportation of the liquid sulfur dioxide involved (drying the sulfur dioxide gas, liquifying, storage in pressure containers, transfer to 7 atm. pressure tank cars, shipping, etc.).

The present invention is concerned with obtaining the advantages that would accompany the use of liquid sulfur dioxide for preparing the cooking acid in the manufacture of sulfite pulp by concentrating a part of the pyrites oven gases

2

to a strength of nearly 100% sulfur dioxide (the rest being water vapor). The concentrated sulfur dioxide gas thus obtained is mixed in suitable proportions with, for example, the main portion of the 9–12% gases from the pyrites oven or with the tower or cooking acid. In this manner it is possible to adjust the sulfur dioxide content of the cooking acid to what the chips or, respectively, the finished pulp demands.

The method presented in this invention does not involve any great expense for construction or operation. There is usually enough space already available, considering the normal high construction of pyrites ovens, and it is easy to make the apparatus automatic in operation, necessitating only a minimum amount of manual labor. The expenses incurred for heat are small, for it is possible to utilize for the purpose, for example, the excess of low-grade heat always available in a pulp mill. Moreover the loss of heat in the method presented in this invention is quite insignificant, inasmuch as it is easy to install heat exchangers to recover the heat liberated in the process.

The expenditures for chemicals constitute only a small fraction of the total costs in the production of liquid sulfur dioxide, and this item of expense is the only one that remains unchanged for the production of highly concentrated sulfur dioxide gas in accordance with the present invention.

We will explain the method according to this invention with reference to the accompanying drawing, which is a schematic representation of a plant for concenrtation of sulfur dioxide gas.

In connection with the pyrites oven there is erected an absorption tower 1 equipped with plates or grates and filled with Raschig rings or the like or in some other way so arranged as to bring about as great a contacct surface as possible between gas and liquid. The gas mixture coming from the pyrites oven, containing, for example, 10% sulfur dioxide gas, is introduced into the bottom of the absorption tower 2. By means of a pump 3 a mixture of water and absorbent at suitably 30° C. is pumped from container 4 through the pipeline 5 to the top of the absorption tower, where the absorption mixture is distributed evenly over the tower fill by means of spray nozzles or the like, and trickling down absorbs the sulfur dioxide from the gas mixture coming up in counterstream.

From the bottom of the absorption tower the absorpion mixture, which has now taken up the

sulfur dioxide, is conducted through pipeline 6 to container 7.

The absorbent used according to this invention is 2-aminocymene, suitably mixed with water in the proportion of 1:1. The aggregate is so dimensioned and the flow of gas and absorbent mixture so regulated that the gas mixture issuing from the upper end of the tower through pipeline 8 has a residual sulfur dioxide content of about 0.1% and can thus be released into the air without causing trouble. The gas stream carries with it small amounts of amine, corresponding to the partial pressure of the latter. These latter are recovered in a scrubber 9 by the aid of sulfuric acid (which forms solid compounds with them), alkali bisulfite, or oily substances. From the two first-named of these scrubber substances the aminocymene may be separated in separator 9*a* by heating with alkali, and from the last-named it may be separated, depending on the nature of the oil, by fractional distillation or some other known method. After separation, the sulfuric acid, bisulfite solution, or oil is transferred to container 28 and thence put into the process again by pump 29 via pipeline 30.

The heat developed in the absorption tower by the solution of the sulfur dioxide is removed by means of a cooling arrangement 10 inserted between the different units of the tower. In this manner it is possible to avoid the expense attendant on the otherwise necessary numerous conduits for gas and absorbent fluid between a plurality of towers.

The sulfur dioxide solution received in container 7 is suitably at a temperature of about 30° C. and contains 100–130 gm. sulfur dioxide (that can be boiled off) per 1 liter absorption mixture (water: aminocymene in proportion of 1:1).

Wherever sulfur dioxide comes into contact with water sulfur trioxide is formed. This reaction is catalysed by a number of substances, such as arsenic and selenium. There are also other substances that retard this reaction. We may reckon with an oxidation of 0.5–1.5% of the sulfur dioxide gas streaming through the absorption tower to sulfur trioxide, in addition to which some thioacids are also formed. In order to bind these we may add to the tower liquid alkali or alkali earth hydroxides or carbonates. It is, however, not so advantageous to use the latter of these as their use leads to the formation of insoluble alkaline earth sulfates.

