

# UNITED STATES PATENT OFFICE.

MAX BAZLEN, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNOR TO BADISCHE ANILIN & SODA FABRIK, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, A CORPORATION.

## PRODUCTION OF ALDEHYDE SULFOXYLATES.

No. 885,566.

Specification of Letters Patent.

Patented April 21, 1908.

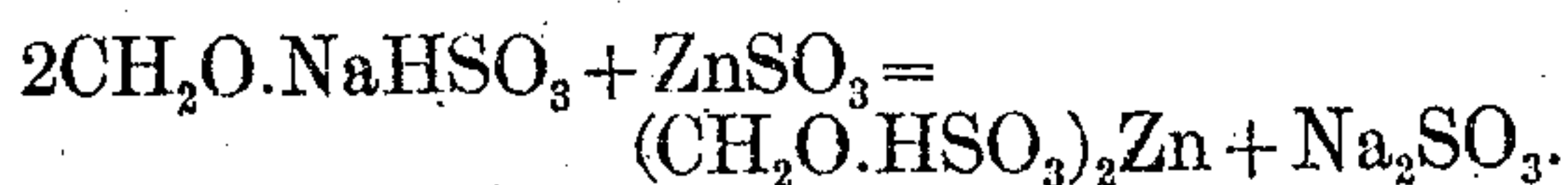
Application filed January 31, 1906. Serial No. 298,867.

*To all whom it may concern:*

Be it known that I, MAX BAZLEN, doctor of philosophy and chemist, a subject of the King of Würtemberg, residing at Ludwigs-  
hafen-on-the-Rhine, in the Kingdom of Bavaria, German Empire, have invented new and useful Improvements in Processes of Producing Aldehyde Sulfoxylates, of which the following is a specification.

My invention relates to the production of aldehyde sulfoxylates.

In the specification of Letters Patent No. 793,610 is described the production of salts of formaldehyde sulfoxylic acid by the reduction of the known aldehyde sulfur oxid compounds, namely formaldehyde bisulfite compound, or formaldehyde hydrosulfite compound. The reducing agent which proved most useful was zinc dust in the presence of acetic acid, although iron, or aluminium, powder, in the presence of acetic acid, or chlorid of tin, could be used. All attempts to reduce, with zinc dust alone, the fixed alkali salts of the said aldehyde sulfur oxid compounds and also the equivalent mixtures of formaldehyde with the fixed alkali sulfites, bisulfites and hydrosulfites have not hitherto been practically successful as only small yields of the sulfoxylate were obtained. I have discovered that these fixed alkali salts of aldehyde sulfur oxid compounds can be reduced by means of zinc dust without the necessity for the presence of acid, if, during the reduction, zinc sulfite, or zinc bisulfite, or a zinc salt of formaldehyde sulfurous acid, or of formaldehyde hydrosulfurous acid, be added. The reason for this appears to be that zinc formaldehyde bisulfite is directly reducible to zinc formaldehyde sulfoxylate by means of zinc dust in the absence of extraneous acid. Thus if zinc sulfite or zinc bisulfite or a zinc salt of formaldehyde hydrosulfurous acid be added to sodium formaldehyde bisulfite, double decomposition takes place, which, taking for instance the case when zinc sulfite is added, can be represented by the equation



The zinc formaldehyde bisulfite which is either thus formed or which has been directly added to the fixed alkali salt of the aldehyde sulfur oxid derivative as the case may be, is then reduced by means of zinc dust yielding

zinc formaldehyde sulfoxylate which then undergoes double decomposition with sodium formaldehyde bisulfite forming sodium formaldehyde sulfoxylate and zinc formaldehyde bisulfite. This latter is then reduced with an additional quantity of zinc dust, and in this way the addition of quite a small quantity of zinc salt enables large quantities of sodium formaldehyde bisulfite to be reduced. When zinc sulfite or zinc bisulfite is added, it is advantageous also to add more formaldehyde so that all the sulfur introduced can be converted into formaldehyde sulfoxylate. This formaldehyde can react with zinc sulfite to form zinc formaldehyde bisulfite which is directly reducible or it can react with the sodium sulfite to form sodium formaldehyde bisulfite which then undergoes the reaction above described. If, instead of zinc sulfite, or zinc bisulfite, a zinc salt of formaldehyde sulfurous acid or of formaldehyde hydrosulfurous acid be employed, it is unnecessary to add any additional formaldehyde, since there is already a sufficient quantity to combine with the whole of the sulfur present when forming sulfoxylate.

