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METHOD OF ELIMINATING ODORS IN KRAFT PULP MILL OPERATION

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It is an object of this invention to provide a method and means whereby the hitherto highly obnoxious odors associated with the production of pulp by any process involving any compound of sulfur as at least one of the digestants can be eliminated.

It is a further object of this invention to provide a method and means as aforesaid, which may be installed in any mill at a reasonable capital investment.

It is a further object of this invention to provide a method and means as aforesaid, which may be operated with a minimum of daily attention and at a minimum daily operating cost.

While the present invention is applicable to all types of pulp mills involving any sort of chemical digestion, it will be described with reference to the operation of a pulp mill using the kraft or sulphate process. In such a mill the cooking liquor contains a mixture of NaOH, the most active ingredient, Na_2CO_3 which is substantially inert and a substantial proportion of Na_2S which in the liquor hydrolizes to NaOH and NaSH. This mixture makes up the so called white liquor. It usually is diluted with a proportion of black liquor before being added to the digester. When the cook is complete, the digester is blown and the now 100% black liquor is separated from the pulp, evaporated to a consistency of 50% to 60% solids and is then burned in a suitable furnace. Usually a certain amount of Na_2SO_4 is added at or just ahead of the furnace. The furnace consumes the organic matter contained in the black liquor, reducing the inorganic solids to a smelt which is redissolved to form green liquor. The green liquor is treated with CaO which reacts with the Na_2CO_3 in the green liquor to produce NaOH and CaCO_3 thus reconstituting the white liquor. The CaCO_3 is burned back to CaO for re-use. It is essential that the combustion in the black liquor furnace be conducted in a reducing atmosphere in order to reduce the Na_2SO_4 to Na_2S .

The foregoing is an extreme simplification of the chemistry of the kraft process. Numerous side reactions occur. Some of these result in the formation of H_2S and of methyl mercaptan (CH_3SH) with some dimethyl disulphide ($\text{CH}_3\text{S.SCH}_3$). The three compounds just named are responsible for the characteristically foul odors emitted by kraft pulp mills. The methyl mercaptan is the chief offender, since its odor is foul even in low concentration and its boiling point is very low, which prevents any possible removal by condensation. It is moreover relatively insoluble and cannot be removed by scrubbing. Flue gases from the recovery furnaces usually carry H_2S as the chief offender. If, however, the evaporators for any reason drop off in efficiency, solids content of the black liquor may drop so low as to cool the furnaces and permit mercaptans to escape combustion and therefore enter the recovery furnace stack. Both H_2S and the mercaptans are relatively insoluble in water and have very low boiling points, for which reason neither

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scrubbing operations nor condensers will remove these objectionable substances.

It is probable that the H_2S is evolved primarily by reaction in the black liquor furnace, of sodium sulphide residual in the black liquor and it has been proposed to oxidize the black liquor before it enters the recovery system. This reaction has been carried out by means of air, the oxygen of which combines with the Na_2S and water to form $\text{Na}_2\text{S}_2\text{O}_3$, while the sodium methyl mercaptide is converted to a less obnoxious dimethyl disulphide.

The primary sources of offensive gases are:

- (1) The stack from the black liquor furnace;
- (2) The vents for relief gases from the digesters and the vents for gases from the blowdown; and
- (3) Noncondensibles from evaporators and the vacuum pump on the washers.

As a matter of fact, there is a considerable body of opinion holding that relief and blowdown gases bear a larger share than the black liquor furnaces gases for kraft mill odors, at least in the southern U. S. and neither such relief gases nor the blowdown gases are mitigated in the least by oxidation of the black liquor, although admittedly if such oxidation be carried out, there will be a mitigation of the odor from the black liquor furnace.

Two fundamental methods have been used to overcome odor problems. The first and best known, involves the principle of "masking." In this case, the undesirable odor literally is overpowered by a more acceptable odor, so that only the more acceptable odor is noticed. Probably the use of perfume to overcome the odor of perspiration is the most familiar example in this category. Such "masking" involves, however, the substitution of one odor for another and in the nature of things, always must leave some characteristic odor.

The second method involves so called "odor counteraction." This treatment is based on the fact that certain pairs of odors, in certain critical proportions, are mutually antagonistic and when mixed within such proportions, the mixture is odorless.

There is of course, a third possible treatment, as by adsorption, involving the use of activated carbon, silica gel and the like but such treatments are quite impractical, considering the daily volume of obnoxious gases emitted by any pulp mill.

Ozone (O_3) has itself a characteristic odor but this odor is by no means pungent and in fact is quite difficult to detect. Ozone is one of the most active oxidizing agents and when mixed with highly active oxidizable material, would be expected to react therewith. I have found, however, that ozone injected into stack gases containing H_2S and/or methyl mercaptans, will emerge from the stack unreacted and in the free state. Nevertheless, the ozone added to such gases, does exercise a deodorant effect, not as one odor overpowering another (masking) or as "odor counteraction." This latter odor counteraction effect, simply would not be expected, because of the low odor value of ozone itself. Moreover, due to ozone's low odor value, the resultant mixture is odorless and the proportion of ozone within broad limits, is not critical. As a result, it is possible to supply ozone in excess of minimum requirements and thereby enable the installation to operate without further adjustment, despite variations in the content of the gases to be treated.