From container 7 the sulfur dioxide solution is pumped by a pump 11 through pipeline 12 through the heat exchangers 13, 14 and 15 to the regeneration tower 16, which is filled with, for example, Raschig rings. The sulfur dioxide containing mixture of aminocymene and water is here met in its downward passage by a stream of steam (and liberated SO_2) generated in the boiler 17 and injected through pipeline 18. Through pipeline 19 issues a mixture of sulfur dioxide and steam including some amino compound, the heat liberated by the condensing steam being recovered in 14. Heat exchanger 15 utilizes partly the heat from the aminocymene-water mixture freed of sulfur dioxide and returning from the regenerating tower through pipeline 20 to boiler 17 and partly heat obtained from the water of condensation in the steam coil of boiler 17 through pipe 21.

The boiler 17 is coupled below to a separatory funnel 22, in which the water and aminocymene are separated from one another after removal of the sulfur dioxide. The water contains sulfur trioxide, the product of oxidation of sulfur dioxide, in the form of for example, sodium sulfate, thio-acids as sodium salts, and the excess alkali, which was changed to bisulfite in the absorption tower, has almost entirely changed to sulfite during the boiling. Giving off its heat in exchanger 13, the aminocymene is returned through pipeline 23 to container 4 to take part in the circulation again.

Either continuously or at intervals determined by analysis a portion of the water solution is transferred through pipeline 24 from 22 to apparatus 25, which is equipped with a reflux condenser and a mixer, and to which is piped also through line 26 the aminocymene recovered from scrubber 9 in separator 9*a*. By adding lye and heating the small quantities of aminocymene contained in the water are liberated, rise to the surface, and are then returned to circulation through pipeline 27. The remaining water solution goes to the drain, possibly after recovering the sodium sulfate still contained therein.

The gas coming from heat exchanger 14 is further cooled in condenser tower 31, from which it issues as about 99% sulfur dioxide.

As mentioned before, the absorbing substance used according to this invention is aminocymene. Cymene, the raw material for this substance, is obtained as a side-product in the production of sulfite pulp and has so far found no other considerable use. The yield of aminocymene in synthesis from cymene is about 90%. About 0.75–1.5 kg. of aminocymene are lost per ton of sulfur dioxide concentrated. Calculated as NaOH about 9–12 kg. of soda are used per ton of sulfur dioxide and about 1.0–1.3 tons of normal steam. This heat may, however, as already mentioned be supplied by utilizing the low-grade heat usually abundantly available in connection with pulp manufacture. Inasmuch as the whole process according to this invention can also easily be made to operate automatically, this method offers many advantages in solving the problem of a strong cooking acid.

The methods described above can, of course, easily be suited also to the use of a sulfite pulp mill burning elemental sulfur for its sulfur dioxide supply. In a like manner the concentration of sulfur dioxide can also be carried through with the gases that at the decompression flow to the acid tower after having passed through the acid cistern, and which often exert a disturbing influence on the operation of the tower, or with the blow-off gases.

The method of concentrating sulfur dioxide gases by means of a mixture of aminocymene and water can naturally be applied in all industries in which gases containing sulfur dioxide are available, for instance the metallurgic industries.

What is claimed is:

1. A method of increasing the sulfur dioxide content of the cooking acid in connection with the manufacture of sulfite pulp which comprises, diverting a portion of the gas supply, concentrating the sulfur dioxide in the said diverted portion of said gas supply by means of absorbing in a mixture of 2-aminocymene and water, boiling off the sulfur dioxide and retaining oxidation products of sulfur dioxide in the absorption liquid, and thereafter introducing said concentrated sulfur dioxide to supplement the sulfur dioxide content of the cooking acid.

2. A method according to claim 1 wherein the absorption liquid mixture is substantially one part of water and one part of 2-aminocymene.

3. A method according to claim 1 wherein the 2-aminocymene used is prepared by synthesis from cymene obtained in the production of sulfite pulp.

VÄINÖ HERMAN SOMER.
TOR ERIK BREHMER.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,740,342	Hansen et al.	Dec. 17, 1929
1,893,385	Wettstein	Jan. 3, 1933
1,941,592	Bacon et al.	Jan. 2, 1934
2,009,757	Bentley et al.	July 30, 1935
2,014,775	McKee	Sept. 17, 1935
2,047,032	Richter	July 7, 1936
2,047,819	Boswell et al.	July 14, 1936
2,186,453	Gleason et al.	Jan. 9, 1940

OTHER REFERENCES

Lucas: "Organic Chemistry," American Book Co., N. Y., 1935, page 350.