Since zinc formaldehyde hydrosulfite behaves, as is known, as if it were composed of equimolecular proportions of zinc formaldehyde bisulfite and zinc formaldehyde sulfoxylate, it can be seen that for the purposes of this invention zinc sulfite, zinc bisulfite and a zinc salt of formaldehyde sulfurous acid or of formaldehyde hydrosulfurous acid are equivalents, all of them giving the desired result, namely, the presence of zinc formaldehyde bisulfite which can be reduced to zinc formaldehyde sulfoxylate by means of zinc alone without the presence of any extraneous acid. Of course the addition of previously prepared zinc formaldehyde sulfoxylate would enable the reduction of the fixed alkali formaldehyde bisulfite to be effected in the manner above described, but I prefer to make use of one of the other above mentioned zinc salts, so that the isolation of zinc formaldehyde sulfoxylate is then unnecessary.

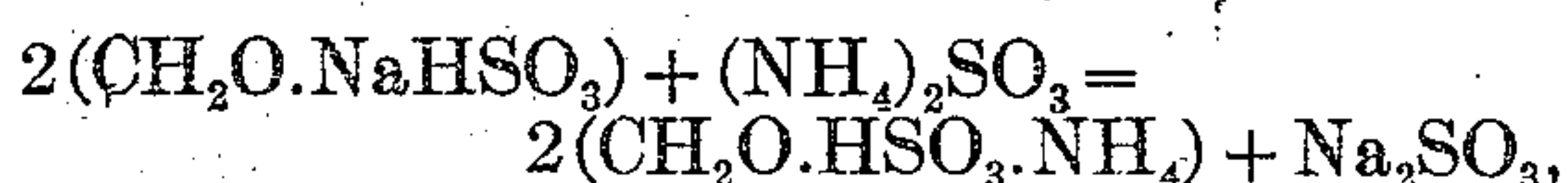
The above description represents my view of the course of the reaction, but I do not wish to be understood as confining my invention to the exact course described or to the equations hereinafter given, since other chemists may hold different views upon the subject.

The reaction should be carried out while



the mixture is hot, even while it is boiling. Any difficultly soluble, or insoluble, zinc salt of formaldehyde sulfoxylic acid obtained can be converted into soluble sulfoxylate by the addition of alkali sulfite either before, or after, the reaction has taken place, or, after the reaction has taken place, any other alkali salt which is convenient for precipitating the zinc, or an alkali hydrate, can be added.

I have discovered that instead of the above named zinc salts, the corresponding ammonium salts can be employed with similar results, so that they are equivalent for this process. The typical reaction when using ammonium sulfite being represented by the following equation:



and the ammonium formaldehyde bisulfite compound resembles the corresponding zinc compound in being capable of reduction by zinc alone without treatment with an extraneous acid. After the formation of the formaldehyde sulfoxylate has taken place, a part of the ammonia combines with the compound formed.

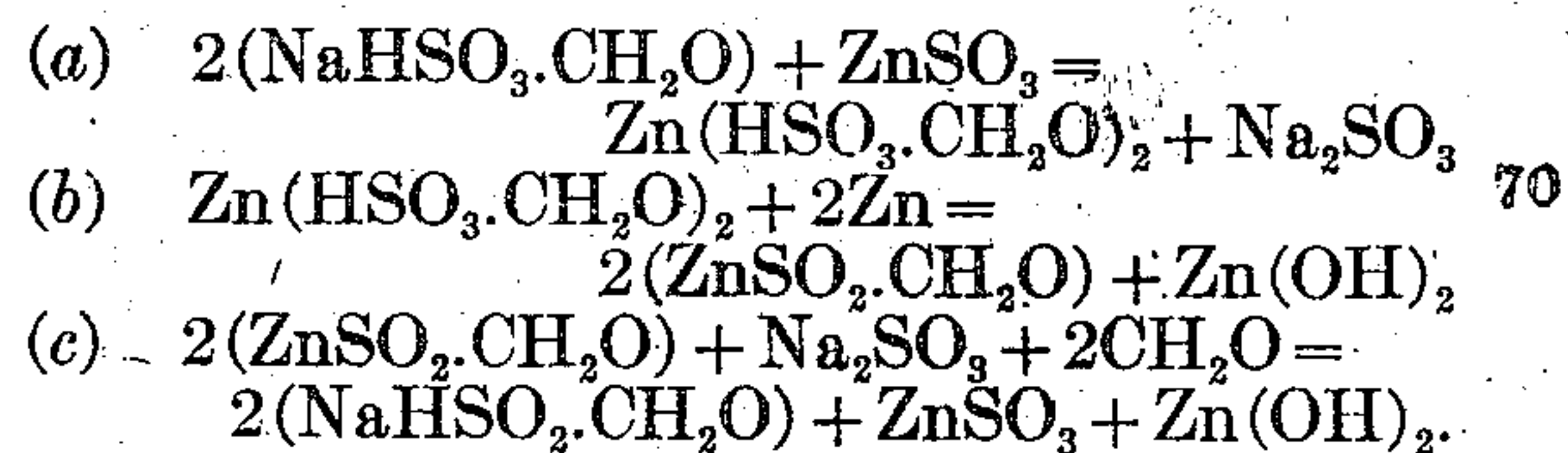
Although I have described my invention taking formaldehyde as a typical aldehyde, yet I do not wish to be understood as limiting my invention to formaldehyde, since other equivalent aldehydes, such for instance as acetaldehyde, may be employed instead.