Throughout this specification and the subjoined claims, all effluent gases will be referred to as "stack gases," whether these be derived from a conventional smoke stack, as from the recovery furnaces or from any other duct venting to the atmosphere gases derived from digester relief, brown stock washer hoods or vacuum pumps, evaporator relief, etc.

The present invention contemplates feeding ozone (O_3) into the stack gases coming from the black liquor furnace and also the supplying of ozone to the gases vented in the digester, blowdown, evaporators, etc. I have found that ozone, added to such gases, has an inexplicable deodorizing effect and eliminates the objectionable odors, even though the quantity of ozone added is far less than enough to meet the theoretical oxidation requirements of the available H_2S and mercaptans. Sampling of the gases at the point of discharge has revealed the presence of unreacted H_2S , on occasion, unreacted mercaptans and free ozone and such samples have been taken while the mill was operating in a virtually odorless condition.

At the present cost of ozone generation, it would be uneconomic to supply the theoretical requirement for complete reaction, let alone the excess which would be needed to insure complete reaction. I have found that if ozone is delivered to the discharging gases in a proportion between 10 and 100 parts per million, the characteristic kraft mill odors may be avoided. The precise proportion will be affected by many factors, such for example as the sulphidity of the cooking liquor; whether the black liquor is oxidized; and the degree of over or underload on the rated capacity of the black liquor furnace. As to the latter, overload conditions increase the proportion of H_2S in the stack gas while under conditions of underload H_2S decreases while SO_2 moves up. At a mill producing 270 tons of kraft pulp per day with a white liquor sulphidity of 28% to 30% and with oxidation of the black liquor, an optimum amount of ozone for controlling the odor from the black liquor furnace was 30 parts per million, based on a total gas flow of 53,400 cubic feet per minute.

It is essential that the ozone be retained for a certain length of time in order to get the maximum effect. In the above case in which 30 parts per million were supplied, the minimum retention time for effective elimination of odor was found to be 2.2 seconds. The retention time of course, is determined by the height of the stack and the velocity of the gases passing therethrough. So far as stack gases from the black liquor furnace are concerned, the H_2S content affords a basis for operation of the ozonator. For example: the 30 parts per million mentioned above with 2.2 seconds of retention time, are based on an H_2S content in the gas of .05 gram per cubic foot. A greater content would indicate a necessity for more parts of ozone and a lesser content correspondingly would reduce the ozone requirement. The retention time, however, should not be much less than the 2.2 seconds above mentioned, since otherwise even an absurdly high proportion of ozone would be ineffectual.

Relief and blowdown gases present a somewhat different problem than do the stack gases from the black liquor furnace. In these gases mercaptans rather than H_2S are the offenders. For example: a Swedish study of such gases showed that for 1000 kilograms of pulp,

there were produced 194.2 grams of H_2S , while 824.1 grams of methyl mercaptan were produced. Most of the mercaptans evolved go to the vents receiving digester relief, blowdown gases and evaporator relief. The mercaptans are formed in the liquor as a sodium salt due to some obscure reaction between the hydrolized sodium sulphide and some constituents of the wood. The sodium mercaptide, however, reacts with the water to release methyl mercaptan as a gas. In most modern kraft mill practice, relief gases of the type above noted, are passed through a condenser system. In deodorizing such gases, ozone should be added both before and after the condenser, if the condenser is of the surface type. Water itself has a considerable affinity for ozone and if ozone consumption is to be held at economic levels, addition of the ozone must be deferred until after the gases have been subjected to the action of any scrubbers or jet-type condensers which may be used in the treatment of the gases. The ozone added ahead of the condenser has the effect, in part at least, of oxidizing the methyl mercaptan to dimethyl disulphide, which not only is less foul smelling but has a much higher boiling point, which means it may be readily condensed from the vapors. Following the condenser, there should be a further addition of ozone, not particularly to react chemically but to produce a deodorant effect.

I claim:

1. In the operation of a kraft pulp mill, the steps of conducting ozone to a line discharging odorous stack gases, mixing the ozone with such gases in a proportion from about 10 to about 100 parts per million of the total gas volume, retaining said ozone and said gases in intimate mixture for not less than about 2 seconds and thereafter discharging said mixture to the atmosphere.

2. In the operation of a black liquor furnace in a kraft pulp mill, the steps of mixing ozone with the stack gases from said furnace in the proportion of from about 10 to about 100 parts per million of the total gas volume, retaining said ozone and said gases in intimate mixture for not less than about 2 seconds and thereafter discharging said mixture to the atmosphere.

3. The process set forth in claim 2 including scrubbing the stock gases to remove soluble and condensable fractions, said scrubbing step being performed prior to the mixture of said ozone with said gases.

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