The following examples will serve to further illustrate the nature of my invention and how it can be carried into practical effect, but my invention is not confined to these examples. The parts are by weight.

Example 1: To a solution of formaldehyde bisulfite, obtained from one hundred and four (104) parts of sodium bisulfite and thirty (30) parts of formaldehyde (used in the form of a thirty (30) per cent. solution) add one hundred and eighty (180) parts of zinc sulfite, one hundred (100) parts of thirty (30) per cent. formaldehyde, two hundred (200) parts of zinc dust, and from fifteen hundred (1500) to two thousand (2000) parts of water, and, while stirring, heat the whole at a temperature of from ninety (90) to one hundred (100) degrees centigrade, until a test portion shows that the reducing power of the mixture is not increasing. During the reaction the water which evaporates off should be replaced.

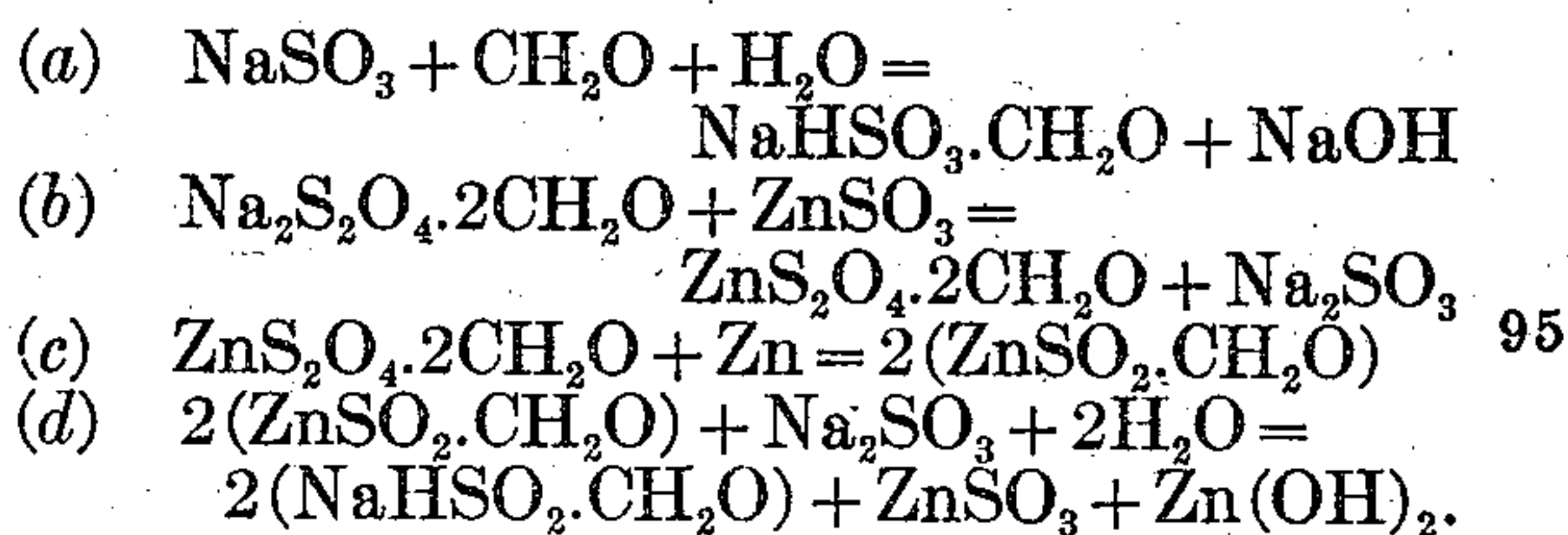
The product obtained consists of a solution containing a precipitate. Part of the formaldehyde sulfoxylic acid formed is contained in the solution in the form of the sodium salt, while the remainder is in the precipitate in the form of a difficultly soluble zinc salt. This can be converted into the sodium salt by boiling with, for instance, sodium sulfite. The reactions which occur in the foregoing

example may be represented by the following equations:



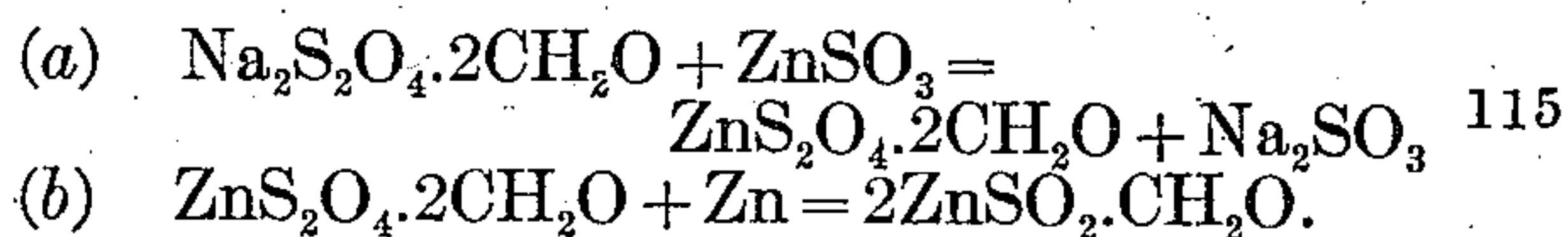
Example 2: Heat together, for some time in the manner described in the foregoing example, two hundred and fifty-two (252) parts of sodium sulfite, one hundred and eighty (180) parts of zinc sulfite, one hundred (100) parts of thirty (30) per cent. formaldehyde solution, one hundred (100) parts of zinc dust and from fifteen hundred (1500) to two thousand (2000) parts of water. After the reaction is complete, the filtrate contains the sodium salt of formaldehyde sulfoxylic acid.

The reactions which proceed in the foregoing example can according to the present view be represented by the following equations:



Example 3: Boil together for some time, three hundred (300) parts of sodium formaldehyde hydrosulfite, one hundred and eighty (180) parts of zinc sulfite, two hundred (200) parts of zinc dust and from fifteen hundred (1500) to two thousand (2000) parts of water. The difficultly soluble zinc salt of formaldehyde sulfoxylic acid which is formed, and which is contained in the precipitate, can be converted into the sodium salt by adding sodium sulfite and boiling for some time.

The reactions which proceed in the foregoing example can according to the present view be represented by the following equations:



Example 4: Boil together for some time, three hundred (300) parts of sodium formaldehyde hydrosulfite, one hundred and eighty (180) parts of zinc sulfite, two hundred and fifty-two (252) parts of sodium sulfite, two hundred (200) parts of zinc dust and two thousand (2000) parts of water. The filtrate contains the sodium salt formaldehyde sulfoxylic acid which can be obtained by evaporation.

The reactions according to the foregoing example are analogous to those taking place in Example 3, the addition of the sodium sul-



fite in this example resulting in the formation of the sodium salt of formaldehyde sulfoxylic acid at once.

Example 5: Mix together four hundred and twenty (420) parts of forty-two (42) per cent. sodium bisulfite solution, three hundred and sixty-five (365) parts of neutral ammonium sulfite solution (containing one hundred and seventy (170) parts of  $(\text{NH}_4)_2\text{SO}_3$ ), three hundred parts of thirty (30) per cent. formaldehyde solution and from fifteen hundred (1500) to two thousand (2000) parts of water; then add three hundred and fifty (350) parts of zinc dust, which has previously been made into a paste with a little water, and heat the mixture, while well stirring, at a temperature of about one hundred (100) degrees centigrade for one hour and a half (1.5). Filter off the zinc mud and precipitate the small amount of zinc which remains in solution and work up the filtrate, which may be done in the usual manner. In this way a mixture of the sodium salt and the ammonium salt of formaldehyde sulfoxylic acid is obtained.

The reactions which occur in the foregoing example are identical with those illustrated at the end of Example 1 with the exception that ammonium sulfite takes the place of zinc sulfite.

In the foregoing examples, instead of being boiled, the mixtures may be heated, while stirring, at a temperature of from ninety (90) to one hundred (100) degrees centigrade, until test portions show that the reducing

power of the mixture is not increasing. If the reaction be carried out at a lower temperature, a correspondingly longer period is required for its completion.

Now what I claim is:

1. The process of producing aldehyde sulfoxylate by reacting with a reducing metal on a fixed alkali salt of an aldehyde sulfur oxid compound in the presence of zinc sulfite while totally avoiding the presence of extraneous acid.

2. The process of producing aldehyde sulfoxylate by reacting with zinc on a fixed alkali salt of an aldehyde sulfur oxid compound in the presence of zinc sulfite while totally avoiding the presence of extraneous acid.

3. The process of producing formaldehyde sulfoxylate by reacting with zinc on a fixed alkali salt of a formaldehyde sulfur oxid compound in the presence of zinc sulfite while totally avoiding the presence of extraneous acid.

4. The process of producing formaldehyde sulfoxylate by reacting with zinc on formaldehyde sodium bisulfite in the presence of zinc sulfite while totally avoiding the presence of extraneous acid.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

MAX BAZLEN.

Witnesses:

J. ALEC. LLOYD,  
JOS. H. LEUTE.